

Thermodynamics of K-Ca exchange in soils. I. Effects of potassium and organic matter residues in soils from the Broadbalk and Saxmundham Rotation I Experiments

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SUMMARY

The standard and differential thermodynamic properties of K-Ca exchange in soils from the Broadbalk (Batcombe series) and Saxmundham Rotation I (Beccles series) Experiments were evaluated for selected manurial treatments, using exchange isotherms and calorimetric measurements. The Beccles soil had a greater preference for K than the Batcombe soil in all the comparable treatments (Nil, PK and FYM). In all the soils, enthalpic forces favoured K preference but entropic forces Ca preference; in all but two cases the magnitude of the enthalpic forces were greater, resulting in K preference (positive $-\Delta G_o$). The $-\Delta H_o$ values of the soils did not vary greatly, and the main cause of variation in $-\Delta G_o$ values was that in $-T\Delta S_o$ values. Residual fertilizer K and FYM residues decreased preference for K at both locations, but more so at Broadbalk than at Saxmundham, presumably because of the greater duration and amount of K manuring at Broadbalk. FYM residues had a very complex effect on the exchange characteristics of Broadbalk soil. It is suggested that these differences are caused by the different pH values of the surface soils before they came into arable usage, which reflect their contrasting parent materials and pedogenic histories, and by the different durations and extents of manuring in the two experiments.

INTRODUCTION

The thermodynamic functions of cation exchange reactions have been used frequently to characterize and compare soils and clay minerals (e.g. Laudelout *et al.*, 1968; Jensen, 1973; Bansal, 1982). In particular Talibudeen (1971, 1972) suggested that, in K-Ca exchange, changes in the activity coefficients of adsorbed K and Ca and in the excess functions, with K saturation, were related to the composition of the phyllosilicate (layer silicate) content of soils. These conclusions have been confirmed by recent calorimetric measurements in which 'pure' phyllosilicate surfaces were identified in clays on the basis of their differential heats of K-Ca exchange, and their known degree of interlayer expansion on adsorbing ethylene glycol (Goulding & Talibudeen, 1980; Talibudeen & Goulding, 1983*a, b*).

This paper describes the extension of such measurements to soils from plots of the Broadbalk (Batcombe series) and Saxmundham Rotation I (Beccles series) Experiments, selected for differences in accumulated potassium and organic matter residues. Walsh (1972) criticized the lack of practical usefulness of thermodynamic functions. In particular, he pointed out that work on the influence of organo-mineral complexes on such properties had not been reported. This paper deals with these points, and suggests reasons for differences in the K exchange characteristics of the Batcombe and Beccles series soils, and anomalies in the K exchange characteristics of the FYM plot soils from the Classical Experiments noted earlier (Williams & Cooke, 1971; Addiscott & Johnston, 1971, 1975).

Table 1. Physical and chemical properties of the soils

Soils	Batcombe Series				Beccles Series		
	Broadbalk Plot				Saxmundham Plot		
	3	5	8	2	6	7	1
Manuring	Nil	PKNaMg	N ₃ PKNaMg	FYM	Nil	PK	FYM
CaCO ₃ (%)*	2.4	1.7	0.5	2.0	1.1	0.8	0.7
pH (0.01 M CaCl ₂)	7.5	7.4	7.0	7.2	7.2	7.1	7.2
Organic carbon (%)*	0.84	0.91	1.04	2.59	0.79	0.82	1.38
K treatment (kg ha ⁻¹ a ⁻¹)*	0	90	90	160	0	53	68
Duration (years)*			137			81	
Approximate K removals (kg ha ⁻¹ a ⁻¹)*	14	19	52	59	25	32	91
CEC (µeq g ⁻¹)	128	145	139	176	149	142	226
%K saturation	2.0	6.4	5.4	9.6	2.2	2.8	3.2
Particle size distribution (%)†							
<0.2 µm			12			22	
<2 µm			22			35	
<20 µm			48			46	
Clay mineralogy‡			m = 13%; k = 19%; iem = 51%		m = 15%; k = 14%; iem = 54%		
Surface area (m ² g ⁻¹)§	101	97	102	95	168	150	153
Surface charge density (µeq m ⁻²)	1.27	1.49	1.36	1.85	0.89	0.95	1.48

* From Johnston (1969) and Williams & Cooke (1971).

† From Weir *et al.* (1969) and Goulding & Talibudeen (1979).

