

## Extractable aluminium, iron and manganese in mineral soils I Dependence of extractability on the pH of oxalate, pyrophosphate and EDTA extractants

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**Abstract.** Al, Fe and Mn in two mineral soils were extracted by 0.05 M and 0.02 M oxalate and pyrophosphate and 0.02 M EDTA solutions the pH of which was adjusted to values ranging from 1.7 to 11.0. The extractability of metals tended to decrease as the pH rose and as the deprotonation of extractant acid, expressed as  $pK_a$  values, progressed. The reduction in extractability of metals by oxalate was rather steep at  $pH > 4$ , whereas the extractability by pyrophosphate remained moderate at a wider pH range. The extractability of metals by EDTA ( $pH\ 3.6-7.3$ ) was lower than that by oxalate and pyrophosphate. Extractability was lower in the absence of the studied oxyacid anions and with 0.01 M KCl as the supporting electrolyte at a pH between 2 and 11 than in their presence.

Index words: amorphous Al, Fe and Mn, acetate-extractable Al, complexing agents, protolysis constants, soil extraction

### Introduction

The removal of aluminium, iron and manganese from soil by solutions of weak acid anions and the adsorption of these anions on soil oxides are based on complexation reactions. At low concentration anions are sorbed on oxides; at high concentration they act as extractants of oxides. The ability of weak acid anions to form metal complexes depends on the form of anions, which in turn depends upon pH. Inflexions in the adsorption 'envelopes' of weak acid anions occur in the vicinity

of pHs corresponding to  $pK_a$  values of acid at issue (HINGSTON et al. 1967, 1968). The extractability of amorphous aluminium, iron and manganese oxides from soil by solutions of weak acid anions is seldom studied as a function of the extractant pH. In a previous study (NISKANEN 1989), the release of soil aluminium and iron by fluoride strongly increased as the pH of the extractant solution decreased. The aim of this paper was to study the effect of the extractant pH on the disso-

Table 1. Soil samples.

	Fine sand	Sand
Sampling depth, cm	0—20	20—40
pH(CaCl <sub>2</sub> )	5.1	4.6
Organic C, %	3.6	0.8
Particle-size distribution:		
<2 µm, %	13	2
2—20 µm, %	20	1
20—60 µm, %	27	7
60—200 µm, %	31	35
>200 µm, %	9	56
Tamm's acid ammonium oxalate-soluble		
Al mmol/kg soil	186	104
Fe mmol/kg soil	53	32
Mn µmol/kg soil	2 200	530
0.1 M Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> -soluble		
Al mmol/kg soil (% of Tamm's oxalate-soluble)	92 (49)	54 (52)
Fe mmol/kg soil (% of Tamm's oxalate-soluble)	23 (44)	10 (30)
Mn µmol/kg soil (% of Tamm's oxalate-soluble)	2 280 (103)	110 (21)
1 M ammonium acetate-soluble		
Al mmol/kg soil (% of Tamm's oxalate-soluble)	6 (3)	10 (9)

lution of aluminium, iron and manganese from soil by solutions of anions of three oxyacids commonly used in soil research.

### Material and methods

The material consisted of a fine sand sample from the surface layer of a cultivated soil (South Karelia, Imatra) and a sand soil sample from a deeper layer of virgin soil (Viikki Experimental Farm, University of Helsinki)

(Table 1). The samples were air-dried and ground to pass through a 2-mm sieve. The pH of the soil was measured in a soil-0.01 M CaCl<sub>2</sub> suspension (1:2.5 v/v) (RYTI 1965). The organic carbon content of the soil was determined by a modified (GRAHAM 1948) ALTEN wet combustion method, the particle-size distribution by the pipette method (ELONEN 1971).

The extraction methods for soil aluminium, iron and manganese are given in Table 2. Extractions 1—3 were used as reference methods. The effect of pH on extractability was studied by using dilute oxalate, pyrophosphate and EDTA solutions. The pK<sub>a</sub> values of the acids are given in Table 3. Acid oxalate solutions were prepared from oxalic acid and ammonium oxalate, basic oxalate solutions from ammonium oxalate by adjusting the pH with 5 % NH<sub>4</sub>OH. The pH of K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> solutions was adjusted with 5 M HCl and NaOH, the pH of EDTA solutions with CH<sub>3</sub>COOH and NaOH. It was not possible to prepare EDTA solutions with pH < 3.6 because at a lower pH the H<sub>2</sub>-EDTA of low solubility precipitated. Extractability without anions of oxyacids was studied by using KCl solutions, the pH of which was adjusted with 5 M HCl and NaOH. The pH of soil-solution suspensions was measured before and after shaking.

