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CONTRIBUTION OF ORGANIC CARBON AND CLAY TO CATION EXCHANGE CAPACITY IN A CHRONOSEQUENCE OF SANDY SOILS

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SUMMARY

CEC and oxidisable carbon content were highly correlated ($r = 0.96$) whereas a lower coefficient was obtained for a correlation of CEC and clay content ($r = 0.57$) in a chronosequence of sandy soils from New Zealand.

Partial regression coefficients for oxidisable carbon were highly significant in multiple regression equations for all soil groupings whereas in only one equation was the coefficient for clay significant. The CEC of the organic matter for all soils was 1.4 me/g and this value decreased from 1.64 me/g in the young soils to 1.22 me/g in old soils.

Peroxidation of selected surface samples caused a reduction in CEC but the results indicated that the clay fractions had a considerably higher CEC (0.57 me/g) than that inferred from multiple regression equations for untreated samples. Selective dissolution analysis indicated that the clay fractions of these soils contained an appreciable amount of amorphous material. Reduction in the CEC of the clay fraction apparently occurs through a blocking by organic matter of the negative charge of the clay components.

INTRODUCTION

Several studies have shown that the cation-exchange capacity (CEC) of soils is closely related to the contents of organic carbon [10 20] and clay [22]. Multiple regression equations have frequently been used to determine the relative contribution of organic carbon and clay to CEC [1 6 7 14 21 22]. The advantages of using multiple regression analyses, whereby the CEC of either the organic or clay fractions is obtained directly from regression coefficients without the removal of each component by chemical treatment, have been discussed by Helling *et al.*[7] As pointed out by Wilding and Rutledge [21], how-

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ever, soils of diverse genesis have usually been included in regression analyses and little or no attempt has been made to control variables such as the texture and mineralogical composition of the parent material and soil drainage properties.

Soil chronosequences offer a unique opportunity to study the contribution of organic carbon and clay to CEC because, by definition [9], the soil-forming factors other than time are held constant or ineffectually varying, and consequently the effects of variations in parent material characteristics and soil drainage properties are largely eliminated.

Since the writers had investigated a chronosequence of weakly-weathered soils developed on wind-blown sand in New Zealand [18], it seemed of interest to study the extent to which the CEC of these soils was determined by organic carbon and clay.

The purpose of this paper is to examine the CEC properties, as a function of organic carbon and clay, of a chronosequence of sandy soils and to investigate the effect of charge blocking by organic matter of exchange sites on the clay.

MATERIALS AND METHODS

The chronosequence of soils developed on wind-blown sand in the Manawatu District of the North Island of New Zealand has been described by Cowie [4]: some aspects of the chemistry of these soils have been discussed previously [18]. The dune-building phases are named Waitarere (50 years), Motuiti (500 years), Foxton (3000 years), and Koputaroa (10,000 years) with the present beach sand being regarded as the stage 'time-zero'. The parent material of the soils is wind-blown sand which is dominated by feldspar and quartz with minor augite, hypersthene, hornblende, mica, and magnetite. In most instances, profiles were sampled approximately half-way down south-facing dune slopes which carried native vegetation.

An ammonium acetate leaching procedure was used for the determination of CEC [13]. Subsequent to leaching with 1 *N* (pH 7) ammonium acetate and 80% ethanol, the NH_4^+ retained by the soil was determined by Kjeldahl digestion and distillation using MgO as the alkaline reagent. Clay content ($< 2\,\mu$) was determined by the pipette method [12] and organic carbon by a modification of the Walkey-Black wet-oxidation method [2]. No correction factor was used in calculating the latter results which are expressed as % oxidisable carbon. Clay ($< 2\,\mu$) and silt 20–2 μ) fractions were separated from the surface soils by conventional procedures [8]. Samples of clay and silt were K-saturated and dried on glass slides at 25°C and heated at 105°C, 300°C, and 550°C. X-ray diffraction patterns were run after each drying treatment using a G.E. XRD unit and CuK_α radiation. To determine whether organic matter was causing a reduction in CEC, either by neutralizing or blocking exchange sites on the clay, the CEC of selected surface samples was determined after prolonged treatment with 6% H_2O_2.

