Estimation of cation-exchange capacity in routine soil testing

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Abstract. The efficiency of the soil testing method used in Finland for predicting the effective cation-exchange capacity was studied in a material of 430 topsoil samples. The effective cation-exchange capacity was estimated 1) by summation of exchangeable Ca, Mg and acidity displaced by unbuffered 1 M KCl and 2) by summation of exchangeable Ca, Mg, K and Na displaced by neutral 1 M ammonium acetate and exchangeable acidity. In soil testing, Ca, Mg and K were extracted by acid ammonium acetate and soil pH measured in water-suspension.

The estimates of the effective CEC were highly correlated and dependent on the clay and organic carbon content and $pH(CaCl_2)$ of the soil, the coefficient of multiple determination being over 80 %. Exchangeable Ca was the dominating cation. The proportion of Ca of the effective CEC was about 80 %.

Acid ammonium acetate-extractable Ca together with $pH(H_2O)$ explained over 80 % of the variation in the effective CEC. For the whole material consisting of mineral soils with great variations in texture, organic carbon content and properties under evaluation, the regression equation predicting the effective CEC (KCl method) was $CEC(mval/kg) = 309—56.8pH(H_2O) + 0.085Ca(mg/l)$. Only 16 % of the estimates of the effective CEC calculated with this regression equation deviated more than 15 % from the measured values.

Index words: exchangeable Ca, Mg, K, Na, exchangeable acidity, effective cation-exchange capacity, soil pH, soil testing

Introduction

In Finnish soil testing, lime requirement has been estimated on the basis of $pH(H_2O)$ and acid ammonium acetate-extractable Ca. According to MÄNTYLAHTI and YLÄRANTA (1980), however, soil pH alone gives a better estimate. The content of extractable Ca in soil cannot be used as an index of liming requirements as long as the cation-exchange capacity and base saturation vary. On the other hand, exchangeable calcium contents together with acidity could estimate cation-exchange capacity of soil. The aim of this study was to examine the relationship between estimates of effective cation-exchange capacity of mineral soils and the possibility of predicting them by soil testing.

Material and methods

The material consisted of 430 plough layer (0—25 cm) samples from the agricultural area of the Viikki Experimental Farm. The soil characteristics have been described previously by JOKINEN (1983, 1984) and NISKANEN and JAAKKOLA (1985). The samples were air-dried and ground to pass a 2-mm sieve. On the basis of the particle-size distribution determined by the pipette method (ELONEN 1971), the material consisted of 230 clay soils with a clay content $\geq$ 30 % and 200 coarser soil samples with a clay content < 30 % (Table 1). The pH of the soil was measured in a soil-0.01 M $CaCl_2$ suspension (1:2.5) (RYTI 1965). The mean pH of the coarser soils was 0.3 pH units higher than that of clay soils (Table 1). The organic carbon content of the soil determined by a modified (GRAHAM 1948) ALTEN's wet combustion method was on the average 1.5 % higher in clay soils (Table 1).

Exchangeable Ca and Mg were extracted from 10 g soil by four successive treatments with 50 ml of neutral 1 M ammonium acetate and 50 ml 1 M KCl and determined by atomic absorption spectrophotometry. Exchangeable K and Na were extracted with neutral 1 M ammonium acetate and determined by flame photometry.

The exchangeable acidity was displaced with 1 M KCl and titrated with 0.01 M NaOH (YUAN 1959). Two estimates for the effective cation-exchange capacity (CEC) were determined according to KAILA (1971 a, 1972). The effective CEC1 was estimated by summation of exchangeable Ca, Mg and acidity displaced by 1 M KCl. The effective CEC2 was estimated by summation of exchangeable Ca, Mg, Na and K extracted by neutral 1 M ammonium acetate with exchangeable acidity displaced by unbuffered 1 M KCl. The pH of the soil-H_2O suspension (1:2.5 v/v) and Ca, Mg and K extracted with acid ammonium acetate (0.5 M acetic acid, 0.5 M ammonium acetate, pH 4.65, ratio 1:10 v/v) (VUORINEN and MÄKITIE 1955) were determined at a commer-cial soil testing laboratory (Viljavuuspalvelu Oy).