Aluminium, iron and manganese in filtrates were determined by atomic absorption spectrophotometry, Fe and Mn with air-acetylene flame and Al with N<sub>2</sub>O-acetylene flame. The experiment was carried out in duplicate.

Table 2. Extraction methods.

Extractant	pH	Extraction ratio, w/v	Shaking time, h	Reference
1. 0.18 M ammonium oxalate, 0.10 M oxalic acid	3.3	1:20	2	TAMM 1922
2. 0.1 M Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	10.0	1:20	4	McKEAGUE 1967
3. 1 M ammonium acetate	4.8	1:10	2	McLEAN et al. 1958
4. 0.05 M oxalate	1.7—9.7	1:200	3	
5. 0.02 M oxalate	2.0—8.4	1:100	3	
6. 0.05 M K <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	2.4—11.0	1:100	3	
7. 0.02 M K <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	2.5—10.1	1:100	3	
8. 0.02 M Na <sub>2</sub> -EDTA	3.6—7.3	1:100	3	
9. 0.01 M KCl	2.3—11.1	1:100	3	

Table 3.  $pK_a$  values of oxalic, pyrophosphoric and ethylenediamine tetraacetic acids (MARTELL and CALVIN 1956, ANON. 1984).

Acid	$pK_1$	$pK_2$	$pK_3$	$pK_4$
Oxalic	1.2	4.2	—	—
Pyrophosphoric	0.9	1.5	5.8	8.2
Ethylenediamine tetraacetic	2.0	2.7	6.2	10.3

## Results and discussion

The removal of metals by 0.05 M oxalate decreased as the pH increased, the reduction in extractability being rather steep at  $pH > 4$  (Figs. 1—3). The minimum extractability of aluminium was measured when pH was about 9 (Fig. 1). At low pH, 0.05 M oxalate extracted more metals than did Tamm's oxalate. The pH at which the removal of metals was equal to the extractability by Tamm's oxalate differed to some extent in both soils, being about 4 for aluminium and iron in fine sand soil and about 4.5 for those in sand soil (Figs. 1—2). The removal of manganese by 0.05 M and Tamm's oxalate was equal at pH 4.3 (fine sand) and 2.0 (sand) (Fig. 3).

The 0.02 M oxalate was a less efficient extractant than 0.05 M oxalate (Figs. 1—3). The extractability of iron in fine sand soil by 0.02 M oxalate was at the highest only 80 % of Tamm's oxalate-extractable iron (Fig. 2).

As pH rose, the decrease in the extractability of metals by  $K_4P_2O_7$  sloped more gently than with oxalate extraction (Figs. 1—3). As compared to oxalate, the extracting ability of pyrophosphate remained moderate at a wider pH range. The iron extracted by 0.05 M  $K_4P_2O_7$  at pH 10 did not deviate much from that extracted by 0.1 M  $Na_4P_2O_7$ , whereas more aluminium was extracted from sand soil by 0.05 M  $K_4P_2O_7$  than by 0.1 M  $Na_4P_2O_7$ . The efficiency of 0.02 M  $K_4P_2O_7$  as the extractant was less than that of 0.05 M  $K_4P_2O_7$ .

As compared to oxalate and pyrophosphate extraction, the extractability of aluminium and iron by 0.02 M EDTA was lower (Figs. 1—2). The extractability was nearly unchanged in the pH range of 5—7; outside this range it slightly increased (Figs. 1—2). In the studied pH range, the extractability of aluminium by EDTA was not much higher than that by ammonium acetate at pH 4.8 (Table 1). The solubility of iron by EDTA was