Regressions were calculated between CEC (me/100 g soil) as the dependent variable and oxidisable carbon (%) and clay (%) as the independent variables: both simple and multiple regression equations were calculated using an IBM data processing computer. In addition to determining a multiple regression equation for all soils of the sequence, the soils were divided for statistical analyses into old soils (Foxton and Koputaroa profiles), young soils (beach sands, Waitarere, and Motuiti profiles), and, within all profiles, into upper horizons (the upper two genetic horizons, usually A and A/B) and lower horizons (down to 100 cm).

EXPERIMENTAL RESULTS

Simple correlation

Simple correlation analyses of the data for all soils, summarized in Table 1, indicated that CEC and oxidisable carbon content were highly correlated (Fig. 1) whereas a lower coefficient was obtained

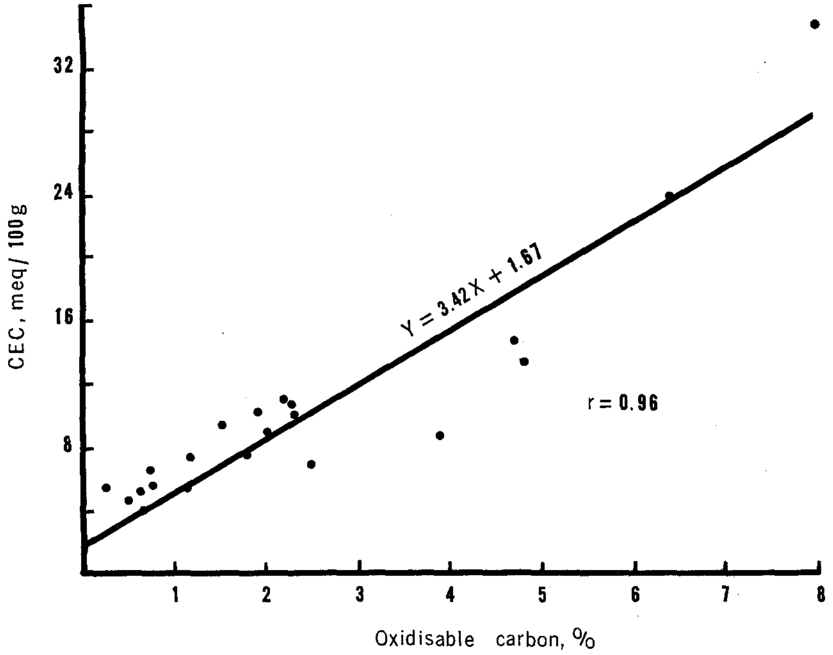

Fig. 1 Relationship between CEC and oxidisable carbon content: data for soils having a CEC less than 4 me/100 g not plotted.

TABLE 1

Means and ranges of CEC, oxidisable carbon, and clay contents of the soils of the chronosequence

Soil groupings	Number of samples used for analysis	CEC me/100 g		Oxidisable Carbon %		Clay %	
		Mean	Range	Mean	Range	Mean	Range
All soils	86	4.0	0.8–34.3	0.68	0.01–7.95	1.4	0.1–14.3
Old soils	32	5.5	2.0–23.9	1.16	0.08–6.36	3.2	0.2–14.3
Young soils	54	3.1	0.8–34.3	0.50	0.01–7.95	0.4	0.1– 2.2
Upper horizons	28	8.7	1.6–34.3	1.91	0.09–7.95	3.2	0.3–14.3
Lower horizons	36	2.4	1.3– 5.6	0.18	0.04– 0.9	0.9	0.1– 8.3

for a correlation of CEC and clay content ($\text{CEC} = 1.05\%$ clay $+ 2.51$, $r = 0.57$). Highly significant correlations between CEC and organic matter have been reported previously for sandy soils by Yuan *et al.*[23] and Kamprath and Welch [10], and for grassland soils low in clay (Walker [20]). It is of interest that simple correlation analysis between oxidizable carbon content and clay content yielded a relatively low coefficient ($\%$ clay $= 1.10\%$ oxidisable carbon $+ 0.67$, $r = 0.57$).