‡ m = mica, k = kaolinite; iem = interstratified expanding minerals; by XRD analysis (Weir *et al.*, 1969; Goulding & Talibudeen, 1979).

§ From the adsorption of ethylene glycol vapour (Rawson, 1969).

MATERIALS AND METHODS

Soils

Relevant details of soils from selected plots of the two Experiments are given in Table 1. The Batcombe soil has been in permanent wheat since 1843, and the Beccles soil in a wheat, beet, barley and beans rotation from 1899 to 1969. The soils were sampled in 1966 from the surface layer (0–20 cm) of all plots. Multiple cores were bulked from each plot to give the main sample, from which subsamples were taken for this experiment.

Heats of K–Ca exchange

These were measured at 30°C by a microcalorimetric method (Talibudeen *et al.*, 1977; Minter & Talibudeen, 1982). Briefly this involves adding successive 5 µl aliquots of 0.5 M KCl to a suspension of about 50 µeq calcium saturated soil, and measuring the heat change following each addition. The heats were thus measured over a concentration range of 0.05–0.18 M. Heats of mixing and dilution were eliminated by a simultaneous reaction without soil. The relationship between the differential heat, $-d(\Delta H_x)/dx$, thus obtained and the fractional K saturation, x , of the soil's negative charge (CEC) was analysed by an iterative procedure to separate regions

Table 2. Standard thermodynamic parameters of Ca→K exchange on the soils*

	Batcombe				Beccles			SE
	Nil	PKNaMg	N ₃ PKNaMg	FYM	Nil	PK	FYM	
$-\Delta G_o$ (kJ eq ⁻¹)	2.0	0.0	1.6	-3.4	5.3	3.8	1.1	± 0.2
$-\Delta H_o^\dagger$ (kJ eq ⁻¹)	10.0	7.5	7.0	8.0	9.0	8.0	10.0	± 0.3
$-T\Delta S_o$ (kJ eq ⁻¹)	8.0	7.5	5.4	11.4	3.7	4.2	8.9	± 0.6

* At 30°C, and over the concentration range 0.05–0.18 M,

† $\Delta H_o = \Delta H_{x=1}$, see text.

of constant $-d(\Delta H_x)/dx$ (Goulding & Talibudeen, 1980). As before, a 'stepped straight lines' (linear spline) fit was considerably better than that of a single smooth curve, the residual mean square of the latter being on average about 7 times that of the former. Progressively integrating $-d(\Delta H_x)/dx$ values gave the integral heat of exchange, $-\Delta H_x$. This was extrapolated to $x=1$ to give $-\Delta H_{x=1}$, which was taken to be equal to the standard heat of exchange, $-\Delta H_o$, within experimental error. This extrapolation was justified previously by measuring the reverse exchange process (i.e. K→Ca exchange; Goulding & Talibudeen, 1980), and by comparing $-\Delta H_{x=1}$ with an independently measured $-\Delta H_o$ value (Maes *et al.*, 1976; Talibudeen *et al.*, 1977).

K-Ca exchange isotherms

The fractional K saturations after the KCl additions during microcalorimetry were obtained in a separate experiment. In this, soil:solution ratios and other experimental conditions were identical to those during microcalorimetry, except that the amounts were increased proportionately to give more precision in the chemical and radiochemical analyses. Adsorbed K and Ca values were obtained by isotopic exchange with ⁴²K and ⁴⁵Ca, and K and Ca in solution by flame photometry. The standard and differential thermodynamic functions were then calculated as before (Deist & Talibudeen, 1967; Goulding & Talibudeen, 1980). The maximum K saturation attained varied from 50% to 65%.

Although the Beccles soil contained less CaCO₃ than the Batcombe soil, isotopically exchangeable Ca from the CaCO₃ greatly increased its apparent CEC, presumably because of its much finer particle size (cf. Arambarri & Talibudeen, 1964; Goulding & Talibudeen, 1979). Its 'real' CEC value was obtained by isotopic exchange with ⁴⁵Ca and ⁴²K after CaCO₃ removal by dilute HCl treatment.

RESULTS

Differences between the soil series

The pH values, calcium carbonate and organic matter contents, and clay mineral compositions (determined by X-ray diffraction, XRD) of the untreated soils (Nil plots) are very similar (Table 1). Differences in crop yields, drainage and ease of cultivation have been ascribed to the different particle size distributions of the soils (Cooke & Williams, 1972). Very relevant to our measurements are differences in geology (Catt, 1969; Hodge, 1972) and that, unlike the Beccles soil, the Batcombe soil is part of the 'originally acid soil of the Chiltern plateau' and was treated with chalk dug from the underlying Upper Chalk before the nineteenth century (Avery & Bullock, 1969). The effects of K and organic matter residues at the two sites may also differ because the amounts and duration of application of fertilizers and FYM, and also crop uptakes and root and stubble residues are not the same.