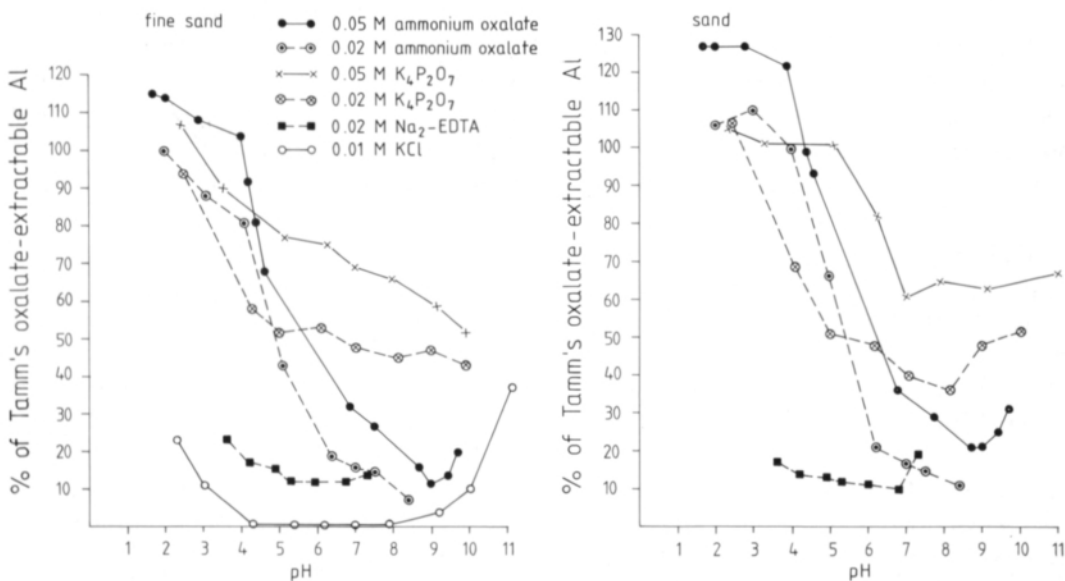


Fig. 1. Extractability of aluminium (% of Tamm's oxalate-extractable Al) versus extractant pH.

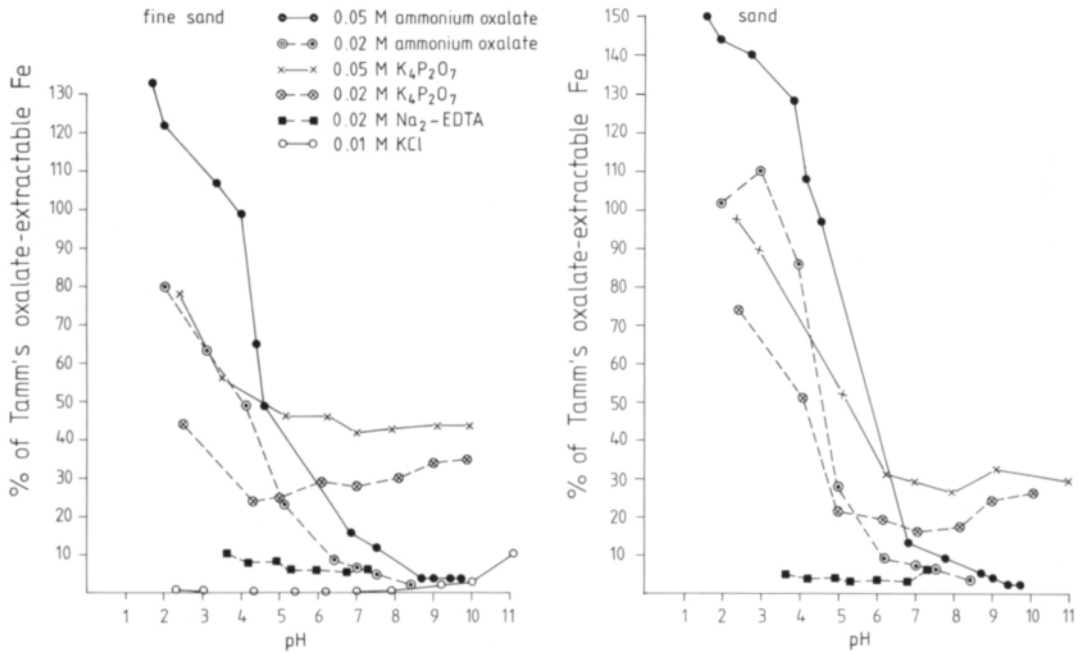


Fig. 2. Extractability of iron (% of Tamm's oxalate-extractable Fe) versus extractant pH.

less than 10 % of that by Tamm's oxalate (Fig. 2). The extractability of manganese in fine sand soil by EDTA decreased as the pH increased, whereas no manganese was extracted from sand soil (Fig. 3).

In the absence of oxyacid anions and with 0.01 M KCl as supporting electrolyte, the solubility of metals was lower than in the presence of those anions (Figs. 1—3). An increasing  $H^+$  concentration in the KCl solution enhanced the dissolution of metals as a result of the formation of aquocations in a reverse hydrolysis reaction. Aluminium and manganese in fine sand soil were solubilized more readily than iron (Figs. 1—3). The method for the selective extraction of 'active' aluminium oxides by 0.5 M  $CaCl_2$  at pH 1.5 used by TWENEBOAH et al. (1967) is actually based on this different solubility of aluminium and iron at low pH.

An increasing  $OH^-$  concentration enhanced the release of metals. The extractability of aluminium and iron in fine sand soil by 0.01 M KCl increased when the pH exceeded 8, that of manganese when the pH exceeded 10 (Figs. 1—3). The release of aluminium by

0.05 M oxalate increased when the pH exceeded about 9 (Fig. 1).

Oxalic, pyrophosphoric and ethylenediamine tetraacetic acids are di- and tetraprotic acids the  $pK_a$  values of which are given in Table 3. According to the theory of HINGSTON et al. (1967, 1968), the adsorption 'envelopes' of anions of these acids should have a maximum at a pH that corresponds to  $pK_1$ . Thereafter the 'envelopes' should have a decreasing slope that is most marked at a pH corresponding to the highest  $pK_a$ . The graphs of the solubility of metals versus pH (Figs. 1—3) showed that extractability by these oxyacid anions also depended on the extractant pH and had a tendency to decrease with rising pH and progressing deprotonation of the extractant acid. The extraction graphs of metals when oxalate was used showed that when the pH was higher than that corresponding to the highest  $pK_a$  of acid, the extractability graphs descended steeply.