Multiple correlation

Multiple regression equations for all soils and for the soil age and soil horizon groupings (Table 2) gave high R^2 values and all the equations were highly significant. The multiple regression solutions yielded lower R^2 values for the upper and lower horizon groupings. The formation of clay-organic complexes in the upper horizons of the soils of the sequence would result in a decrease in the CEC of the

TABLE 2

Multiple-regression data for soils of the chronosequence relating CEC with oxidisable carbon (OC) and clay (C)

Soil groupings	Multiple regression equations	R^2
All soils	$\text{CEC} = 1.68 + 3.33\ \text{OC}^{**} + 0.06\ \text{C}$	0.92^{**}
Old soils	$\text{CEC} = 2.28 + 2.95\ \text{OC}^{**} + 0.11\ \text{C}$	0.92^{**}
Young soils	$\text{CEC} = 1.68 + 3.68\ \text{OC}^{**} - 0.86\ \text{C}$	0.93^{**}
Upper horizons	$\text{CEC} = 2.07 + 3.34\ \text{OC}^{**} - 0.02\ \text{C}$	0.89^{**}
Lower horizons	$\text{CEC} = 1.66 + 2.03\ \text{OC}^{**} + 0.38\ \text{C}^{**}$	0.80^{**}

** Significant at 1% level.

complex as compared to the CEC of the organic and clay components. It is unlikely that clay-organic complexes are responsible for the lower R^2 value obtained for the lower horizon grouping. A reduction in the range of values of the variables in the multiple regression equation could also yield a lower R^2 value.

Partial regression coefficients for oxidisable carbon were highly significant in all equations but only in the case of the lower horizon grouping was the partial regression coefficient for clay significant. The partial regression coefficient for oxidisable carbon was highest for the young soil grouping and lowest for the lower horizon grouping. On the assumption that oxidisable carbon constitutes 77 per cent of the organic carbon (Bremner and Jenkinson [2]) and that organic carbon constitutes 58 per cent of the organic matter (Hallsworth and Wilkinson [6]), the CEC of organic matter ranges from 0.90 me/g in the lower horizon to 1.64 me/g in the young soil grouping. The CEC of the organic matter for all soils was 1.48 me/g which, although lower than the range of 2 to 5 me/g commonly reported for soil organic matter, is similar to the mean value obtained for Coastal Plain soils from North Carolina (Kamprath and Welch [10]), for sandy soils from Florida belonging to the inceptisol and spodosol groups (Yuan *et al.*[23]), and for soils from southern and central Wisconsin (Helling *et al.*[7]). The fact that the CEC of the organic matter was lower in the old soil grouping (1.22 me/g) than in the young soil grouping (1.64 me/g) reflects a change in the inherent composition of the organic matter. A progressive increase in C/N and C/organic P ratios with an increase in soil development in this chronosequence has been reported previously (Syers, Adams, and Walker [19]).

The partial regression coefficients for clay were considerably lower than those for oxidisable carbon. The low intensities obtained in x-ray diffraction studies of the clay fraction of these soils suggested the presence of amorphous material. The amount of amorphous material, determined by dissolution in 0.5 *N* NaOH (Jackson [8]), in the clay fraction of the surface horizon of modal Waitarere, Motuiti, Foxton, and Koputaroa profiles varied within the narrow range of 50 to 55 percent. Only the clays from the Motuiti and Koputaroa profiles, however, gave a positive reaction to the allophane test with sodium fluoride (Fieldes and Perrott [5]). Claridge [3] has previously commented on the presence of amorphous material in the clay fraction of these soils. Layer silicates identified in the clay fraction of the surface horizons of the soils of the sequence were mica, vermiculite, and mafic chlorite in the younger soils, and vermiculite, pedogenic chlorite, and metahalloysite in the older soils. Small amounts of quartz, cristobalite, and feldspar were identified in all samples.

Positive values for the constant in the multiple regression equations (Table 2) could be due to organic-clay complexes which confound the relationship of CEC of oxidisable carbon and clay (Wilding and Rutledge [21]), to the CEC of the coarser fractions, or to non-linearity near the origin.

