

SOIL SCIENCE

Exchange Equilibria of Sodium on Some British Soils

BECKETT^{1,2} has discussed potassium-calcium exchange energies in soil suspensions, using a development of a thermodynamic approach suggested by Woodruff³ and Schofield and Taylor⁴. He showed that a graph of the "activity ratio"

$$\frac{a_K}{\sqrt{a_{(Ca+Mg)}}}$$

(called AR_K) in the solution plotted against the changes in exchangeable soil potassium (ΔK) is usually linear except at small values of AR_K , where it curves sharply and becomes asymptotic to the ΔK axis (Fig. 2). AR_K is directly related to the change in free energy when equivalent amounts of potassium and calcium are exchanged between the soil and solution phases. Beckett³ considers that the curvature is produced by a small proportion of potassium ions held on discrete exchange sites with a greater preference for potassium relative to calcium. These sites determine the exchange energy when nearly all the exchangeable potassium is removed. Very recently he has found evidence of similar behaviour for calcium and magnesium⁵.

We have used the same approach to investigate the $Na - (Ca + Mg)$ exchange in several British soils. Soil samples were equilibrated at 20° C with solutions with calcium chloride concentrations of 0.01 molar containing various amounts of sodium. The suspensions were centrifuged and the solutions analysed by flame photometer and EDTA titration.

$$\frac{a_{Na}}{\sqrt{a_{(Ca+Mg)}}}$$

(AR_{Na}) and ΔNa were then calculated. The graphs obtained with both mineral soils in Fig. 1, and with all others tested, show a clear curvature at small amounts of exchangeable sodium, whereas no curvature could be found for an organic peat soil (C). The peat soil was converted to the calcium form by leaching with calcium chloride and again tested to give greater accuracy at small values of AR_{Na} , but the measurements again gave a straight line graph (Fig. 1D). These results imply the presence of a few exchange sites where sodium is held more strongly, relative to calcium, than it is elsewhere, and that these sites are probably associated with the soil minerals rather than the soil organic matter. It seems likely that any clay mineral will have a small proportion of exchange sites where the surface configuration will preferentially favour the adsorption of a particular ion relative to others. Sodium held on exchange sites at greater exchange energies than expected corresponds to less than 0.6 per cent of the exchange capacity in the soils used to obtain the results in Fig. 1; however, a significant proportion of the exchangeable sodium found in all the mineral soils tested is held on these "preferred sites".

Curvatures in the plots of $AR_{Na} - \Delta Na$ at low levels of exchangeable sodium have not previously been reported, probably because other workers⁶⁻⁸ have worked with relatively large amounts of exchangeable sodium on the

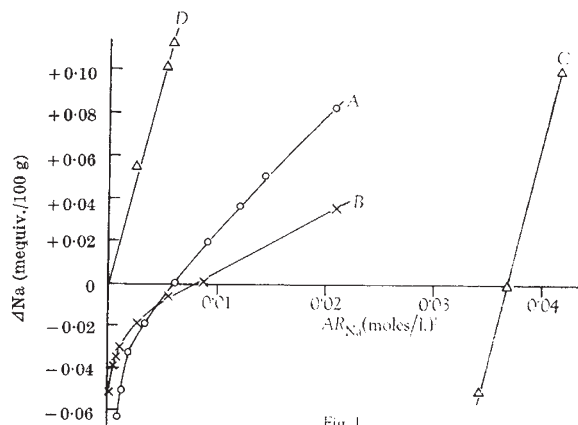


Fig. 1

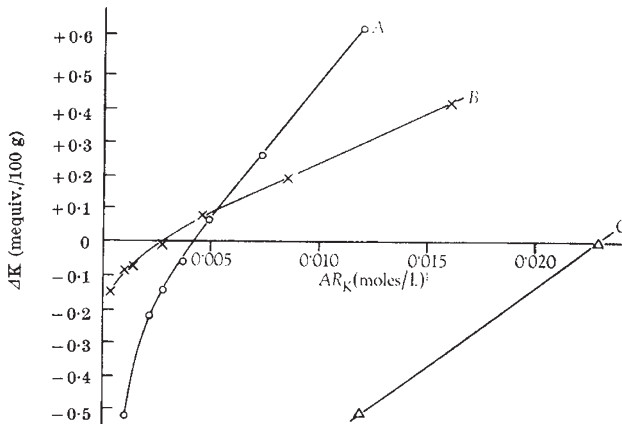


Fig. 2

Figs. 1 and 2. Activity ratios and changes in exchangeable ions for sodium (Fig. 1) and potassium (Fig. 2) in three soils. ○, Soil A; ×, soil B; △, soil C.

soil, when this effect would not be noticed. However, Levy and Mor⁹ recently showed that a graph of the "sodium absorption ratio" (SAR)

$$\frac{Na}{\sqrt{\frac{1}{2}(Ca+Mg)}}$$

and the "exchangeable sodium percentage" (ESP) for an Israeli soil gave an SAR of zero when the ESP was still 5.5 per cent. This is analogous to our results, though with much more sodium in both soil and solution. Their results may possibly be explained by the presence of a zeolite with exchange sites from which calcium cannot displace sodium such as analcime which Schultz *et al.*¹⁰ found recently in some saline soils.

The slopes of the linear part of the $AR_{Na} - \Delta Na$ graphs were much smaller than those of the $AR_K - \Delta K$ graphs (Fig. 2) for all soils. This agrees with the usual finding that potassium is held on the soil more strongly than sodium.

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³ Woodruff, C. M., *Soil Sci. Soc. Amer. Proc.*, **19**, 36, 98 and 167 (1955).

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⁷ Bower, C. A., *Soil Sci.*, **88**, 32 (1959).

⁸ Pratt, P. F., Whittig, L. D., and Grover, B. L., *Soil Sci. Soc. Amer. Proc.*, **26**, 227 (1962).

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¹⁰ Schultz, R. K., Overstreet, R., and Barshad, I., *Soil Sci.*, **99**, 161 (1964).

Table 1. SOIL ANALYSIS RESULTS

Soil	(A) Rothamsted (Barnfield)	(B) Brooms Barn	(C) Feltwell Fen
Texture	Clay loam	Sandy loam	Peat
Coarse sand (%)	11	39	<1
Fine sand (%)	35	41	3
Silt (%)	20	9	17
Clay (%)	32	10	<1
Exchangeable sodium, mequiv./100 g	0.17	0.06	0.78
Exchangeable potassium, mequiv./100 g	0.51	0.20	0.95
Exchange capacity (ammonium saturation) mequiv./100 g	24.3	11.0	146.0
pH (water)	8.1	7.1	7.5
Loss on ignition (%)	—	—	75