Standard free energy

The order of K preference, expressed by $-\Delta G_o$ values (Table 2), was: Beccles Nil > Beccles PK > Batcombe Nil > Batcombe N₃PKNaMg > Beccles FYM > Batcombe PKNaMg >

Batcombe FYM. This correlates with the per cent K saturation of the soils (Table 1), showing that the K selectivity of a soil decreases as its accumulated K residues increase

$$-\Delta G_o = -0.88 (\%K) + 5.47; \text{variance accounted for} = 74.0\% (P \leq 0.01)$$

The regressions for the two soils are, however, very different:

$$\text{Batcombe, } -\Delta G_o = -0.72 (\%K) + 4.26; \text{variance accounted for} = 76.3\%$$

$$\text{Beccles, } -\Delta G_o = -4.07 (\%K) + 14.51; \text{variance accounted for} = 84.9\%$$

Thus the $-\Delta G_o : \%K$ relationship for the Beccles soil has a much greater negative slope, indicating that changes in K saturation have a much greater effect on the K selectivity of the Beccles than the Batcombe soil. This may well be due to the much greater clay and fine clay content of the Beccles soil.

Of special interest are the observations that (a) in the Batcombe PKNaMg soil, residual K from 137 years' K manuring increased K-saturation by 4.4% and decreased $-\Delta G_o$ by 2 kJ eq^{-1} such that neither ion was preferred in K-Ca exchange, (b) in the Batcombe FYM soil, K and organic matter residues combined to make the soil matrix 'prefer' the Ca ion, and (c) the Beccles soil preferred the K ion more than did the Batcombe soil in all comparable treatments, i.e. the Nil, PK and FYM pairs.

Standard heat

The heat of Ca \rightarrow K exchange is the sum of all the heats of bond formation and dissolution in the reaction, including those caused by changes in cation and surface hydration. It is therefore a direct measurement of the difference in the relative bond strengths of a Ca-clay and a K-clay. The standard heats measured here (Table 2) indicate that K is bound more strongly than Ca to the exchange complex in all these soils in the order: Batcombe Nil = Beccles FYM > Beccles Nil > Batcombe FYM = Beccles PK > Batcombe PKNaMg > Batcombe N₃PKNaMg, although the differences between the soils are not very great. This order differs from that of the K selectivities, which indicates that in these soil samples, enthalpic and entropic forces interact in different ways to determine overall K selectivity. All K treatments decrease binding strength for K.

Standard entropies

The $-T\Delta S_o$ values (Table 2) reflect the extent and nature of the rearrangement of cations and surfaces, and of their water of hydration. A positive $-T\Delta S_o$ value for Ca \rightarrow K exchange implies greater disorder of these components in the Ca-saturated than in the K-saturated soil. A comparative 'disorder' scale is

Batcombe FYM > Beccles FYM > Batcombe PKNaMg = Batcombe Nil > Batcombe N₃PKNaMg > Beccles PK = Beccles Nil

Thus the Batcombe soil has, in all comparable manurial treatments, a more highly disordered matrix than its Beccles counterpart. It is suggested (J. A. Catt, personal communication) that this results either from differences in the nature of the soil parent materials, or from the different weathering histories of the two soils. Thus the Batcombe parent material was mainly Reading Beds Clay deposited in a tropical terrestrial environment, whereas the Beccles parent material was mainly Chalky Boulder Clay deposited subglacially. Likewise, the Batcombe soil was developed over at least 300 000 years and under fluctuating climatic conditions (Catt, 1969) whereas the Beccles soil has probably formed over the last 10 000 years when the climate differed little from the present day. Both factors helped make the Batcombe soil much more acid than the Beccles soil prior to modern cultivation, and a long period of acidity could account for the greater thermodynamic disorder of the Batcombe soil.

The 'disorder' scale also shows that (a) residual K accumulated after many years at the two locations has had little effect on their degree of disorder if the K treated plots are compared with the Nil plots at each site; and (b) the organic residues from long-term FYM treatments have greatly increased this degree of disorder.

