

Soil response to acid input in a titration experiment

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Cultivated surface soil samples of an acid Gleysol (soil 1, pH 4.9) and a slightly acid Podzol (soil 2, pH 6.7) were equilibrated for 48 h with 0 to 144 meq H^+ kg^{-1} by a batch technique designed to simulate reactions of acid load with soil constituents. The pH of the titration suspensions ranged in soil 1 from 5.6 to 3.3, in soil 2 from 7.2 to 4.7. The exchange reaction with base cations on variable charge sites was an important mechanism for H^+ inactivation. The quantities of cation equivalents released were, however, lower than the proton equivalents added. Calcium dominated the supernatant solutions, but as related to exchangeable reserves, Mg seemed to be more susceptible to acidification at high soil pH. Protons were also consumed in the mobilization of divalent base cations from a non-exchangeable pool to an exchangeable one.

The experimental soils differed in their response of acid cation fractions to proton loading. In the rather neutral soil 2, the quantities of soluble and exchangeable acid cations were very low and not affected by acidification. The Al dissolved by proton attack was immobilized by complexation reactions. This mechanism did not operate in the acid soil 1 where the proton loading markedly increased the exchangeable Al pool and, consequently, the soluble Al in the supernatant solution. This was associated with a simultaneous reduction in the complexed Al and a small increase in complexed Fe. Furthermore, acidification diminished the effective cation exchange capacity (ECEC) decisively less in soil 1 than in soil 2, because the increase in exchangeable Al markedly compensated the reduction in the exchangeable base cations. As compared to freely-drained systems, the batch titration overestimated the release of Al to solution phase.

Key words: pH-buffering, acidification, cation exchange, complexation

Introduction

Soil acidification is characterized by intensity and capacity factors. Intensity factors are determined by chemical properties and are independent of the size of the system considered, whereas capacity factors are a function of the size of the system (VAN BREE-MEN et al. 1983). Soil pH is an attribute indicating the intensity of acidity as well as the chemical and

biological conditions of a soil. Its alteration in response to acid loading is determined by the buffering properties of the respective soil. The impact of acid precipitation in a special edaphic ecosystem is dependent on the type of buffering reactions involved. Buffering by certain mechanisms can be ample but ecologically harmful (e.g. ULRICH 1981, SCHWERTMANN et al. 1987).

In Finland, the soil factors responsible for the

Table 1. Characteristics of the test soils.

Soil	Clay %	Silt %	pH (CaCl ₂)	Org. C %	CEC _{pot} meq kg ⁻¹	Fe _{ox}	Al _{ox}	Mn _{ox}
						mmol kg ⁻¹		
1	27	22	4.9	4.6	268	88	95	1
2	13	15	6.7	3.6	168	61	178	1

buffer action have been previously investigated statistically in a study carried out with 84 non-calcareous mineral soils (HARTIKAINEN 1986). The present paper reports the first part of a series of experiments aimed to monitor experimentally the acid-induced changes in soils and soil extracts as well as the role of various soil components in buffering reactions. In this study, the effect of acidification on soil elements and on their mobilization was investigated by a titration procedure. A titration curve for soil combines the two soil acidification characteristics: acid addition refers to the capacity and pH shows the intensity factor. In addition, it integrates these factors to describe buffering reactions by soil.

Material and methods

The titration experiment was carried out with two cultivated fine sand soils of very different pH. The samples taken from the surface layers are described in Table 1. Soil 1, a Gleysol from the postglacial sediment, was taken from the Viikki Experimental Farm (University of Helsinki) near the Gulf of Finland, and soil 2, a Podzol from the glacial till, from Northern Karelia. The clay fraction of the soils in both regions are dominated by illite, the other clay minerals being chlorite and vermiculite (CARLSON and HARTIKAINEN, unpublished). Soil samples were analyzed for pH in a 1:2.5 0.01 M CaCl₂ suspension, organic carbon by a CHN analyzer and soil texture according to ELONEN (1971). Potential CEC was determined at pH 7.0 by using NH₄OAc

solution (four extractions). Adsorbed NH₄⁺ replaced by KCl was determined by distillation. Semiamorphous Al_{ox}, Fe_{ox} and Mn_{ox} were extracted according to a modified Tamm's method (NISKANEN 1989) with 0.05 M NH₄-oxalate (pH 3.3) at a soil to solution ratio of 1:20 and determined by atomic absorption spectrophotometry (AAS).

