

BASIC EXCHANGEABLE CATIONS IN FINNISH MINERAL SOILS

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Abstract. The content of exchangeable Ca, Mg, K and Na replaced by neutral ammonium acetate was determined in 470 samples of mineral soils from various parts of Finland, except from Lapland.

The amount of all these cations tended to increase with an increase in the clay content, but variation within each textural class was large, and the ranges usually overlapped those of the other classes.

The higher acidity of virgin surface soils was connected with a lower average degree of saturation by Ca as compared with the corresponding textural classes of cultivated soils. No significant difference in the respective contents of other cations was detected.

The samples of various textural groups from deeper layers were usually poorer in exchangeable Ca and K than the corresponding groups of plough layer. The mean content of exchangeable Mg was equal or even higher in the samples from deeper layers than in the samples from plough layer, except in the group of sand soils.

The percentage of Mg of the effective CEC increased, as an average, from 9 in the sand and fine sand soils of plough layer to 30 in the heavy clay soils; in the heavy clay soils from deeper layers its mean value was $38 \pm 4\%$.

In the samples of plough layer, the mean ratio of Ca to Mg in sand and fine sand soils was about 9, in silt and loam soils about 6, in the coarser clay soils about 4, and in heavy clay about 2.

Chemical and physical properties of a soil may largely depend on the quality and quantity of exchangeable cations in it. The degree of saturation by basic cations is of particular importance, but also the proportions of various basic cations and their amounts in soil exert marked effect on plant nutrition and, especially, on properties of clay soils.

Information about basic exchangeable cations in Finnish soils obtained by modern analytical methods is not particularly abundant. HEINONEN (1956) has reported results of exchangeable Ca, Mg, and K in the plough layer of about 50 mineral or organic soils. MARTILA (1965) published data of a material consisting of 100 samples from surface and deeper layers of both cultivated and virgin soils, and MÄKITIE and VIRRI (1965) studied 10 clay soil profiles of Southern Finland. Their results do not differ from the

general rule that the content of exchangeable Ca is usually higher than that of Mg, and both of them markedly higher than those of K and Na. Clay soils, especially their deeper layers appeared to be fairly rich in Mg.

In the present paper the content of basic exchangeable cations in Finnish soils of different textural classes is studied on the basis of a larger material. Attention is also paid to differences between cultivated and virgin soils on the one hand, and between surface soils and deeper layers on the other hand. In order to get a more realistic idea about the conditions in the field, the degree of saturation by the various cations is calculated using the effective cation exchange capacity instead of some potential value determined at a higher pH than those existing in our more or less acid soils.

Material and methods

The material consists of 470 soil samples collected from various parts of Finland, except from Lapland. The surface samples were taken down to about 20 cm, the samples of the deeper layers mainly from depths between 20 and 70 cm.

The samples were air-dried and ground, and the particles larger than 2 mm were separated by sieving. On the basis of the particle size composition of mineral matter, the samples were grouped according to the classification used in Finland. Soils containing the fraction $< 2 \mu\text{m}$ more than 60 % are listed as heavy clays. Of the other clay soils with 30 to 60 % clay, the silt clay soils contain 20 to 70 % silt (2–20 μm) and less than 20 % fine sand (20–200 μm), clay loam contains both these fractions 20 to 50 %, and the sandy clay soils less than 20 % silt and 20 to 70 % fine sand. Since there were only 11 samples of sandy clay soils in this material, they were pooled with the clay loam soils. The non-clay soils with less than 30 % clay are silt soils with more than 50 % silt, fine sand soils with more than 50 % fine sand, or loam soils with 20 to 50 % of both these fractions. The sand soils are mainly composed of the fraction 0.2 to 2 mm. The moraine soils got into the groups of sand or fine sand soils.

Soil pH was measured in 1 to 2.5 suspension in 0.01 M CaCl_2 , organic C was determined by wet combustion and iodometric titration.

The basic exchangeable cations were extracted by washing with centrifuge 10 g-samples of soil with five 50 ml-portions of neutral ammonium acetate. Ca and Mg were measured by a Perkin Elmer atomic absorption spectrophotometer 290, and K and Na with an EEL flame photometer.

The effective CEC was calculated as the sum of the basic exchangeable cations and exchange acidity displaced by successive extractions with unbuffered N KCl.

The soil samples are characterized by data in Table 1. Because no statistically significant differences could be detected in this work between the subsurface samples of the same textural classes in cultivated and virgin soils, this part of material is treated without attention to its origin. There were 74 samples of clay soils and 52 samples of non-clay soils from the deeper layers of cultivated land, 39 samples of clay soils and 61 samples of non-clay soils from virgin land.

It is of interest to note that the average clay content is equal in the sand and fine sand soils, in the loam and silt soils, and in the two groups of coarser clay soils, respectively. Corresponding equality is also reflected by the mean values of effective CEC. The heavy clay soils have a markedly higher mean CEC than the other clay soils.