Comparing $-\Delta H_o$ and $-T\Delta S_o$ values shows that $-T\Delta S_o$ values are much more variable than $-\Delta H_o$ values, and are the main cause of the variation in $-\Delta G_o$ values. However, this

Table 3. Groups of cation exchange sites with constant differential heat, $-d(\Delta H_x)/dx$ (kJ eq⁻¹), in the soils for the first 50-60% of their CEC (x =fractional K saturation at which a transition occurs*)

Groups of sites	Batcombe				Beccles				Mean ± SE
	Nil†	PKNaMgt	N ₃ PKNaMgt	FYM†	Nil†	PK†	FYM†		
1	—	—	—	7.6 (0.115)	—	—	—	0.3	
2	12.9 (up to $x=0.50$)	—	—	17.3 (0.291)	12.3 (0.254)	—	—	0.3	
3	—	9.7 (0.337)	—	—	9.8 (0.487)	10.8 (0.380)	10.0 (up to $x=0.52$)	0.3	
4	—	—	8.6 (0.333)	—	—	8.1 (up to $x=0.55$)	—	0.3	
5	—	7.0 (up to $x=0.50$)	6.7 (up to $x=0.50$)	11.5 (up to $x=0.45$)	6.7 (up to $x=0.55$)	—	—	0.3	

* Mean SE for transitional x values = ± 2.4%.

† Manuring.

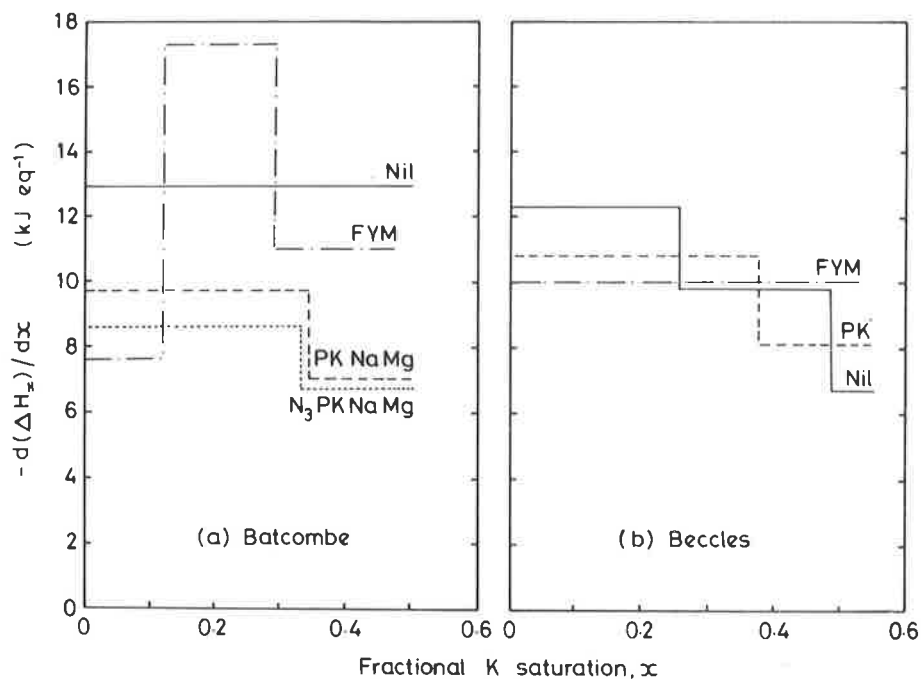


Fig. 1. Differential heat of Ca→K exchange, $-d(\Delta H_x)/dx$, versus fractional K saturation, x , for the soils.

comparison shows that, in all soil treatments except Batcombe PKNaMg and FYM, stronger binding of K outweighs the effect of a more regular rearrangement of the components of exchange on replacement of Ca by K in determining the sign of $-\Delta G_0$, giving the soil a preference for K.