A set of 5 g soil samples (three replicates) was weighed into centrifuge tubes and 50 ml of water or a H₂SO₄ solution of a concentration of 0.0012, 0.0024, 0.0036, 0.0048, 0.0060 or 0.0072 M was added. The suspensions were shaken for one min and allowed to stand for 48 h. The pH of the suspensions was measured after manual reshaking. The supernatant solution obtained after centrifugation was filtered through a hard filter paper (Schleicher & Schuell 589³) and analyzed for Ca, Mg, Fe and Mn by AAS, for K and Na by flame photometry and for Al by the Aluminon method (YUAN and FISKELL 1959). The soil samples treated with water or acid were washed with 30 ml of ethanol and analyzed for exchangeable cations extracted with four 25 ml portions of 1 M NH₄Cl. Another set of soil samples was treated similarly with water and acid. After washing with ethanol the soil samples were analyzed for exchangeable and complexed cations according to a modified JUO and KAMPRATH's method (1979) by extracting with four 25 ml portions of 0.33 M CuCl₂. Similarly to the study of NÄTSCHER (1987), the CuCl₂ solution was adjusted to the same ionic strength as the NH₄Cl solution. The soil cations were determined as described above, except for Al which was determined by AAS.

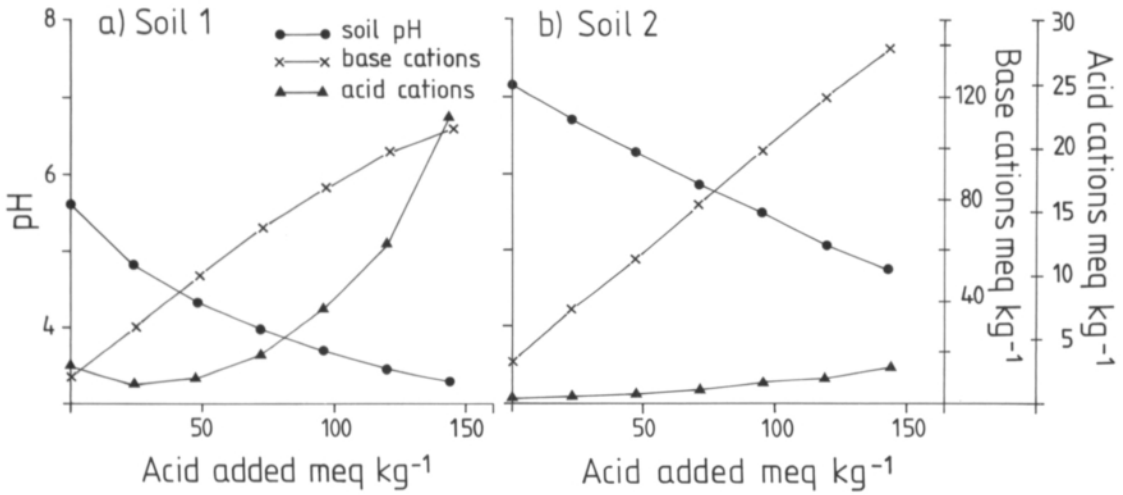


Fig. 1a-b. Suspension pH and the release of the base and acid cations from the soil to solution in the titration experiment.

Results

Titration solutions

The effect of increasing acid load on the pH of the soil suspensions and on the release of cations from soil to solution is described in Figure 1a-b. The cation species non-hydrolyzable at pH values prevailing in soils (Ca, Mg, K, Na) are referred to as basic cations, the hydrolyzable species (Al, Fe, Mn) as acid cations. When calculating the equivalents of the acid species, Fe and Mn were assumed to appear as divalent ions and Al as a trivalent one.

The reciprocal of the slope of the titration graph stands for the buffer capacity (BC), defined as the number of mmols or meq of H⁺ that must be added to 1 kg of soil to lower pH by one unit. When using pH of the zero point of titration (i.e. pH in H₂O) as a reference pH, the buffer capacity was higher for soil 2 (55 meq) than for soil 1 (33 meq). The experimental soils differed also in the shape of the titration curves. At high pH's obtained for soil 2 (range 7.2-4.7) the graph was linear implying the BC to be rather independent of pH. In soil 1, on the contrary, the pH was lower (range 5.6 - 3.3) and BC increased with decreasing pH. However, pH being a logarithmic measure the BC values of various

soils are comparable only at the same pH level. The comparison of the graphs at a coincident pH range (5.6-4.7) revealed the slope to be steeper for soil 1 than for soil 2. This suggests that, at this pH range, soil 2 was more effectively buffered against acid.