Results

The mean contents of basic exchangeable cations in the various soil groups are listed

Table 1. Soil samples.

	Number of samples	pH*	Org. C %*	Clay %*	Effective CEC mc/100 g*
<i>Surface samples</i>					
cultivated soils					
Sand	20	5.4 ± 0.2	3.3 ± 0.7	11 ± 3	9.8 ± 1.8
Fine sand	29	5.2 ± 0.2	2.9 ± 0.4	10 ± 2	9.1 ± 1.6
Loam	58	5.2 ± 0.1	2.7 ± 0.2	21 ± 1	10.2 ± 0.7
Silt	16	5.3 ± 0.2	3.4 ± 0.7	20 ± 3	13.0 ± 2.1
Clay loam	35	5.2 ± 0.2	4.2 ± 0.5	39 ± 2	16.6 ± 1.7
Silty clay	36	5.2 ± 0.1	4.0 ± 0.4	42 ± 3	15.7 ± 1.8
Heavy clay	13	5.1 ± 0.2	4.6 ± 1.4	71 ± 6	22.6 ± 3.3
virgin soils					
Sand and fine sand	26	4.4 ± 0.2	4.8 ± 0.9	11 ± 2	9.3 ± 1.2
Loam and silt	12	4.5 ± 0.2	4.0 ± 1.4	20 ± 3	9.9 ± 2.2
Clay	9	4.5 ± 0.5	3.4 ± 1.8	59 ± 12	18.6 ± 0.3
<i>Deeper layers</i>					
Sand	26	4.6 ± 0.1	0.9 ± 0.2	8 ± 2	2.7 ± 0.4
Fine sand	37	5.1 ± 0.2	0.7 ± 0.2	6 ± 2	3.2 ± 0.9
Loam	25	5.1 ± 0.2	0.9 ± 0.3	20 ± 3	7.0 ± 0.1
Silt	25	5.2 ± 0.3	0.9 ± 0.4	20 ± 3	7.1 ± 0.1
Clay loam	19	5.1 ± 0.5	1.0 ± 0.4	42 ± 4	14.5 ± 2.5
Silty clay	40	5.4 ± 0.2	0.8 ± 0.2	44 ± 3	13.7 ± 1.6
Heavy clay	44	5.7 ± 0.2	0.9 ± 0.3	76 ± 3	25.5 ± 2.3

*Means with the confidence limits at the 95 per cent level.

in Table 2. The increase in the effective CEC from sand to heavy clay soils appears to be due to increases in the amounts of all four cations.

The content of exchangeable Ca ranged in these samples from 0.1 mc/100 g in the A₂-horizon of a podsol soil to more than 20 mc/100 g in some cultivated clay soils. There seems to be a higher average content of Ca in the plough layers of the cultivated soils than in the corresponding groups from deeper layers or from the surface soils of virgin lands. Only the 44 samples of heavy clay from the deeper layers have a mean content of exchangeable Ca as high as the 13 samples from plough layer.

The mean content of exchangeable Mg seems to increase from sand to heavy clay soils even more markedly than that of exchangeable Ca. The lowest values, less than 0.1 mc/100 g, were found in deeper layers of sand soils, and the highest, about 20 mc/100 g, in the deeper layers of heavy clay soils. Contrary to the occurrence of exchangeable Ca, the content of exchangeable Mg does not seem to be higher in the plough layer than in the deeper layers; in the clay soils even higher average content is found in the subsurface samples. No significant difference exists between the corresponding kinds of virgin and cultivated soils.

Table 2. Basic exchangeable cations, me/100 g of soil.