Results

The effective CEC1 averaged 150 mval/kg soil in clay soils (range 74—250 mval/kg soil) and 108 mval/kg soil in coarser soils (range 43—288 mval/kg soil) (Table 1). On the average, more than 80 % of the effective CEC1 was saturated with exchangeable Ca, 10 % with exchangeable Mg and less than 10 % with exchangeable acidity (Table 2).

Exchangeable Ca was rather closely correlated with calcium extracted by the routine soil-testing method (r = 0.74***). So was exchangeable magnesium with extractable magnesium (r = 0.83***). The variation in the sum of KCl-extractable calcium and magnesium was fairly well explained by acid ammonium acetate-extractable calcium (R^2 = 0.66, n = 430).

The relationship between exchangeable acidity and soil pH was curvilinear, but the logarithmic values of exchangeable acidity were linearly correlated with soil pH. With pH(H_2O) as an independent variable, the regression equation for the whole material (n = 430) was log(acidity) = 4.66—0.68 pH(H_2O), R^2 = 0.83.

The dependence of the effective CEC1 on soil properties was studied using clay and silt content (%), organic carbon content (%) and pH($CaCl_2$) as independent variables in the regression analysis. Clay content, organic carbon content and pH($CaCl_2$) together explained 83.4 % of the variation in the effective CEC1 of the whole material, the regression equation being CEC1 (mval/kg) = —227 + 1.85clay-% + 45.6pH + 11.2org.C-%. The silt content was an insignificant explainer. The content of clay fraction explained 67.5 %, organic carbon content 62.9 % and pH($CaCl_2$) 65.4 % of the variation in the effective CEC1, when the effect of the other two independent variables was eliminated.

The sum of exchangeable cations extracted by neutral 1 M ammonium acetate averaged

161 mval/kg soil in clay soils (range 55—303 mval/kg soil) and 125 mval/kg soil in coarser soils (range 49—329 mval/kg soil) (Table 1). The effective CEC2 estimated by summation of exchangeable acidity displaced by unbuffered 1 M KCl and exchangeable cations extracted by neutral 1 M ammonium acetate averaged 172 mval/kg soil in clay soils (range 94—305 mval/kg soil) and 129 mval/kg soil in coarser soils (range 55—333 mval/kg soil).

On the average, 75 % of the effective CEC2 was saturated with exchangeable Ca in clay soils (range 21—92 %) and 81 % in coarser soils (range 43—93 %). The proportion of Mg, K and Na in the saturation of the effective CEC2 was only slightly higher in clay soils than in coarser soils. In the whole material, on the average 10 % of the effective CEC2 was saturated with Mg (range 3—34 %), 5.3 % with K (range 0.6—22 %) and 1.2 % with Na (range 0.4—8.5 %). The proportion

Table 1. Soil characteristics.