Charge blocking

Because the CEC of the clay fraction was apparently very low, organic matter was removed to determine whether the negative charge of the clay was being blocked or neutralized by organic matter. Although a decrease in the CEC of selected surface samples was obtained following peroxidation (Table 3) the results indicate that the clay fractions have a considerably higher CEC than would be inferred from the multiple regression equations for untreated samples (Table 2). The CEC of these peroxidised samples was highly correlated with clay content (Fig. 2) and a mean value of 57 me/100 g was obtained for the CEC of the clay fraction. The value obtained for the constant in the simple regression equation for CEC and clay

TABLE 3

Cation exchange capacity of untreated and peroxidised samples

Soil *		Horizon	CEC	
			Untreated me/100 g	Peroxidised me/100 g
Motuiti	(10)	A1	7.5	3.1
Motuiti	(10)	B1	2.6	1.4
Foxton	(14)	A1	9.1	4.7
Foxton	(14)	A/B	5.6	4.8
Koputaroa	(17)	A1	23.9	9.9
Koputaroa	(17)	A/B	9.7	7.8
Koputaroa	(18)	A1	13.3	6.6
Koputaroa	(18)	A/B	7.6	6.5

* Number in parenthesis indicates soil profile number.

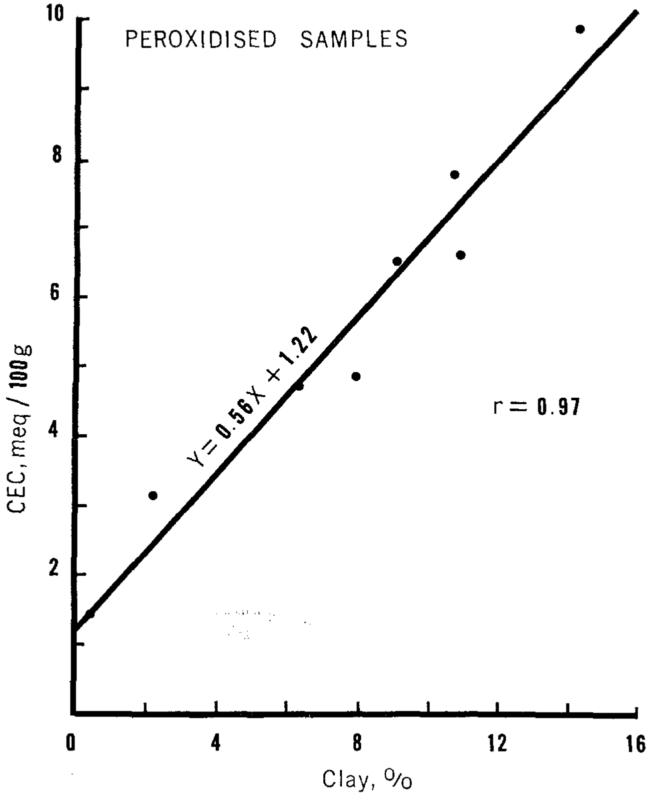

Fig. 2. Relationship between CEC and clay content for peroxidised surface samples.

content indicates the contribution of the silt and sand fractions to the CEC of the surface samples.

Several investigators have objected to the use of H_2O_2 for removal of organic matter on the grounds that this treatment results in incomplete oxidation of the organic matter or partial dehydration of the clay minerals (Kelley *et al.*[11]; Olson and Bray[15]). The fact that the correlation between the CEC of peroxidised samples and clay content was highly significant for the present samples suggests that either organic matter removal was complete or that the organic matter remaining had a negligible CEC. Also, recent studies have shown that the CEC of vermiculite (Roth *et al.*[16]), nontronite, biotite, and muscovite (Roth *et al.*[17]) is not affected by peroxidation.

These latter findings may suggest that the effect of H_2O_2 on the CEC of clay minerals has been overestimated in the past.

The present results indicate that the clay fraction of the soils of the chronosequence contribute very little to the CEC of the soils. Blocking by organic matter of the negative charge of the clay fraction apparently reduces the CEC of the clay to such a level that the organic matter contributes by far the major part of the CEC of these sandy soils.

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