

## Effect of liming on basic exchangeable cations of soil

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**Abstract.** The effect of liming on the basic exchangeable cations in a sand, a heavy clay and a muddy clay soil was studied with a 9 month's incubation experiment under laboratory conditions. Besides, observations were made in connection with some other incubation and field experiments.

It was found that application of  $\text{CaCO}_3$  in amounts which reduced the acidity to about pH 7, decreased the content of exchangeable Mg in all experiments, and even a lower application effectively prevented any net release of nonexchangeable Mg which occurred in the muddy clay samples incubated without lime. Some fixation of K was also usually detected, but liming increased the amount of exchangeable Na.

Essential differences apparently exist between the mechanisms of the retention of Mg and K induced by liming: Significantly lower amounts of Mg was extracted by 0.5 HCl from the limed samples of the heavy clay and muddy clay soil than from the original ones, while the contrary was true with K.

The mechanisms connected with the Mg fixation were discussed. Attention was paid to the possibility that the usually poor Mg supporting ability of Finnish muddy clay soils may be partly connected with the heavy liming necessary for the cultivation of these acid soils.

The decrease in soil acidity as a result of liming is likely to increase the effective cation exchange capacity of the soil and also to exert some effect on the exchangeability of the basic cations. Fixation of some cations in non-exchangeable forms may occur, but also release of cations from organic matter or minerals is possible, particularly, during prolonged periods. In the field, losses of cations by leaching or uptake of cations by plant roots will complicate the processes.

In the present paper the effect of application of calcium carbonate on the basic exchangeable cations of three mineral soils is studied on the basis of an incubation experiment under laboratory conditions. Besides, results of some laboratory and field experiments are examined from this point of view.

### *Experimental*

Samples of a sand soil, a heavy clay soil and a muddy clay or gyttja clay soil were collected from virgin land of the university farm in Helsinki. The

samples were air-dried and ground to pass 2 mm sieve. 5 kg samples of the sand and heavy clay soils and 4 kg samples of the muddy clay soil were incubated in Mitscherlich pots at about field capacity and at room temperature (19–24° C) for nine months. All three soils were incubated without any application and with CaCO<sub>3</sub> corresponding to 7.5 me/100 g of dry soil. To the muddy clay, CaCO<sub>3</sub> was also added in amounts of 15, 22.5, 30, or 60 me/100 g. All treatments were in triplicates. At the end of the experimental period the samples were air-dried and passed through a 2 mm sieve.

The exchangeable cations were extracted by washing 5 g of soil with four 50 ml-portions of several buffered or unbuffered one normal salt solutions: NH<sub>4</sub>OAc at pH 7, 0.9 N CaOAc + 0.1 N CaCl<sub>2</sub> at pH 7, NH<sub>4</sub>Cl, KCl and CaCl<sub>2</sub>. Acid-soluble Ca, Mg, K, and Na were extracted with 0.5 N HCl by shaking for one hour in the ratio of 1 part of soil to 20 parts of the solution. Ca and Mg in the extracts were measured by a Perkin Elmer atomic absorption spectrophotometer 290, K and Na by an EEL-flame photometer.

Table 1. Soil samples

	Sand	Heavy clay	Muddy clay
Sampling depth cm .....	0–30	0–40	0–100
Org. C % .....	2.89	0.67	2.94
Particle size fractions %			
< 2 μm .....	14	78	59
2– 20 μm .....	6	14	28
20– 200 μm .....	24	7	11
200–2000 μm .....	56	1	2
Soil pH .....	6.0	5.7	3.5
Acidity me/100 g			
N KCl .....	0.2	0.4	11.0
N NH <sub>4</sub> OAc at pH 7 .....	5.8	8.5	27.5

The results were treated by DUNCAN's new multiple range test. (DUNCAN 1955).

The soils are characterized by data in Table 1. Soil pH was measured in a 0.01 M CaCl<sub>2</sub> suspension in the ratio of 1 to 2.5. Soil acidity was titrated in connection with the determination of the exchangeable cations with N KCl and N NH<sub>4</sub>OAc at pH 7.

The heavy clay sample is poor in organic C because of the high sampling depth. The muddy clay sample, on the other hand, has its typical high content of organic matter even down to the depth of one meter. The sand soil is exceptionally rich in the clay fraction as is also the case with the muddy clay soil. The very low pH-value of the muddy clay sample is in accordance with its high exchange acidity which exceeds the lowest amount of CaCO<sub>3</sub> applied. The exchange acidity is very low in the sand and heavy clay soils. The titratable acidity at pH 7 is in the former soil lower and in the latter soil only slightly higher than the amount of lime applied in the experiment.