In both soils, the basic cations dominated the titration solutions, Ca being the main cation, followed by Mg and K. The difference between the cation quantities dissolved in the acid and water treatments was taken to describe the acid-induced release into supernatant. Similarly, the differences calculated for each acid increment of 24 meq kg⁻¹ were considered to measure the gradual dissolution as response to progressing acidification. The results in Table 2 (only the statistically significant differences are recorded) reveal that with increasing acid load the differential release of Mg decreased proportionately most. The release of Ca diminished clearly in soil 1 but remained rather constant in soil 2. Na was not affected.

The portion of acid cations in the solutions, mainly Al, distinctly increased with progressing acidification in soil 1, but very slightly in soil 2 where the release of Al was of the same magnitude as that of Mn (on the equivalent basis). No Fe was dissolved.

Table 2. Differential dissolution of cations (meq kg⁻¹) calculated for each acid increment of 24 meq kg⁻¹

Increment of acid meq kg ⁻¹	Ca	Mg	K	Na	Al	Fe	Mn	Σ
	Soil 1							
0→24	16.7	2.1	0.7	–	–0.3	–1.2	0.2	18.2
24→48	18.4	2.1	0.7	–	0.5	0.2	0.1	22.0
48→72	16.0	1.7	0.5	–	1.5	–0.1	0.2	19.8
72→96	14.2	1.3	0.5	–	3.6	0.2	0.1	19.9
96→120	11.2	1.1	0.4	0.2	5.2	0.1	0.1	18.3
120→144	7.9	0.9	0.3	0.1	9.1	0.4	0.2	18.9
	Soil 2							
0→24	15.0	3.9	0.7	–	–	–0.1	0.2	19.7
24→48	16.3	3.0	0.5	0.2	–	–	0.3	20.3
48→72	20.2	2.7	0.6	0.4	0.1	–	0.3	24.3
72→96	18.4	2.0	0.4	–0.1	0.3	–	0.3	21.3
96→120	18.4	2.0	0.2	0.1	0.3	–	0.2	21.2
120→144	18.2	0.7	0.4	0.2	0.5	–	0.5	20.5

Table 3. Cations (meq kg⁻¹) replaced by NH₄Cl in soil samples after titration treatment.

Acid added meq kg ⁻¹	Ca	Mg	K	Na	Al	Fe	Mn	Σ
	Soil 1							
0	101.8	11.7	7.4	2.3	4.1	2.2	1.1	130.6
24	88.5	9.5	6.4	2.5	9.2	1.7	0.9	118.7
48	75.4	7.6	5.8	2.1	20.6	0.9	0.8	113.2
72	64.3	6.5	5.4	2.3	31.1	0.9	0.7	111.2
96	53.6	5.2	5.0	2.2	40.8	0.8	0.6	108.2
120	45.6	4.6	4.8	2.3	51.4	0.9	0.5	110.1
144	41.5	4.0	4.6	2.3	58.5	0.9	0.5	112.3
	Soil 2							
0	124.0	16.6	5.0	2.3	0.0	0.1	1.2	149.2
24	117.9	14.2	4.4	2.2	0.0	0.1	1.6	140.4
48	108.3	11.5	3.9	1.9	0.1	0.1	2.0	127.8
72	104.0	9.8	3.7	2.3	0.2	0.1	2.0	122.1
96	95.0	7.9	3.5	2.2	0.3	0.2	2.3	111.4
120	86.9	6.8	3.1	2.1	0.7	0.1	2.1	101.8
144	74.1	5.7	2.9	2.2	1.4	0.2	2.1	88.6

Soil samples

Acidification markedly depleted the reserves of the basic exchangeable cations (Table 3). Magnesium was reduced proportionately more than Ca and K, but no changes were found for Na. The total quantity of NH₄Cl-replaceable cations, taken to represent

effective cation exchange capacity (ECEC), diminished decisively more in soil 2 than in soil 1. This was attributable to the fact that in soil 1 the decrease in the exchangeable basic cations was to a marked degree compensated by an increase in the exchangeable Al. The exchangeable Fe and Mn, on the other hand, were lower in the acidified subsamples than

Table 4. The sums (meq kg⁻¹) of base cations dissolved in the supernatant solution and left in the exchangeable form in soil after titration.