Differential heat of exchange

The variation in differential heat of Ca→K exchange, $-d(\Delta H_x)/dx$, with K saturation was used earlier to show heterogeneity in some standard phyllosilicate minerals (Goulding & Talibudeen, 1980; Talibudeen & Goulding, 1983*a, b*). Altogether six groups of exchange sites were observed, up to four in any one mineral. These groups were ascribed to pure 2:1 phyllosilicate surfaces: mica, $-d(\Delta H_x)/dx \approx 10-11 \text{ kJ eq}^{-1}$; illite or hydrous mica, $-d(\Delta H_x)/dx \approx 8-9 \text{ kJ eq}^{-1}$; vermiculite, $-d(\Delta H_x)/dx \approx 15-16 \text{ kJ eq}^{-1}$; montmorillonite, $-d(\Delta H_x)/dx \approx 5-7.5 \text{ kJ eq}^{-1}$. Similar heterogeneity is observed in the Batcombe and Beccles soils (Table 3, Fig. 1). Up to three groups of sites occur in any one soil, and altogether there are five groups of sites whose differential heats differ only in minor detail from those of the standard phyllosilicates. Based on the $-d(\Delta H_x)/dx : x$ analysis, and following the method of calculation used earlier (Talibudeen & Goulding, 1983*a*), the types of mineral surfaces in the soils from the nil plots were calculated (Table 4). Measurements were made up to K saturations of 50–60% only. At K saturations greater than this exchange sites will have similar or lower binding strengths than the group of sites with the lowest binding strength recorded. In Table 4, therefore, the content of montmorillonite in the whole soil, and that in the clay fraction derived from that in the whole soil, includes true montmorillonite layers that account for the remaining fraction of the CEC not covered by the calorimetric measurements. Also, as before (Talibudeen & Goulding, 1983*b*), kaolinite is considered to have no permanent negative charge, its CEC being ascribed to 2:1 phyllosilicate impurities.

According to XRD evidence, the dominant minerals in the clay fractions of both soils are interstratified expanding minerals (iem) with some mica and kaolinite, consisting mainly of a modified vermiculite in the Batcombe soil (Weir *et al.*, 1969). This is supported to some extent by the $-d(\Delta H_x)/dx$ evidence. When compared with differential heat analyses given

Table 4. Mineralogical composition of the whole soil and the <2 μm fraction of soils from the Nil plots, calculated from their $-d(\Delta H_x)/dx$: x relationship for the first 50–60% of their CEC

2 : 1 phyllosilicate (on EG adsorption*)	Batcombe series		Beccles series	
	Whole soil	<2 μm fraction†	Whole soil	<2 μm fraction†
Mica (no expansion)	—	—	1.4%	4.0%
Vermiculitic mica (1/4 expansion)	2.6%	11.8%	1.5%	4.4%
Montmorillonite (full expansion)	4.9%	22.4%	5.2%	16.8%
Uncharged minerals (by difference)	92.5%	65.8%	91.9%	74.8%

* This refers to the known interlayer expansion of the 2 : 1 phyllosilicates by ethylene glycol adsorption. The calculation of these mineral compositions was described earlier (Talibudeen & Goulding, 1983a, b).

† Calculated from the values for the whole soil and the <2 μm clay content (Table 1).

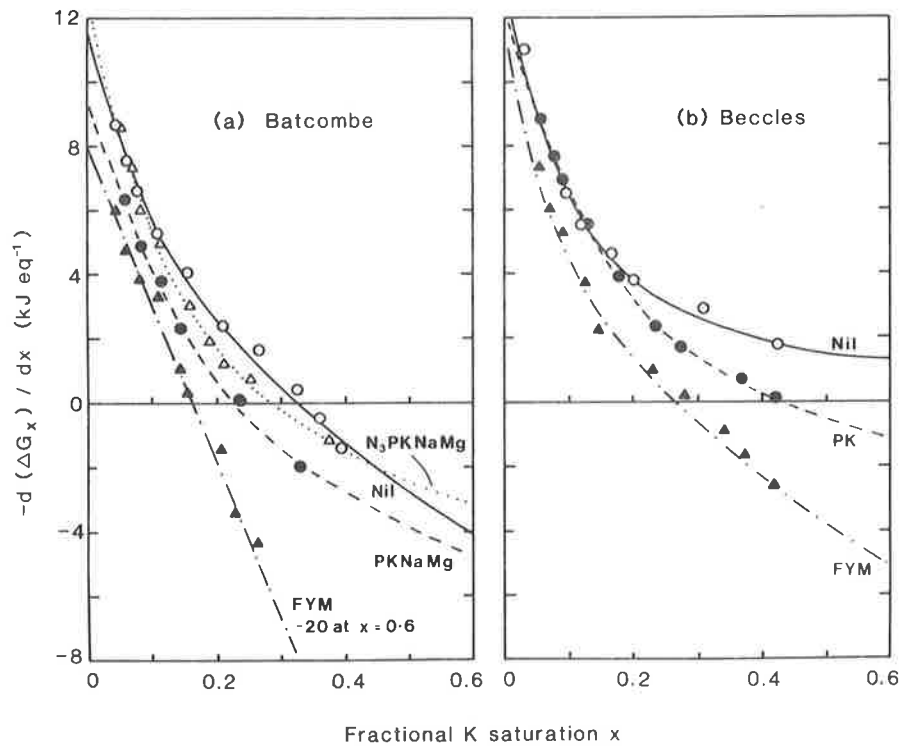


Fig. 2. Differential free energy of Ca→K exchange, $-d(\Delta G_x)/dx$, versus fractional K saturation, x , for the soils: Nil (O), PK or PKNaMg (●), N₃PKNaMg (Δ), FYM (▲).