	Ca*	Mg*	K*	Na*
<i>Surface samples</i>				
cultivated soils				
Sand	7.7 ± 1.5	0.9 ± 0.3	0.44 ± 0.14	0.16 ± 0.06
Fine sand	7.2 ± 1.6	0.8 ± 0.2	0.35 ± 0.08	0.15 ± 0.06
Loam	7.8 ± 0.7	1.2 ± 0.2	0.32 ± 0.05	0.16 ± 0.06
Silt	10.0 ± 2.0	1.6 ± 0.5	0.52 ± 0.29	0.21 ± 0.10
Clay loam	11.6 ± 1.2	2.8 ± 0.7	0.67 ± 0.14	0.24 ± 0.03
Silty clay	11.3 ± 1.4	2.6 ± 0.5	0.62 ± 0.09	0.24 ± 0.02
Heavy clay	14.0 ± 2.7	6.7 ± 1.1	0.81 ± 0.19	0.33 ± 0.09
virgin soils				
Sand and fine sand	5.3 ± 1.2	1.2 ± 0.2	0.30 ± 0.10	0.15 ± 0.03
Loam and silt	4.9 ± 2.3	1.5 ± 0.5	0.41 ± 0.11	0.17 ± 0.06
Clay	8.7 ± 3.0	4.7 ± 2.9	0.89 ± 0.66	0.34 ± 0.15
<i>Deeper layers</i>				
Sand	1.1 ± 0.3	0.3 ± 0.1	0.09 ± 0.03	0.06 ± 0.01
Fine sand	1.7 ± 0.8	0.5 ± 0.4	0.14 ± 0.04	0.14 ± 0.06
Loam	3.9 ± 1.2	1.7 ± 0.5	0.26 ± 0.05	0.17 ± 0.03
Silt	4.0 ± 0.6	1.9 ± 0.4	0.19 ± 0.05	0.18 ± 0.03
Clay loam	7.7 ± 2.9	3.6 ± 1.1	0.38 ± 0.09	0.42 ± 0.15
Silty clay	7.2 ± 1.1	4.5 ± 0.9	0.40 ± 0.08	0.31 ± 0.06
Heavy clay	13.2 ± 1.3	10.1 ± 1.6	0.73 ± 0.07	0.56 ± 0.07

*Means with the confidence limits at the 95 per cent level.

The average ratio of exchangeable Ca to Mg in the plough layers is in sand and fine sand soils about 9, in silt and loam soils about 6, in clay loam and silt clay about 4 and in heavy clay soils about 2. In the deeper layers the corresponding ratios are about 3.5, 2, 2, and less than 1.5, respectively. The surface samples of virgin soils stand halfway between these.

The surface layers seem to be markedly richer in exchangeable K than the deeper layers. The minimum content, 0.01 me/100 g, was found in the deeper layers of virgin fine sand soil, and the highest contents, 1.9 me/100 g in the plough layer of a silt and clay loam soil. The content of exchangeable K seems to increase with the increase in the content of clay, though less markedly than does Mg.

In the mineral soils there is roughly twenty times as much exchangeable Ca as exchangeable K. The average ratio of exchangeable Mg to K varies from about 2 in the plough layer of sand and fine sand soils to more than 8 in the heavy clay soils. In the virgin soils and in the deeper layers the ratio tends to be higher.

In the surface layers of the mineral soils the mean content of exchangeable Na in the respective textural classes is distinctly lower than that of exchangeable K, but in the

Table 3. Basic exchangeable cations as a per cent of effective cation exchange capacity.

	Ca*	Mg*	K*	Na*
<i>Surface samples</i>				
cultivated soils				
Sand	78 ± 2	9 ± 2	4 ± 1	2 ± 0.5
Fine sand	76 ± 4	9 ± 2	4 ± 2	2 ± 1
Loam	76 ± 2	12 ± 1	3 ± 0.5	1 ± 0.2
Silt	75 ± 6	12 ± 3	5 ± 2.5	2 ± 0.5
Clay loam	70 ± 3	11 ± 3	4 ± 1	1 ± 0.2
Silty clay	71 ± 3	15 ± 2	5 ± 1	2 ± 0.2
Heavy clay	61 ± 5	30 ± 4	4 ± 1	1 ± 0.3
virgin soils				
Sand and fine sand	55 ± 8	13 ± 2	3 ± 1	2 ± 0.3
Loam and silt	45 ± 15	13 ± 3	4 ± 1	2 ± 0.5
Clay	47 ± 16	24 ± 11	5 ± 1	2 ± 1
<i>Deeper layers</i>				
Sand	41 ± 5	10 ± 2	4 ± 0.5	2 ± 0.4
Fine sand	42 ± 7	13 ± 3	5 ± 1.5	6 ± 3
Loam	50 ± 7	21 ± 4	4 ± 1	3 ± 0.5
Silt	54 ± 5	25 ± 4	3 ± 1.5	3 ± 0.5
Clay loam	50 ± 11	15 ± 7	3 ± 0.5	3 ± 1
Silty clay	52 ± 5	31 ± 4	3 ± 0.5	2 ± 0.4
Heavy clay	52 ± 4	38 ± 4	3 ± 0.5	2 ± 0.3

*Means with the confidence limits at the 95 per cent level.

deeper layers the difference is smaller or there is no difference. In some exceptional cases the content of exchangeable Na is even markedly higher than that of K.

The variation in the content of exchangeable Ca, Mg, K and Na is large in all textural classes, and individual values of one group are overlapping the range of other ones. This is, of course, true also in the variation of the degree of saturation of the exchange capacity by the basic cations. Yet, the average saturation percentages may significantly differ at least between more distant textural classes, as shown by the data in Table 3.