	Acid added meq kg ⁻¹	Ca	Mg	K	Na	Σ
Soil 1	0	105.8	13.6	9.4	5.1	133.9
	72	119.5	14.2	9.2	5.0	147.9
	144	130.4	15.1	9.6	5.2	160.3
Soil 2	0	132.0	19.2	7.9	4.7	163.8
	72	163.5	21.9	8.4	5.4	199.0
	144	188.6	22.5	8.5	5.3	224.9

Table 5. Cations in complexed form (meq kg⁻¹) in the soil samples after titration.

Acid added meq kg ⁻¹	Ca	Mg	Al	Fe	Mn
Soil 1					
0	10.2	0.8	84.1	-0.7	0.1
24	9.1	1.4	84.2	0.2	0.1
48	5.1	0.7	82.4	1.6	0.1
72	4.3	0.3	80.9	2.1	0.1
96	3.3	0.5	77.8	2.4	0.1
120	1.0	0.5	70.9	2.9	0.1
144	-0.3	0.3	66.1	3.3	0.1
Soil 2					
0	32.4	1.0	37.7	0.0	4.4
24	31.4	1.0	39.8	0.0	4.2
48	30.0	0.9	45.1	0.0	3.8
72	21.2	0.7	52.3	0.1	3.7
96	22.5	1.3	51.6	0.0	3.4
120	13.7	0.7	57.3	0.1	3.5
144	12.4	0.8	66.7	0.1	3.5

in the water-treated ones. In soil 2, the exchangeable Al was found in very small quantities and only at the highest acid doses. In this soil, the highest acid addition almost doubled the exchangeable Mn but had no effect on Fe.

For quantitative estimation of the acid-derived changes in the basic cations, the cation equivalents dissolved in the supernatant solutions were summed up to the residual exchangeable reserves (compiled data given in Table 4). The lower sums for the water-treated subsamples as compared to those for the acid-loaded ones indicate that proton additions

evoked mobilization from a non-exchangeable pool to the exchangeable and/or soluble fraction. For Ca, and to a lesser extent for Mg, release from these reserves was enhanced with progressing acidification. For the monovalent species, the phenomenon was less pronounced. Furthermore, the cation supply from non-exchangeable reserves appeared to be of greater significance in soil 2.

The differences between the CuCl₂- and NH₄Cl-extractable cations were considered to represent non-exchangeable reactive reserves, mainly organically bound ones. Acidification gradually exhausted Ca in this fraction in soil 1 and markedly decreased it in soil 2. Complexation of Mg was immaterial and very slightly influenced by acid additions. For acidic cations, Al dominated the complexed reserves. In soil 1, acidification reduced this Al pool but increased the corresponding Fe pool. In soil 2, on the contrary, increasing proton load resulted in an accumulation of Al in a complexed form and a slight decrease in complexed Mn.

Discussion

In order to monitor acid-evoked changes in the soil and solution cations, the titration was performed without background electrolyte. This technique, previously used e.g. by WELLS and DAVEY (1966) and FEDERER and HORNBECK (1985), obviously underestimates the buffer capacity (BC). The present experiment produced lower values than obtained in

a parallel percolation experiment with the same soils (HARTIKAINEN 1992a) where soil pH was measured in a CaCl_2 suspension after elution. Obviously, in the titration experiment without background electrolyte the matrix solution affected dissimilarly soil pH in the various treatments, the pH being erroneously high in the water and maybe in the most dilute acid solution suspensions. This hypothesis is supported by the finding that the difference between the titration and percolation experiment was more pronounced for soil 1 in which the portion of salt replaceable acid cations was high. Also the higher BC for soil 2 of higher pH is in contradiction with general response of non-calcareous soils, confirmed e.g. in the earlier titration study at a constant ionic strength (HARTIKAINEN 1986), that the acid buffering is lowest in soils with the highest pH. This behaviour is attributable to the logarithmic nature of pH.

The marked reduction in the exchangeable base cations in the acid-treated soils evidences inactivation of H^+ by cation exchange. Furthermore, the decrease in ECEC indicates the buffering to have taken place by protonation of variable charge sites. The reduction in ECEC was mainly attributable to the depletion in the divalent base cations. The buffering by exchange reactions can be concluded to be mainly attributable to humic material. It is known that added H^+ ions will associate first with the conjugate base of the weakest acid in the soil. Owing to the weak-acid nature, organic matter with variable charge has a preference as a proton acceptor.