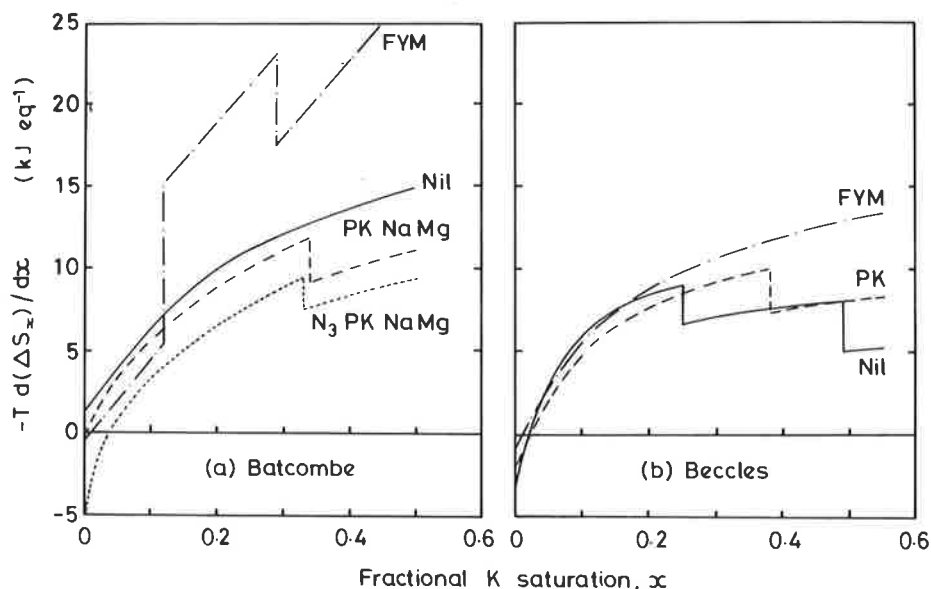


Fig. 3. Differential entropy of Ca→K exchange, $-Td(\Delta S_e)/dx$, versus fractional K saturation, x , for the soils.

previously (Goulding & Talibudeen, 1980; Talibudeen & Goulding, 1983a, b), the single group of sites in the Batcombe Nil soil with a $-d(\Delta H_e)/dx$ value of 12.9 kJ eq^{-1} can be assigned to an interstratified 2:1 phyllosilicate, with mixed true mica, vermiculite and montmorillonite layers. It is most likely that, at K saturations $>50\%$, true montmorillonite layers with $-d(\Delta H_e)/dx$ values of $5.5\text{--}7.5 \text{ kJ eq}^{-1}$ would be observed. In the Beccles soil, by contrast, 26% of the exchange sites can be assigned to a hydrous mica (mica-montmorillonite interstratification), 23% to true mica layers, and the remainder to true montmorillonite layers. As with the Batcombe soil, at K saturations $>55\%$ the negative charge can be attributed to true montmorillonite layers. So there are considerable differences in the surfaces involved in Ca→K exchange which are not apparent from XRD evidence.

The FYM treated soil from Broadbalk exhibited an abnormal $-d(\Delta H_e)/dx : x$ curve (Fig. 1, Table 3), in that up to a fractional K saturation of 0.115, a $-d(\Delta H_e)/dx$ value of 7.6 kJ eq^{-1} occurred, which increased to 17.3 kJ eq^{-1} at higher K saturations. Replicate runs confirmed these observations to be correct, and that equilibrium had been achieved. No such abnormal effect was seen in the Beccles FYM soil. Here, residual K had merely eliminated the 12.3 kJ eq^{-1} group of sites observed in the Nil plot soil such that only a homogeneous group of sites with a $-d(\Delta H_e)/dx$ value of 10.0 kJ eq^{-1} was observed. To interpret, albeit speculatively, the contrasting differential heat patterns of the FYM treated soils it is necessary to refer to those of the Nil soils. Also relevant to the interpretation is that FYM treatment increased the organic carbon content of the Batcombe soil from 0.84% to 2.59% over 123 years, but of the Beccles soil from 0.79% to only 1.38% over 80 years. The rate of increase of organic carbon in the Batcombe soil ($0.0142\% \text{ a}^{-1}$) was therefore exactly twice that in the Beccles soil ($0.0074\% \text{ a}^{-1}$) because the rate of application of FYM was almost 2:1 (Table 1).