## Results

The basic exchangeable cations replaced by unbuffered N  $\text{NH}_4\text{Cl}$  are recorded in Table 2. The figures for Ca in the limed samples are in parenthesis, since it is likely that, at least at the higher pH-values,  $\text{CaCO}_3$  had not completely reacted with the soil, and a part of it may only have been dissolved by  $\text{NH}_4\text{Cl}$ .

In the limed samples of sand and heavy clay soils pH is 6.9, but in the muddy clay soil only an eightfold amount of  $\text{CaCO}_3$  was enough to keep the reaction at about neutrality. The pH-values in this soil measured after one week of incubation were pH 3.5, 4.1, 4.7, 5.6, 6.9, and 7.2 for the treatments with 0, 7.5, 15, 22.5, 30, and 60 me/100 g, respectively. In the following weeks the acidity increased rapidly in samples limed with 7.5 to 22.5 me/100 g, but 30 me/100 g was able to keep the pH of the muddy clay for four weeks higher than pH 6 and for 13 weeks higher than pH 5.

In all soils incubation with lime which kept the soil pH at about 7 distinctly decreased the amount of Mg replaced by washing with N  $\text{NH}_4\text{Cl}$ . In the sand and heavy clay soils, this decrease was about 30 %, in the muddy clay soil only slightly lower than 50 % of the content of exchangeable Mg in the original sample. In the highly acid muddy clay soil incubated without lime or with 7.5 me/100 g, some release of nonexchangeable Mg is apparent. This net release was completely prevented by 15 me/100 g, and a statistically significant decrease in the content of exchangeable Mg is detectable in sample incubated with 30 me/100 g, which was enough to keep the soil only slightly acid for several weeks.

Table 2. Basic exchangeable cations in soil samples replaced by N  $\text{NH}_4\text{Cl}$  (me/100 g)

	$\text{CaCO}_3$ me/100 g	Soil pH*	Ca*	Mg*	K*	Na*
Sand						
Original		6.0 <sup>b</sup>	10.1 <sup>a</sup>	0.47 <sup>b</sup>	0.35 <sup>b</sup>	0.18 <sup>a</sup>
Incubated	0	5.8 <sup>a</sup>	10.0 <sup>a</sup>	0.49 <sup>b</sup>	0.33 <sup>ab</sup>	0.18 <sup>a</sup>
	7.5	6.9 <sup>c</sup>	(15.8)	0.32 <sup>a</sup>	0.30 <sup>a</sup>	0.26 <sup>b</sup>
Heavy clay						
Original		5.7 <sup>b</sup>	10.1 <sup>a</sup>	8.2 <sup>b</sup>	0.79 <sup>a</sup>	0.44 <sup>a</sup>
Incubated	0	5.6 <sup>a</sup>	10.3 <sup>a</sup>	8.2 <sup>b</sup>	0.85 <sup>b</sup>	0.47 <sup>b</sup>
	7.5	6.9 <sup>c</sup>	(17.0)	6.0 <sup>a</sup>	0.78 <sup>a</sup>	0.55 <sup>c</sup>
Muddy clay						
Original		3.6 <sup>b</sup>	4.9 <sup>a</sup>	3.6 <sup>c</sup>	0.92 <sup>d</sup>	0.85 <sup>a</sup>
Incubated	0	3.5 <sup>a</sup>	4.2 <sup>a</sup>	4.4 <sup>c</sup>	0.37 <sup>a</sup>	0.85 <sup>a</sup>
	7.5	3.6 <sup>b</sup>	(12.9)	4.0 <sup>d</sup>	0.92 <sup>d</sup>	1.01 <sup>b</sup>
	15	3.8 <sup>c</sup>	(21.0)	3.6 <sup>c</sup>	1.09 <sup>e</sup>	1.04 <sup>b</sup>
	22.5	4.3 <sup>d</sup>	(25.5)	3.4 <sup>bc</sup>	0.98 <sup>d</sup>	1.14 <sup>c</sup>
	30	4.9 <sup>e</sup>	(34.4)	3.2 <sup>b</sup>	0.82 <sup>c</sup>	1.16 <sup>c</sup>
	60	7.1 <sup>f</sup>	(57.1)	1.9 <sup>a</sup>	0.62 <sup>b</sup>	1.44 <sup>d</sup>

\* Means in each column of the respective soils do not differ at  $P = 0.01$  when they are followed by a common letter.