	All soils (n = 430)			Clay soils (n = 230)			Coarser soils (n = 200)		
	$\bar{x}$	s	range	$\bar{x}$	s	range	$\bar{x}$	s	range
pH(CaCl$_2$)	5.3	0.6	4.0—6.8	5.2	0.6	4.0—6.8	5.5	0.5	4.5—6.8
pH(H$_2$O)	5.8	0.5	4.2—7.1	5.7	0.5	4.2—7.1	6.0	0.5	4.8—7.1
Org.C, %	5.2	2.2	1.8—14.6	5.9	2.2	2.5—14.4	4.4	2.0	1.8—14.6
Clay (< 0.002 mm), %	31	3	6—65	41	6	30—65	19	6	6—30
Silt (0.002—0.02 mm), %	17	8	3—43	22	7	9—43	13	6	3—37
Coarser fractions (0.02—2 mm), %	52	18	20—91	38	9	20—59	69	10	40—91
Exchangeable cations (mval/kg soil) extracted by 1 M KCl:									
Ca	109	36	0—257	122	35	27—237	93	29	0—257
Mg	14	11	0—72	17	13	4—72	11	6	0—44
Acidity	8	10	1—82	11	11	1—66	5	7	1—82
Sum of cations = Effective CEC1	131	38	43—288	150	33	74—250	108	30	43—288
Exchangeable cations (mval/kg soil) extracted by neutral 1 M ammonium acetate:									
Ca	119	39	25—292	131	38	25—280	105	35	38—292
Mg	16	12	3—79	19	14	5—79	12	5	3—31
K	8	4	1—37	9	4	3—37	6	3	1—21
Na	1.8	1.9	0.4—18.7	2.3	2.4	0.6—18.7	1.3	0.6	0.4—5.5
Sum of cations	144	45	49—329	161	43	55—303	125	38	49—329
Effective CEC2									
mval/kg soil	152	43	55—333	172	36	94—305	129	37	55—333
Cations (mval/l soil) extracted by acid ammonium acetate:									
Ca	89	28	14—193	93	31	14—185	85	24	35—193
Mg	14	13	2—154	16	15	3—79	11	11	2—154
K	6	3	1—32	6	3	2—32	5	2	1—16
Sum of cations	108	37	27—274	115	42	27—224	101	30	42—274

Table 2. Exchangeable cations extracted by 1 M KCl, % of effective CEC1.

	All soils (n = 430)			Clay soils (n = 230)			Coarser soils (n = 200)		
	$\bar{x}$	s	range	$\bar{x}$	s	range	$\bar{x}$	s	range
Ca	83	10	0—94	80	10	26—94	85	9	0—95
Mg	10	7	0—54	11	7	3—37	10	6	0—54
Acidity	7	9	0.4—100	9	10	0.4—63	5	8	0.6—100

of exchangeable acidity averaged 7.5 % in clay soils (range 0.3—55 %) and 3.9 % in coarser soils (range 0.5—52 %).

Clay content, organic carbon content and pH(CaCl$_2$) together explained 84.4 % of the variation in the effective CEC2, the regression equation being CEC2 (mval/kg) = —296 + 1.97clay-% + 60.6pH + 12.5org.C-%. The clay content explained 66.6 %, pH(CaCl$_2$) 73.8 % and organic carbon content 64.1 % of the variation in the effective CEC2, when the effect of the other two independent variables was eliminated.

The values of the effective CEC1 were about 85 % of the effective CEC2 (Table 1), because exchangeable K and Na were not included in the CEC1, and more Ca was extracted with neutral ammonium acetate than with KCl. The effective CEC1 and CEC2 were highly correlated (r = 0.96***, n = 430).

The sum of Ca, Mg and K extracted by acid ammonium acetate averaged 115 mval/l soil in clay soils (range 27—224 mval/l soil) and 101 mval/l soil in coarser soils (range 42—274 mval/l soil) (Table 1). In the whole material, 83 % of the cation sum, on the average, was saturated with Ca (range 41—94 %). The proportion of Mg averaged 11 % (range 4—56 %) and that of K 6 % (range 1—27 %). Clay and silt content, organic carbon content and pH(CaCl$_2$) explained 86.8 % of the cation sum, the regression equation being cation sum (mval/l) = —264 + 1.76clay-% — 1.03silt-% + 60.2pH + 3.11org.C-%. The content of clay fraction explained 65.6 %, silt content 19.0 %, pH(CaCl$_2$) 80 % and organic carbon content 14.3 % of the variation in the cation sum, when the

effect of the other three independent variables was eliminated. The sum of cations extracted with acid ammonium acetate was not very closely correlated with the estimates of effective CEC. The correlation coefficient with CEC1 was r = 0.65*** (n = 430).