The elimination of the 12.3 kJ eq^{-1} group of sites observed in the Beccles FYM soil points to a decrease in K binding strength due to the adsorption of K residues on sites that bind K strongly (but see 'Effect of organic matter residues' below). The exchange was not taken far enough to show whether the 6.7 kJ eq^{-1} true montmorillonite sites observed in the Nil soil also occurred in the FYM soil. The very long period of interaction of the Batcombe soil with large amounts of fresh and degraded FYM residues seems to have separated the components of the exchange process, such that the vermiculitic, micaceous and montmorillonitic surfaces, which are interstratified in the Nil soil, were observed distinctly in the FYM

soil. However, the increase in the differential heat with K saturation points to effects induced by organic matter in addition to such a separation. The effects are discussed below.

Differential free energy and entropy

Preference for K, shown by $-d(\Delta G_x)/dx$, decreased as K saturation increased in all the soils (Fig. 2) as would be expected. Furthermore, residual K decreased the K preference of all exchange sites.

The derived $-Td(\Delta S_x)/dx : x$ relationship (Fig. 3) reinforces the conclusion for the Nil treatment soils, at least up to $x=0.5$, that the Batcombe soil has only one homogeneous group of sites whereas the Beccles soil has three such groups. The differences between the soils from the FYM treatments at the two locations are again apparent. Between $x=0.12$ and 0.29 a much-disordered group of sites was exposed in the Batcombe soil whose differential entropy decreased sharply with increasing K saturation. This contrasts with the smooth decrease in the Beccles soil reflecting the homogeneous character of its organo-mineral complex.

DISCUSSION

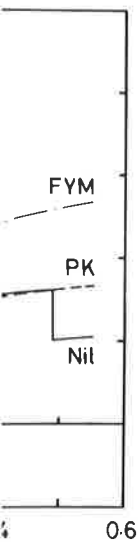
Effect of K residues

The $-\Delta H_0$ and $-\Delta G_0$ values (Table 2) are considerably less on the PK or PKNaMg plots than on the Nil plots, and the $-d(\Delta G_x)/dx : x$ relationships show a decrease in K preference over all exchange sites (Fig. 2). The $-T\Delta S_0$ values and $-Td(\Delta S_x)/dx : x$ relationships (Fig. 3) of these plots are not significantly different, however. This suggests that K residues decrease K binding strength and hence K preference without rearranging the cation exchange matrix of the soil greatly. Addiscott & Johnston (1975) and Goulding (1981) concluded that the decrease in K binding strength and preference, accompanying a build-up of K reserves, reflects a slowly reversible adsorption of K on the K-selective sites at the weathered periphery (frayed-edges) of 2:1 phyllosilicates in soils. They inferred that, on adsorbing K, frayed-edges collapse, eliminating the highly K selective sites and thus decreasing K selectivity. However, the differential heats and free energies observed in the present work show a stepped decrease in K binding strength and a gradual decrease in K preference to at least $x=0.55$, not just the disappearance of a group or groups of sites. Also, if only frayed-edges collapsed, causing a considerable rearrangement of cation exchange surfaces, one might expect a large change in entropy that is not observed here. Again, the decrease in K selectivity by such a method would be accompanied by a significant decrease in CEC. The data in Table 1 suggest that there is no such decrease in these two soils, and Addiscott (1970) found only a very small decrease in CEC of the mineral fraction of the Batcombe PKNaMg soil after 100 years of K fertilizer treatment. Thus the decrease in K selectivity observed here is not caused by K fixation at frayed edges but by the gradual modification of exchange sites.

Effect of organic matter residues

The effect of organic matter (OM) residues on the soils of the FYM plots is complicated by the fact that FYM also adds much soluble potassium to the soil. However, it was shown in the previous section that K residues affect principally the binding strength of K and hence K selectivity, and so the effect of OM can be isolated.