In the sand and heavy clay soils, liming at least prevented any release of nonexchangeable K. In the muddy clay soil, the highest amount of lime brought about a relatively high net fixation of K: one third of the exchangeable K in the original sample seems to be fixed. Some decrease in the exchangeable K is obvious also in the muddy clay soil incubated with 30 me  $\text{CaCO}_3$ .

Incubation without lime slightly increased the amount of exchangeable K in the heavy clay soil, no statistically significant effect can be found in the low values of the sand soil, but in the muddy clay soil a very marked decrease in the exchangeable K occurred. This somewhat surprising result which may be partly connected with the accumulation of  $\text{NH}_4^+$ -ions in this soil, will be studied more thoroughly in an other work.

In all soils, the amount of exchangeable Na is increased by liming, but not at all, or only slightly, by the somewhat higher acidity produced during incubation without lime.

Washing with the other buffered or unbuffered solutions gave results which, in respect of the basic exchangeable cations which could be determined, did not markedly differ from those obtained by N  $\text{NH}_4\text{Cl}$ . At least, the mutual sequence of the respective cations in the differently treated samples was equal. In all soils, incubation with lime decreased the amount of exchangeable Mg and increased that of Na, while the effect on exchangeable K was more complicated but similar to that reported in Table 2. Therefore, these data are not separately recorded in this connection.

Extraction with 0.5 N HCl was employed in order to get some more information about the effect of liming on the release or fixation of Mg, K, and Na. Results in Table 3 indicate that these acid soluble quantities are higher than the corresponding amounts of exchangeable form, though those of Na in sand and muddy clay soils are not much higher.  $\text{CaCO}_3$  applied is fairly well recovered by this extraction.

Acid soluble Mg is in the samples incubated with lime significantly lower than in the unlimed samples. In the heavy clay and muddy clay soils, differences in the acid soluble Mg between the original samples and the variously treated incubated samples are mainly of the same size as the corresponding differences in the exchangeable Mg. This may be taken to indicate that fixation of Mg induced by application of  $\text{CaCO}_3$ , to a large part occurred as compounds or complexes which are not readily dissolved by acid.

On the other hand, K retained unexchangeable in the samples limed to a high pH-value seems to be quite readily soluble in 0.5 N HCl, or at least K in the limed samples is more easily soluble than K in the unlimed samples of the both clay soils. In the muddy clay soil this is particularly marked, since K fixed in the sample incubated without lime seems to be bound in acid-insoluble forms. Apparently, there are different mechanisms not only between the lime induced fixation of Mg and K, but also between the retention of K in unexchangeable position in the limed and unlimed samples of the muddy clay soil.

The positive effect of liming on the acid soluble Na is equal to its effect on the exchangeable Na in the sand and muddy clay soil. In the heavy clay soil, the tendency towards the same direction is not statistically significant.

Table 3. Ca, Mg, K, and Na extracted by 0.5 N HCl at room temperature (me/100 g)

	CaCO <sub>3</sub> me/100 g	Ca*	Mg*	K*	Na*
Sand					
Original .....		14.0 <sup>a</sup>	0.93 <sup>a</sup>	0.55 <sup>a</sup>	0.22 <sup>a</sup>
Incubated .....	0	14.5 <sup>a</sup>	1.00 <sup>b</sup>	0.55 <sup>a</sup>	0.21 <sup>a</sup>
	7.5	21.8 <sup>b</sup>	0.90 <sup>a</sup>	0.55 <sup>a</sup>	0.27 <sup>b</sup>
Heavy clay					
Original .....		13.9 <sup>a</sup>	18.0 <sup>b</sup>	1.86 <sup>a</sup>	0.75 <sup>a</sup>
Incubated .....	0	13.2 <sup>a</sup>	18.3 <sup>b</sup>	2.33 <sup>b</sup>	0.85 <sup>b</sup>
	7.5	20.8 <sup>b</sup>	16.8 <sup>a</sup>	2.54 <sup>c</sup>	0.89 <sup>b</sup>
Muddy clay					
Original .....		6.9 <sup>a</sup>	7.0 <sup>c</sup>	1.34 <sup>c</sup>	0.95 <sup>a</sup>
Incubated .....	0	6.3 <sup>a</sup>	6.9 <sup>d</sup>	0.71 <sup>a</sup>	0.95 <sup>a</sup>
	7.5	14.3 <sup>b</sup>	6.3 <sup>c</sup>	1.26 <sup>b</sup>	1.06 <sup>b</sup>
	15	22.3 <sup>c</sup>	5.5 <sup>b</sup>	1.42 <sup>d</sup>	1.13 <sup>c</sup>
	30	37.1 <sup>b</sup>	5.4 <sup>b</sup>	1.58 <sup>e</sup>	1.25 <sup>d</sup>
	60	66.6 <sup>e</sup>	5.0 <sup>a</sup>	1.58 <sup>e</sup>	1.62 <sup>e</sup>