The usability of pH(H$_2$O) and Ca, Mg and K extracted by acid ammonium acetate in predicting the effective CEC was tested with clay soils, coarser soils and the whole material. The sum of Ca, Mg and K together with pH(H$_2$O) explained the variation in the effective CEC as follows:

	clay soils	coarser soils	all soils
effective CEC1	63.0 %	63.2 %	72.3 %
effective CEC2	68.4 %	68.9 %	74.1 %

The coefficients of determination slightly increased when K was omitted from the sum of cations. The sum of Ca and Mg together with pH(H$_2$O) explained the variation in the effective CEC as follows:

	clay soils	coarser soils	all soils
effective CEC1	69.3 %	65.0 %	74.8 %
effective CEC2	71.5 %	70.0 %	75.3 %

The highest values of the coefficient of determination were obtained by using acid ammonium acetate-extractable Ca instead of cation sum as an independent variable. With Ca and pH(H$_2$O) as independent variables explaining the variation in the effective CEC1, the coefficients of determination and corresponding regression equations were as follows:

clay soils	81.6 %	CEC1(mval/kg) = 274 — 47.6pH + 1.58Ca(mval/l)
coarser soils	75.8 %	CEC1(mval/kg) = 251 — 44.2pH + 1.43Ca(mval/l)
all soils	82.6 %	CEC1(mval/kg) = 309 — 56.8pH + 1.70Ca(mval/l)

With the effective CEC2 as a dependent variable, the coefficients of determination and corresponding regression equations were as follows:

clay soils	80.4 %	CEC2(mval/kg) = 242 — 38.4pH + 1.59Ca(mval/l)
coarser soils	84.5 %	CEC2(mval/kg) = 223 — 41.2pH + 1.79Ca(mval/l)
all soils	84.0 %	CEC2(mval/kg) = 292 — 52.9pH + 1.88Ca(mval/l)

The partial correlation coefficients for the relation between the effective CEC1 (1) or CEC2 (2), pH(H₂O) (3) and acid ammonium acetate-extractable Ca (4) were as follows:

	$r_{13.4}$	$r_{14.3}$	$r_{23.4}$	$r_{24.3}$
clay soils	—0.69***	0.88***	—0.56***	0.84***
coarser soils	—0.72***	0.87***	—0.70***	0.92***
all soils	—0.81***	0.91***	—0.76***	0.91***

Omitting pH(H₂O) from the regression analysis decreased the coefficient of determination considerably. With acid ammonium acetate-extractable Ca as the only independent variable, 50.2 % of the variation in the effective CEC1 for the whole material was explained.

Theoretically it was justified to test the relationship between effective CEC, pH(H₂O) and acid ammonium acetate-extractable Ca also with a regression model in which all variables were logarithmic. However, this model was not superior to the model tested before. According to the logarithmic model, the relationship between the effective CEC1, pH(H₂O) and Ca in the whole material was described by the equation logCEC1 = 1.12 + 1.08logCa — 0.19pH, R^2 = 0.75.

