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 pKₐ values, progressed. The reduction in ex-
tractability 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 reac-
tions. 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 'enve-
lopes' of weak acid anions occur in the vicinity of pHs corresponding to pKₐ 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 in-
creased 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.

<table>
<thead>
<tr>
<th>Sampling depth, cm</th>
<th>Fine sand</th>
<th>Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH(CaCl₂)</td>
<td>5.1</td>
<td>4.6</td>
</tr>
<tr>
<td>Organic C, %</td>
<td>3.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Particle-size distribution:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;2 μm, %</td>
<td>13</td>
<td>2</td>
</tr>
<tr>
<td>2—20 μm, %</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>20—60 μm, %</td>
<td>27</td>
<td>7</td>
</tr>
<tr>
<td>60—200 μm, %</td>
<td>31</td>
<td>35</td>
</tr>
<tr>
<td>&gt;200 μm, %</td>
<td>9</td>
<td>56</td>
</tr>
</tbody>
</table>

Tamm's acid ammonium oxalate-soluble

<table>
<thead>
<tr>
<th>Extractant</th>
<th>pH</th>
<th>Extraction ratio, w/v</th>
<th>Shaking time, h</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al mmol/kg soil</td>
<td>1.08</td>
<td>92 (49)</td>
<td>54 (52)</td>
<td>1:20</td>
</tr>
<tr>
<td>Fe mmol/kg soil</td>
<td>1.08</td>
<td>23 (44)</td>
<td>10 (30)</td>
<td>1:20</td>
</tr>
<tr>
<td>Mn μmol/kg soil</td>
<td>1.08</td>
<td>2 280 (103)</td>
<td>110 (21)</td>
<td>1:10</td>
</tr>
<tr>
<td>0.1 M Na₃P₂O₅-soluble</td>
<td>1.08</td>
<td>6 (3)</td>
<td>10 (9)</td>
<td>1:20</td>
</tr>
</tbody>
</table>

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 pK₃ 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% NH₄OH. The pH of K₃P₂O₅ solutions was adjusted with 5 M HCl and NaOH, the pH of EDTA solutions with CH₃COOH and NaOH. It was not possible to prepare EDTA solutions with pH < 3.6 because at a lower pH the H₂-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 N₂O-acetylene flame. The experiment was carried out in duplicate.

(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 CaCl₂ 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 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 3. pK\textsubscript{a} values of oxalic, pyrophosphoric and ethylenediamine tetraacetic acids (Martell and Calvin 1956, Anon. 1984).

<table>
<thead>
<tr>
<th>Acid</th>
<th>pK\textsubscript{1}</th>
<th>pK\textsubscript{2}</th>
<th>pK\textsubscript{3}</th>
<th>pK\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic</td>
<td>1.2</td>
<td>4.2</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Pyrophosphoric</td>
<td>0.9</td>
<td>1.5</td>
<td>5.8</td>
<td>8.2</td>
</tr>
<tr>
<td>Ethylenediamine tetraacetic</td>
<td>2.0</td>
<td>2.7</td>
<td>6.2</td>
<td>10.3</td>
</tr>
</tbody>
</table>

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\textsubscript{4}P\textsubscript{2}O\textsubscript{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\textsubscript{4}P\textsubscript{2}O\textsubscript{7} at pH 10 did not deviate much from that extracted by 0.1 M Na\textsubscript{4}P\textsubscript{2}O\textsubscript{7}, whereas more aluminium was extracted from sand soil by 0.05 M K\textsubscript{4}P\textsubscript{2}O\textsubscript{7} than by 0.1 M Na\textsubscript{4}P\textsubscript{2}O\textsubscript{7}. The efficiency of 0.02 M K\textsubscript{4}P\textsubscript{2}O\textsubscript{7} as the extractant was less than that of 0.05 M K\textsubscript{4}P\textsubscript{2}O\textsubscript{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.](image-url)
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 CaCl₂ 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 tetracetic acids are di- and tetraprotic acids the pKₐ 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 pK₁. Thereafter the ‘envelopes’ should have a decreasing slope that is most marked at a pH corresponding to the highest pKₐ. 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 pKₐ 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
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.

References


McLean, E.O., Heddleston, M.R., Bartlett, R.J. & 77


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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 pyrofosfaatti-liuosilla sekä 0,02 M EDTA-liuosilla, joiden pH oli 1,7—11,0. Suuntauksena oli, että metallien uuttuminen vähensi uuttoliuoksen pH:n ja uuttavan hapon dissoiaatioasteen kohotossa. Uuttuvuus aleni jyrkästi oksalaatti-liuosken pH:n ollessa yli 4, kun uuttuvuus pyrofosfaatiilla 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 uuttoliuokset.