The buffering by the exchange on the permanent charges can be concluded to be rather ineffective because these sites act like strongly acidic anions so that H^+ ions linked to them are strongly ionized. The H^+ ion has to compete with other cations present in ambient solution for the permanently charged exchange sites. Its preference for mineral sites has been found to be between K and Na (GILBERT and LAUDELOUT 1965, TALIBUDEEN 1981). Actually, H^+ ions are weakly adsorbed on the permanent charge sites and will remain in a salt-replaceable

form and, thus, are not really buffered. Therefore, base cations on the permanently charged sites are hardly exchanged directly by H^+ ions but by lattice cations (mainly Al) (VEITH and SCHWERTMANN 1972) or oxide cations (HARTIKAINEN 1986) released by proton attack.

Extraction with NH_4Cl is known to replace Al only from the permanent charge surfaces. Thus, the significant increase in NH_4Cl -replaceable Al upon progressing acidification in soil 1 evidences that, in this soil, exchange occurred markedly also on the mineral surfaces. It is noteworthy that with increasing Al saturation the exchangeable divalent base cations were highly reduced, whereas the monovalent species were only slightly affected. This suggests that, on permanent charges, exchangeable Al replaced mainly divalent species dominating the cation composition. The increase in the Al saturation was reflected as a marked increase in solution Al^{3+} . In the parallel percolation experiment (HARTIKAINEN 1992b) the increased Al saturation enhanced the Al leaching immaterially. This difference in the reaction patterns is due to a higher increase in the ionic strength (due to H_2SO_4) in the titration solutions, which is shown to enhance the displacement of Al^{3+} from exchange sites (REUSS 1983, BRUCE et al. 1989). This reveals that the results obtained for cation exchange in a batch titration are not applicable to freely-drained systems.

The titration results imply that in addition to exchange reactions also other buffering mechanisms were involved. Firstly, the quantities of cations released by acid were lower than the proton equivalents added. Secondly, the depletion in the exchangeable basic cations was smaller than a respective mobilization to solution. The contribution by other buffering reactions in mineral soils of Finland can be concluded also from the titration data published by MÄNTYLÄHTI and NISKANEN (1986) showing the H^+ consumption to be greater than the corresponding reduction in CEC.

In fact, it can be calculated from the data in Table 4 that the highest acid load dissolved 24.6 and 56.6

meq kg⁻¹ non-exchangeable Ca from soil 1 and 2, respectively. A concomitant increase in P mobilization (6.7 mg kg⁻¹ in soil 1 and 39.0 mg kg⁻¹ in soil 2) observed in a parallel titration study (HARTIKAINEN 1992, unpublished data) gives reason to suppose that acid dissolved some Ca from primary or secondary Ca-phosphates, especially in soil 2.

Magnesium and monovalent cations were released mainly from exchangeable reserves. As found also in earlier studies (JEFFREY and WEBER 1982, HAUN et al. 1988), Na did not respond to acidification. When related to the exchangeable pool, the mobilization of Mg in soil 2 was proportionately more pronounced than that of Ca. The result suggests that in a soil of high pH Mg may be more susceptible to proton load, and in the first phase of acidification it will be lost proportionately more effectively than Ca. The acid-induced impoverishment of Mg has been reported in numerous studies on forest soils (e.g. ABRAHAMSEN 1980, JEFFREY and WEBER 1982, BOSCH et al. 1983, ZECH and POPP 1983) and also on acid sulphate soils (HARTIKAINEN and YLI-HALLA 1986).

The difference between CuCl₂- and NH₄Cl-extractable cations was assumed to represent non-exchangeable reactive reserves, mainly organically bound ones. Cu²⁺ has a high affinity for functional groups of humic compounds and is able to replace complexed cations (BLOOM et al. 1979). Being acidic, the CuCl₂ solution may extract also some inorganic polymerized metals, but according to OATES and KAMPRATH (1983), it hardly markedly enhances the replacement of Al from the mineral fraction. Furthermore, because CuCl₂ determines the pH of the extraction mixture (OATES and KAMPRATH 1983), it can be concluded that in the present study the same Al pool was affected in all treatments.

The role of organic matter in regulating the acid-derived changes in soil cations was dependent on the soil pH. In both soils, the acid loading resulted in replacement of the complexed Ca by Al³⁺ or H⁺. The reduction in the complexed Ca explained a small part of the total mobilization from non-

exchangeable reserves. In the slightly acid soil 2 (pH 6.7), acidification enhanced the accumulation of Al into the non-exchangeable complexed fraction. At the same time some dissolution of weaker Mn complexes appeared to take place.