The coefficients of determination for clay and coarser soil groups obtained with Ca and pH(H₂O) as independent variables did not deviate very much from each other. Therefore the examination of the material as a whole was appropriate. The variation in the estimates of the effective CEC was explained equally well. The measured values of the effective CEC1 were compared with the values calculated according to the regression equation CEC1(mval/kg) = 309 — 56.8pH + 1.70Ca(mval/l). The relationship between measured and predicted values is presented in Figures 1 and 2. The proportion of samples with the predicted value deviating more than 15 % from the measured value was 16 % of the whole material. This proportion included 11 % of the clay soil samples and 22.5 % of the coarser soil samples. In clay soils, the deviation did not exceed 30 % of the measured value. Coarser soil samples with the predicted value much below the measured value (No. 1—3) were
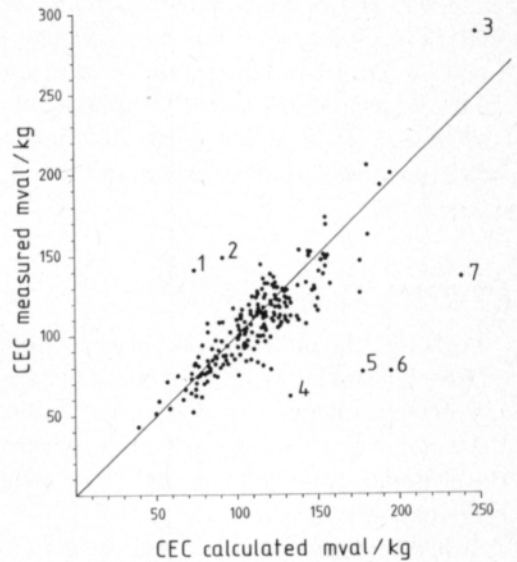

Fig. 1. Relationship between measured effective CEC1 (Ca + Mg + acidity) and its estimate calculated on the basis of soil testing data (Ca + pH) in coarse mineral soils.
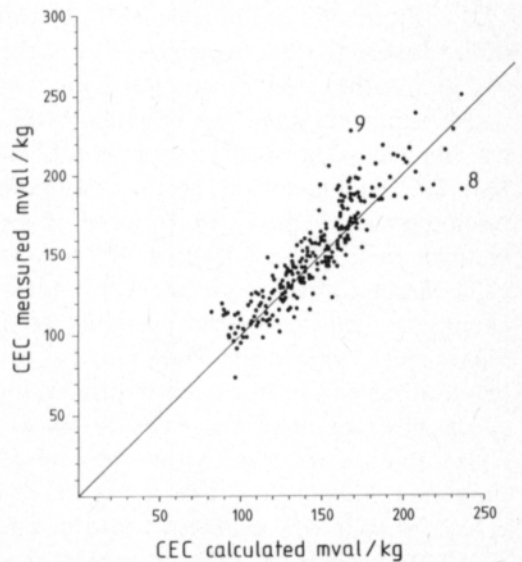

Fig. 2. Relationship between measured effective CEC1 (Ca + Mg + acidity) and its estimate calculated on the basis of soil testing data (Ca + pH) in clay soils.

characterized by high clay and organic carbon content. In clay soils the sample with the greatest underestimation of the measured value (No. 9) was characterized by high organic carbon content. Samples with the predicted value much above the measured value (No. 4—8) were characterized by low or moderate clay and organic carbon content. The $pH(H_2O)$ of these soils were 6.0—7.0 and in two cases (No. 7—8) the content of acid ammonium acetate-extractable Ca was high, over 160 mval/l. It is possible that some undissolved calcium carbonate existed in the soil.

Discussion

Although the material was collected from a restricted area, it was characterized by relatively great variations in soil properties. Under these circumstances it is justified to consider the material quite suitable for the present examination.

It has been shown earlier that the cation-exchange capacity of Finnish mineral soils is largely dependent on clay and organic carbon content (HEINONEN 1960, MARTTILA 1965, JOKINEN 1984) together with soil pH (KAILA 1971 a, b). In the study of KAILA (1971 b), the three variables together explained 83 % of the variation in the effective cation-exchange capacity estimated as the sum of exchangeable Ca, Mg and acidity displaced by unbuffered KCl. The result is in good agreement with the results obtained in this study. However, in the material (n = 230) of KAILA (1971 b), organic carbon content was a lesser explainer as compared with the present material with higher mean content and wider range of organic carbon and smaller range of $pH(CaCl_2)$.