The average degree of saturation by exchangeable Ca is distinctly lower in the plough layer samples of heavy clay soils than in those of a coarser texture. It varies from about 80 % in sand soils to about 60 % in the heavy clay samples, while the degree of saturation with Mg increases from an average of about 10 % to 30 %. Together these two basic cations saturate, on an average, 80 to 90 % of the effective CEC of these cultivated soils.

In the virgin samples and in the soils from deeper layers the degree of saturation by Mg is of the same order as in the corresponding textural classes of plough layer samples,

but the mean proportion of Ca is distinctly lower in the former groups. In all the samples of the plough layer at least 50 % of the exchangeable cations are Ca, but in the virgin soils the minimum may be about 10 % in particularly acid soils.

The proportions of exchangeable K and Na do not show any distinct tendency to be connected with the textural class or sampling depth. Cultivation does not seem to have any significant effect on them.

Discussion

The contents of exchangeable Ca, Mg, K and Na, replaced by neutral ammonium acetate varied in the present material markedly. The contents of all these cations tended to increase from sand soils to heavy clay soils, but in spite of the statistically significant differences found between the mean values of some textural classes, no reliable estimation of the content of exchangeable basic cations in an individual sample can be made on the basis of the soil texture alone.

Samples of virgin soils of the present material do not represent sampling places adjacent to those of cultivated lands. Therefore, it is not allowable to claim that differences between them would arise only from cultivation. In this material no statistically significant differences existed between the respective textural groups of virgin and cultivated soils in the mean contents of exchangeable Mg, K and Na, when expressed as me/100 g of soil or as a percentage of effective CEC. Because of the large variation, not even the mean content of exchangeable Ca as me/100 g was significantly lower in the virgin soils, but their higher acidity was characterized more distinctly by the lower average degree of saturation by Ca. Even in this case the ranges were overlapping.

It was found in a previous paper (KAILA 1971) that the mean effective CEC was in the surface layers in our more or less acid clay soils about two thirds, in deeper layers of sandy soils about one third, and in all other groups about one half of the corresponding average potential CEC determined by neutral ammonium acetate. Therefore, the mean values reported in the present paper for the degree of saturation by the various exchangeable cations may be about 1.5 to 3 times as high as would be those calculated on the basis of the potential CEC.

Attention is often paid to the ratio of exchangeable cations, particularly to that of Ca to Mg. According to SCHMID (1965) their ideal ratio would be 5—8 to 1. In the present material, only in the plough layer of the sand and fine sand soils the mean ratio of Ca to Mg was somewhat higher than this, in the clay soils, and particularly in the heavy clay soils, it was even markedly lower. It seems that our acid soils of a finer texture are more in need of liming with ordinary limestone than with dolomitic limestone, as already suggested by KERÄNEN and JOKINEN (1964).

As far as the exchangeable Mg represent an estimation of plant available Mg in soil, the conditions in clay soils are, according to the present material, satisfactory with a minimum content of about 200—250 kg/ha and a maximum of about 3000 kg/ha. In the plough layer of the coarser mineral soils the content of exchangeable Mg ranges from 30 to 1000 kg/ha, indicating that there are soils in which Mg-deficiency may be expected.

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SELOSTUS

SUOMEN KIVENNÄISMAIDEN EMÄKSISET VAIHTUVAT KATIONIT

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Tiipiston maanviljelyskemian laitos, Viikki

Neutraalilla ammoniumasetaatilla vaihdettavissa oleva Ca, Mg, K ja Na määritettiin 470 kivennäismaan näytteestä, jotka oli kerätty eri puolilta maata Lappia lukuunottamatta.

Vaihtuvien emäksisten kationien määrä kasvoi maan saveksen pitoisuuden mukana, mutta eri maalajien puitteissa vaihtelu oli niin suurta, että vaihtelurajat yleensä ylittivät toisensa.

Luonnontilaisten pintamaitten happamuus liittyi viljelymaita matalampaan Ca-kyllästysasteeseen; muiden kationien kohdalla ei vastaavissa maalajiryhmissä ollut merkitseviä eroja.

Syvämpien kerrosten näytteissä oli eri maalajeissa yleensä keskimäärin vähemmän sekä vaihtuvaa Ca että K kuin muokkauskerroksen näytteissä. Sen sijaan Mg:n määrä oli hiekkamaita lukuunottamatta joko keskimäärin sama tai hiukan korkeampikin syvämmässä kerroksissa kuin muokkauskerroksessa.

Keskimääräinen Mg-kyllästysaste nousi muokkauskerroksen hiekka- ja hietamaiden 9 %:sta aitosaven 30 %:iin. Pohjamaiden aitosavien ryhmässä se oli jopa 38 ± 4 %.

Muokkauskerroksessa vaihtuvan Ca:n suhde Mg:iin oli hiekka- ja hietamaissa keskimäärin noin 9, hie- ja hiesumaissa 6, karkeammassa savimaissa 4 ja aitosavissa vain 2.