In the Beccles FYM soil, preference for K is less than that of the Nil soil because of (i) a lower K binding strength over the first 25% of K saturation (Fig. 1b), and (ii) a much greater degree of randomness, in the arrangement of the components of the exchange, causing a large increase in their order upon Ca \rightarrow K exchange, over 25–52% K saturation (Fig. 3). In the Batcombe FYM soil, an abnormal situation is observed. Its preference for K is very much less than that of the Batcombe Nil plot soil, especially at high K saturations (Fig. 2a). Sites of low binding strength adsorb K at lower K saturations than sites of higher binding strength (i.e. the differential heat increases with K saturation, Fig. 1a), the reverse of what one would expect, and a large increase in order occurs from $x=0.12$ onwards (Fig. 3a). Overall, therefore,



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In both soil series there is much greater disorder in the Ca-forms of the FYM soils than those of the Nil soils (cf. also $-T\Delta S_0$ values in Table 2). This is presumably caused by OM residues, which may be adsorbed to form a surface coating on the clay minerals, or associated with them by means of a bridging complex with Ca ions (Greenland & Mott, 1978, p. 336).

The complicated effects observed with the Batcombe FYM soil are difficult to explain. While twice the amount of FYM has been added to this soil, and residues of OM have increased at twice the rate of those in Beccles FYM soil, the different amounts of OM are unlikely to be the sole cause of the differences in behaviour. It is possible that the behaviour of Batcombe FYM soil reflects the adsorption of some K on organic exchange sites—the differences in behaviour between the two soils being due to differences in the structural composition of the OM residues at the two sites. Alternatively, the behaviour of Batcombe FYM soil may be due to an association of OM with exchange surfaces, modifying their reactivity towards K by preventing K ions from reaching the most reactive sites (cf. Beckett & Nafady, 1967; Greenland & Mott, 1978, p. 322). As the equivalent fraction of K on the surface and in solution increases, the 'bridging' between adsorbed Ca and organic matter will weaken, the OM will be desorbed—an endothermic reaction—so that K is then adsorbed on 'high-energy' sites thus exposed; a similar modifying effect of OM was noted previously (Imai *et al.*, 1981). The destabilizing effect of monovalent cations on clay-OM complexes, and the mechanisms of association and dissociation were reviewed by Theng (1979). That this complicated picture is not observed with the Beccles FYM soil is presumably due to the appreciable differences between the two soils at the beginning of the experiments, i.e. different parent materials and periods of weathering, and different types and amounts of organic residues from the FYM treatment.

Others have observed anomalies in the K exchange characteristics of the FYM plot soils. Williams & Cooke (1971) found that the K exchangeable to M ammonium acetate of the Beccles FYM soil was more available to crops than that of mineral plots. They attributed this to either an underestimation of K in FYM, or to FYM greatly increasing the solubility of K. Addiscott & Johnston (1971) found this effect in the FYM plot soils of all the Classical Experiments at Rothamsted, and attributed this to extra K held in a form more available to plants on these plots. They later found that the relationship between exchangeable and non-exchangeable K on the FYM plots of several of the Classical Experiments was not the same as that on the mineral plots (Addiscott & Johnston, 1975). They ascribed this to K on the FYM plots being held on organic exchange sites not in equilibrium with non-exchangeable K on clay mineral exchange sites. Equally possible, and favoured by the data presented here, is a modifying effect of well-degraded OM as a coating on mineral surfaces.

CONCLUSIONS

There are considerable differences in the K-Ca exchange characteristics of the Batcombe and Beccles soils which would not be expected from their very similar clay mineral compositions based on XRD. The $-d(\Delta H_e)/dx : x$ relationship points to the presence of an appreciable amount of mica in the Beccles soil, but none in the Batcombe soil. The $-Td(\Delta S_e)/dx : x$ curves indicate considerably more disorder in the Batcombe soil. The Batcombe soil therefore appears to be far more weathered than the Beccles soil, and thus has less preference for K over Ca. These differences could be related to the nature of the parent materials, the weathering history of the soils, or their husbandry before they were put to arable and experimental usage. To distinguish between these possible causes, we need to examine by the same methods the parent materials of the two soils, which we hope to report later.

Differential heats and entropies of exchange also show differences in the way in which inorganic K and FYM residues react with the soils. Whereas K residues from inorganic fertilizers decrease preference for K by reducing K binding strength, FYM residues reduce K preference to an even greater extent by causing increased disorder in the clay matrix, and possibly by blocking the most K selective sites.

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