The fact that the extracting ability of organic acid anions depends on pH is not significant only in choosing the pH of the extractant solution; it is also important when soil

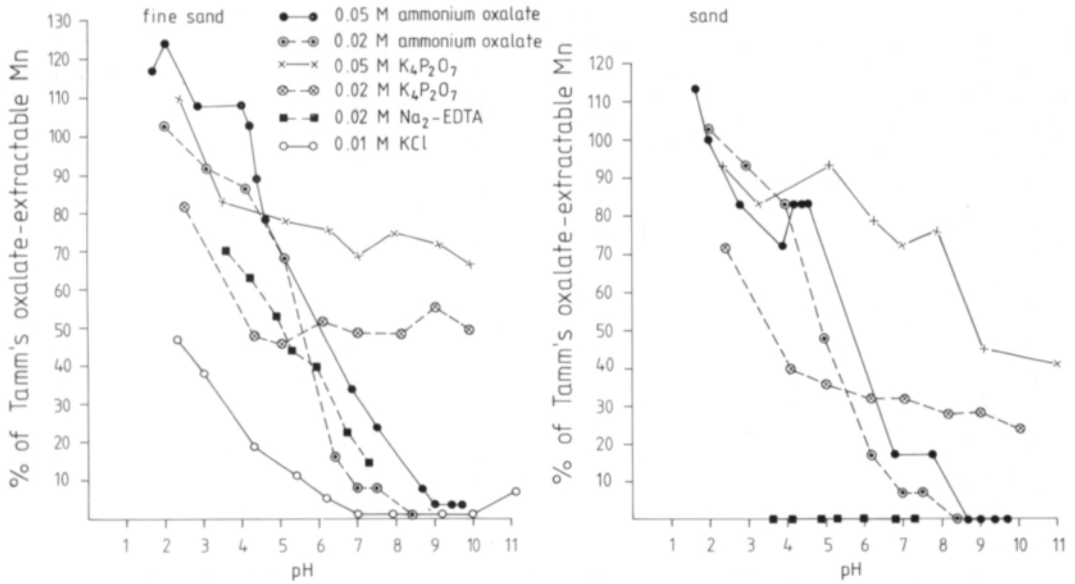


Fig. 3. Extractability of manganese (% of Tamm's oxalate-extractable Mn) versus extractant pH.

conditions are considered. Organic acids are present in soil as a consequence of root exudation and microbial activity in the rhizosphere (CURL and TRUELOVE 1986), they act as chelators in soil formation processes (SCHNITZER 1959, HINGSTON 1962), and they affect the availability of plant nutrients, e.g. phosphorus. In acid soil, the removal of phosphate by organic acid anions is pH-dependent and occurs largely through dissolution and

chelation of iron and aluminium (LOPEZ-HERNANDEZ et al. 1979). Organic anions enhance the solubility of metals; thus, for example, the concentration of aluminium increases more than would be expected only on the basis of the pH (REUSS and JOHNSON 1986). The effect of soil acidification is to enhance the ability of organic acid anions to solubilize metals through complexation.

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## SELOSTUS

### **Kivennäismaiden uuttuva alumiini, rauta ja mangaani I Uuttuvuuden riippuvuus oksalaatti-, pyrofosfaatti- ja EDTA-uuttoliuosten pH:sta**

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Kahden kivennäismaan alumiinia, rautaa ja mangaania uutettiin 0,05 M ja 0,02 M oksalaatti- ja pyrofosfaattiliuksilla sekä 0,02 M EDTA-liuksilla, joiden pH oli 1,7—11,0. Suuntauksena oli, että metallien uuttuminen väheni uuttoliuoksen pH:n ja uuttavan hapon dissosiaatioasteen kohotessa. Uuttuvuus aleni jyrkästi oksalaatti-

liuoksen pH:n ollessa yli 4, kun uuttuvuus pyrofosfaatilla pysyi kohtalaisena laajalla pH-alueella. EDTA (pH 3,6—7,3) uutti vähemmän metalleja kuin oksalaatti ja pyrofosfaatti. Pelkkä 0,01 M KCl uutti pH-alueella 2—11 vähemmän metalleja kuin tutkittavat uuttoliukset.