In the acid soil 1 (pH 4.9), on the contrary, complexed Al began to decrease and exchangeable Al to increase from the second acid increment on (suspension pH 4.3). This response, demonstrating a gradual shift from a non-labile complexed pool to a labile one, was similar to that found by JAMES and RIHA (1984) in soil extracts. The reduction in the complexed reserves was, however, lower than the concomitant increase in the exchangeable and dissolved fractions, which indicates that Al was mobilized also from mineral components of soil. The decrease in complexed Al coincided with an accumulation of Fe in the complexed form, which gives reason to suppose that Fe dissolved by acid began to replace Al from the complexation sites. This hypothesis is supported e.g. by the results of SCHNITZER and SKINNER (1965) showing that organic matter has a higher affinity for Fe than for Al, even though the retention of both metals decreases when pH is lowered. The replacement of Al by Fe did not, however, quantitatively explain the depletion in the complexed Al. This indicates that with increasing acid load, also H⁺ began to compete more effectively with Al³⁺ for ligand binding sites. Also BLOOM et al. (1979) concluded the Al replacement by H⁺ on organic matter exchange sites to be an important source of pH buffering.

The experimental soils differed in their buffering mechanisms, as concluded from the dissimilar shapes of their titration graphs. The results demonstrate that the role of humic material as H⁺ buffering agent is limited at low pH's. Also the complexation of detrimental metals alleviates the effects of proton loading more effectively in soils of high pH, because the stability of the metal complexes decreases with lowering pH. A common feature was that the release of soil elements to supernatant due to acidification did not quantitatively explain the changes in soil chemistry. More detailed studies are

needed, e.g. to qualify and quantify the role of organic matter in buffering.

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SELOSTUS

Maa-aineksen reaktiot happotitrauksessa

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Laboratoriossa tehdyssä titrauskokeessa seurattiin kasvavien happolisäysten aiheuttamia muutoksia maa-aineksessa ja sitä ympäröivässä liuoksessa. Kokeessa käytettiin kahta viljelymaan muokkauserroksista otettua hietänäytettä, joista toinen (maa 1) oli selvästi hapan (CaCl₂-pH 4,9) ja toinen (maa 2) vain heikosti hapan (pH 6,7). Ilmakuivaa maata (5 g) punnittiin sentrifugiputkiin, joihin lisättiin 50 ml vettä tai rikkihappoliuosta (0,0012 - 0,0072 M). Suspensioiden pH mitattiin 48 tunnin kuluttua, minkä jälkeen maa-aines ja liuosfaasi erotettiin sentrifugoimalla ja analysoitiin erikseen.

Vety-ionien sitoutuminen pH:sta riippuville varauspaikoille (pääasiassa humukseen) emäskationeja syrjäyttämällä oli tärkeä puskurointimekanismi, minkä seurauksena efektiivinen kationinvaihtokapasiteetti (EKVK) pieneni. EKVK:n lasku jäi kuitenkin pienemmäksi alunperin happamassa maanäytteessä 1, jossa vaihtoreaktioita tapahtui merkittävässä määrin myös mineraaliaineksen pysyvän negatiivisen varauksen omaavilla vaihtopaikoilla. Niihin sitoutuneita vaihtuvia emäskationeja korvautui alumiinilla, jota vapautui maasta vaihtuvaan muotoon happamoitumisen seurauksena. Titraus-

liuokseen liukeni eniten kalsiumia, mutta vaihtuviin varoihin suhteutettuna magnesiumia näytti vapautuvan maasta herkemmin etenkin pH:n ollessa korkea. Happamoituminen edisti myös vaihtumattomana olevien emäskationien (lähinnä 2-arvoisten) mobilisoitumista vaihtuvaan muotoon. Happamien kationien osalta maanäytteet poikkesivat selvästi toisistaan. Maanäytteessä 2, joka oli alunperin melko neutraali, happamoitumisen seurauksena liennut alumiini näytti sitoutuvan orgaanisiksi komplekseiksi ja sitä vapautui suurillakin happokuormilla liuokseen erittäin vähän. Sen sijaan maanäytteessä 1 liukoisen alumiinin määrä kasvoi happamoitumisen myötä samanaikaisesti kun vaihtuvan alumiinin määrä maassa lisääntyi merkittävästi ja kompleksoituneen alumiinin määrä pyrki laskemaan. Eri kationien vapautuminen liuosfaasiin ei kuitenkaan kvantitatiivisesti selittänyt maan kemiassa havaittuja muutoksia. Kun titrauskokeen tuloksia verrattiin huuhtomiskokeessa vastaavilla happokäsittelyillä saatuihin tuloksiin, havaittiin mm., että eräitras yliarvioi alumiinin vapautumista liuosfaasiin.