The observation of KAILA (1972) that exchangeable Ca and Mg together saturate on the average 80—90 % of the effective CEC of cultivated soils was manifested also in this study. The proportion of exchangeable acidity was of minor importance in most soils. The average ratio of exchangeable Ca to Mg was

about 7 in clay soils and nearly 9 in coarser soils. In the study of KAILA (1972), the ratio in sand and fine sand soils was about 9 and in clay soils (clay-% < 60) about 4. According to SCHMID (1965), the ratio of Ca to Mg would be 5—8 to 1. The average ratio of exchangeable Mg to K was about 2 both in clay soils and in coarser soils. The average ratio of exchangeable K to Na was higher in coarser soils than in clay soils, the values being 4.6 and 3.9, respectively. In the study of KAILA (1972), the ratio of Mg to K was 2—8 and the ratio of K to Na 2—2.8.

On the basis of soil testing, the cation-exchange capacity of soil was to some extent predictable. The variation in the effective CEC was best explained by pH in soil-water suspension and Ca extracted by acid ammonium acetate. Indeed, additional variation can be caused by the fact that cation-exchange capacity was expressed on a weight basis and acid ammonium acetate-extractable Ca on a volume basis. Using the sum of Ca and Mg or Ca, Mg and K extracted by acid ammonium acetate instead of Ca did not increase the coefficient of determination. This was largely due to the fact that K and Mg were only minor components of CEC.

The effective CEC was adequately predictable by a regression equation in which $pH(H_2O)$ and acid ammonium acetate-extractable Ca were independent variables. The same equation could be applied to all mineral soils. When Ca is expressed as mg/l, the equation takes the form CEC(mval/kg) = 309 — $56.8pH(H_2O)$ + 0.085Ca(mg/l). Most of the material was such that the predicted CEC value did not deviate more than 15 % from the measured value. Some characteristics common to the samples with a great deviation were observed. High content of organic carbon, e.g., seemed to be associated with a great underestimation of CEC. The immediate reason in this case might be the smaller bulk density which affects the relationship between values given on weight and volume basis.

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SELOSTUS

Kationinvaihtokapasiteetin likiarvon laskeminen viljavuustutkimuksen perusteella

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Tutkimuksessa selviteltiin, voidaanko viljavuustutkimuksessa määritettävien happamaan ammoniumasetaattiin uuttuvien kalsiumin, magnesiumin ja kaliumin pitoisuuksien sekä maa-vesisuspensiosta määritetyn pH:n avulla laskea likiarvo maan efektiiviselle kationinvaihtokapasiteetille. Aineisto käsitti 430 kivennäismaiden muokkauskerroksesta otettua näytettä. Efektiivinen kationinvaihtokapasiteetti määritettiin 1 M kaliumkloridilla vaihtuvan kalsiumin, magnesiumin ja happamuuden summana sekä vaihtuvan happamuuden ja neutraalilla 1 M ammoniumasetaatilla uuttuvan kalsiumin, magnesiumin, kaliumin ja natriumin summana.

Molemmilla menetelmillä saadut efektiivisen kationinvaihtokapasiteetin arvot korreloivat voimakkaasti keskenään. Saveksen ja orgaanisen hiilen pitoisuus yhdessä pH($CaCl_2$):n kanssa selitti yli 80 % efektiivisen kationinvaihtokapasiteetin vaihtelusta. Vaihtuvan kalsiumin keskimääräinen osuus efektiivisestä kationinvaihtokapasiteetista oli noin 80 %.

Happamalla ammoniumasetaatilla uuttuva kalsium yhdessä maa-vesisuspensiosta mitatun pH:n kanssa selitti yli 80 % efektiivisen kationinvaihtokapasiteetin vaihtelusta. Koko maa-aineistolle voitiin käyttää samaa regressioyhtälöä, joka KCl-menetelmällä määritetylle efektiiviselle kationinvaihtokapasiteetille oli seuraava: KVK(mval/kg) = 309 — 56.8pH(H_2O) + 0.085Ca(mg/l). Vain 16 % näytteistä oli sellaisia, että regressioyhtälöstä laskettu KVK:n arvo poikkesi määritetystä arvosta enemmän kuin 15 %.

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