\* Means in each column of the respective soils do not differ at  $P = 0.01$  when they are followed by a common letter.

#### Other observations

Results obtained in connection of some other incubation and field experiments largely corroborated that heavy liming of an acid soil is likely to decrease the amount of exchangeable Mg and often also to some extent that of exchangeable K, while the content of exchangeable Na tends to increase with liming.

In a field trial on a clay loam soil of pH 5.4, liming in the spring with 14 000 kg CaCO<sub>3</sub> per hectare, until autumn decreased the acidity to pH 6.8. In samples collected in autumn or after 3 months from the fallow plots, the content of exchangeable Mg in the unlimed samples was 0.89 me/100 g, in the limed ones 0.57 me/100 g. The corresponding figures for exchangeable K were 0.23 and 0.18 me/100 g, respectively, and those for exchangeable Na 0.20 and 0.33 me/100 g. The respective differences were statistically highly significant.

In an incubation experiment under laboratory conditions with three acid muddy clay soils sampled both from the surface layer and from the depth of 40 to 60 cm, incubation for 6 months with 0, 0.5, 1.0, and 2.0 % CaCO<sub>3</sub> resulted in average pH-values of 3.9, 5.1, 5.9, and 6.8, respectively. The content of exchangeable Mg was at the lowest rate of liming about 85 %, at the second rate about 70 %, and at the highest rate of liming about 50 % of the content of exchangeable Mg in the samples incubated without lime. The corresponding decrease in the exchangeable K was less regular, but in some samples the increase in the exchangeable Na with liming was quite distinct.

There was an incubation experiment on nine loam and silt soils in which besides the effect of both liming and an application of KCl, also the effect of

alternate freezing and thawing on the exchangeable Mg could be studied. It was found that treatment with 0.5 %  $\text{CaCO}_3$  again distinctly decreased the amount of exchangeable Mg: the drop varied from 20 to 50 % of Mg in the samples incubated for three months without liming. No difference in exchangeable Mg was detectable as a result of the presence of KCl in an amount of 2.5 me/100 g of soil, neither did the alternate freezing or thawing bring about any net changes in Mg.

### *Discussion*

In all these experiments, heavy liming markedly decreased the amount of Mg which could be exchanged by various methods, and often also the content of exchangeable K was lowered. Since losses by leaching were excluded in the incubation experiments, fixation, or at least some kind of reduction in the exchangeability of these cations apparently occurred.

Liming has been found to increase fixation of K (KERÄNEN 1946, WIKLANDER 1954, KAILA 1965 etc.). This is most likely connected with release of aluminium hydroxide polymers from the interlayer position of clay minerals by the increase in soil pH, but also other mechanisms may be involved.

Though fixation of K has been the subject of numerous papers, rather little is reported about the fixation of Mg. Studies on the effect of liming on Mg usually treat the equilibrium between Mg in the soil solution and Mg sorbed as an exchangeable cation.

WIKLANDER and KOUTLER-ANDERSSON (1959) found that in a 30 years' field trial liming with 12 000 kg/ha of  $\text{CaCO}_3$  decreased the content of exchangeable Mg from 2.7 me/100 g in the unlimed plots to 2.2 me/100 g. They supposed this to be connected with losses of Mg by a higher leaching rate from the limed plots. On the other hand, they reported that air-drying of the soil samples decreased the exchangeable Mg in the limed plots by about 8 % of that in the undried samples from the surface layers down to the depth of 35 cm; in the samples from the unlimed plots the effect of drying was detectable first in deeper layers. The authors refer to a previous work (MALQUORI and WIKLANDER 1950) which proved that both aluminium and iron silicates fixed K and particularly Mg in nonexchangeable form, probably as insoluble K- and Mg-silicates. In addition to the formation of Mg-silicates, Mg-Al-silicates, or Mg-Fe-silicates, also binding into the mineral structure is suggested as possible mechanism for this fixation brought about by drying of soil samples.

Also EATON et al. (1968) showed that  $\text{MgSiO}_4$  precipitates in soils at high pH. HUNSAKER and PRATT (1970), on the other hand, demonstrated the formation of mixed Mg-Al-hydroxides in soils when raised to alkaline pH-levels. DONER (1967, ref. HUNSAKER and PRATT 1970) confirmed the inclusion of Mg in  $\text{CaCO}_3$  as it precipitated. McLEAN and CARBONELL (1972) again, suggested that conversion of Mg to nonexchangeable forms as a result of liming of a silt soil to pH 6.8 may have been primarily by chelation via organic components or by precipitation as oxalates, fatty acids or phosphates rather than by precipitation as silicates or aluminosilicates.



It is difficult to see which of these mechanisms was responsible for the fixation of Mg in the soils of the present study. The samples were air-dried before analysing, and it probably intensified the retention of Mg. In any case, the combined effect of incubation, liming and air-drying bound Mg as compounds or complexes which were not readily soluble in 0.5 N HCl, contrary to K fixed under the same conditions. Further studies are needed to ascertain the nature and importance of Mg fixation induced by liming.

It is of interest to note that in an experiment carried out by WIKLANDER and KOUTLER-ANDERSSON (1963), the amount of Mg transferred from non-exchangeable to exchangeable form during one year's storage was rather low in soil samples saturated with Ca-ions as compared to samples saturated with H-ions. Release of nonexchangeable Na tended to be slightly higher in samples saturated with Ca-ions than in those saturated with H-ions, but the contrary seemed to be true with changes in K. The present results do not disagree with these data, if differences in the treatments are taken into account.

In a previous work (KAILA and KETTUNEN 1973), it was found that while some slight release of nonexchangeable Mg was detectable in most soils applied to exhaustive cultivation in greenhouse, the muddy clay soil which was the only sample treated with lime, did not show any net release of nonexchangeable Mg. It is likely that one reason for the rather low amounts of plant-available Mg in the Finnish muddy clay soils is the effect of the fairly heavy liming which is usually needed for profitable cultivation of these acid soils.

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## Kalkituksen vaikutus maan emäksisiin vaihtuviin kationeihin

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Kalkituksen vaikutusta hiekkamaan, aitosaven ja liejusaven emäksisiin vaihtuviin kationeihin tutkittiin 9 kk:n muhituskokeessa laboratorion olosuhteissa. Lisäksi tarkasteltiin eräitten muitten muhitus- ja kenttäkokeitten analyysitietoja.

Todettiin, että  $\text{CaCO}_3$  annettuna määrinä, jotka nostivat maan reaktioltaan suunnilleen neutraaliksi, alensi kaikissa kokeissa merkittävästi vaihtuvan Mg:n pitoisuutta. Heikompikin kalkitus näytti estävän liejusaven vaihtumattoman Mg:n nettomobilisoitumisen, jota oli havaittavissa, kun maata muhitettiin ilman kalkitusta. Useimmissa maissa oli havaittavissa myös K:n pidättymistä kalkituksen tuloksena, mutta vaihtuva Na yleensä lisääntyi kalkituksen myötä.

Kalkituksen aikaansaama K:n ja Mg:n pidättäminen oli mekanismiltaan erilaista: ainakin aitosavi- ja liejusavinäytteistä 0.5 n HCl uutti kalkituista ja muhitetuista maista merkittävästi vähemmän Mg kuin alkuperäisistä, mutta K:n kohdalta tulos oli päinvastainen.

Tulosten tarkastelussa käsiteltiin Mg:n pidätyksen mekanisme kirjallisuuden melko niukkojen olettamusten perusteella. Esitettiin, että mahdollisesti eräänä syynä liejusaviemme yleensä heikohkoon Mg-tilaan saattaa olla näiden maiden tavallisesti vaatima verraten voimakas kalkitus, joka voi johtaa Mg:n pidättymiseen vaihtumattomaksi.