Water soluble phosphorus in Finnish mineral soils and its dependence on soil properties

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Abstract. Water soluble phosphorus ranged from 0.2 mg to 117.8 mg/kg in 104 surface soil samples studied. On the average, water extracted less P from the heavy clay soils (4.8 ± 2.2 mg/kg) than from the coarser clays (12.8 ± 4.6 mg/kg) and non-clay soils (13.3 ± 7.2 mg/kg).

Water extraction seemed to illustrate "the effective" P status, it is that determined by the quantity and quality of sorption components in soil, soil pH and the content of organic carbon. These factors did not affect the amounts of P dissolved in water directly but indirectly by controlling the nature of P bonding which, in turn, seems to be of decisive importance in the extractability of P into water.

The P supplying power of a given fraction is obviously controlled by the quantity of corresponding sorption agent. Water extractable P correlated most closely with the molar ratio of NH₄F soluble P to oxalate extractable Al (r=0.93**, n=103). However, according to the theory presented, with progressing desorption, P starts to mobilize also from the NaOH soluble fraction, its significance being the more apparent the greater the corresponding molar ratio NaOH-P/Fe is. In addition, the role and significance of other inorganic P fractions were discussed.

Introduction

The availability of soil phosphorus to plants essentially depends on the solubility of phosphorus compounds or surface complexes. A great deal of effort has been expended on trying to find suitable chemical extraction methods for the determination of phosphorus resources in soils available to plants.

In Europe, the lactat method is commonly being used, but recently also the water extraction method of van der PAAUW (1971) and SISSINGH (1971) has become general. According to SCHACHTSCHABEL and BEYME (1980), water soluble phosphorus reflects the quantity of total phosphorus relatively easily dissolved and, thus, the phosphorus supplying power of the soil. In the pot experiment made by AURA (1978) with some Finnish soils, the phosphorus extracted by water quite well correlated with the phosphorus uptake by the oats.
Water treatment is superior to strong extractants, because it does not alter the microstructure of the soil decisively. Further, water soluble, inorganic phosphorus is biologically immediately available and therefore the method can be used also for estimating the ability of eroded soil material to load surface waters with phosphorus or quantities of phosphorus possible to be dissolved in runoff waters.

The purpose of the present study was to investigate the amount of water soluble phosphorus in Finnish mineral soils and its dependence on soil properties. The results were assumed to give intimations also about factors regulating phosphorus exchange between the bottom sediment and overlying water in lakes.

Material and methods

The material consisted of 104 mineral soil samples from southern and middle Finland. Most of the samples were taken from the plough layer of cultivated soils and only a few ones from the surface layer of virgin soils. All the samples were air-dried and ground to pass a 2-mm sieve. They were divided into three groups on the basis of the results of mechanical analysis. The heavy clay soils (19) were samples containing 60 % or more clay (<2 μm) and the coarser clays (51) those containing 30–59 % clay. The group of non-clay soils consisted of 27 silt soil samples in which the particle size fraction 2–20 μm was dominating and of 7 fine sand soils with the main fraction 20–200 μm.

The chemical characteristics of the soil samples are presented in Table 1. Soil pH was measured by a Beckman pH-meter in a 0.01 M CaCl₂ suspension in the ratio of 1 to 2.5. The content of organic carbon was determined by a modified WALKLEY and BLACK wet combustion method (GRAHAM 1948). Amorphous aluminium, iron and manganese were extracted by shaking the samples for two hours in a 0.05 M ammoniumoxalate solution (pH 3.3) in the ratio of soil to solution of 1:20 (w/v). Aluminium, iron and manganese concentrations were determined by a Varian Techtron atomic absorption spectrophotometer.

The inorganic phosphorus status of the soils was studied by a modified CHANG and JACKSON fractionation method (HARTIKAINEN 1979). The various extracts were analysed for phosphorus by a molybdenum blue method, modified by KAILA (1955). Water soluble phosphorus was extracted by a modified van der PAAUW (1971) and SISSINGH (1971) method. Deionized water was used at a water-soil ratio of 60:1 on volume/weight basis. Premoistening was replaced by prolonged shaking: an hour after addition of water and 15 minutes after standing for 23 hours. The suspensions were centrifuged and filtered through a filter of 0.2-μm pore size. The phosphorus concentrations in the filtrates were determined by the ascorbic acid method (ANON. 1969).

Results

The amount of water soluble P ranged very widely: 0.2–117.8 mg/kg soil, the average being 11.5 mg/kg and the median 5.8 mg/kg. Table 2 shows the quantities of water extractable P and the inorganic P fractions in the various soil sample groups. The water soluble reserves in the heavy clay soils were generally smaller and ranged less than those in the coarser soils. The total fractionated P varied from 160 to 1453 mg/kg soil, the average being 564 mg/kg. As a rule, NH₄Cl and H₂SO₄ extracted less P from the heavy clay soils than from the samples belonging to the other groups. With regard to the other extractants, the differences between the soil groups were not statistically significant. Only in a few soil samples did the quantity of NH₄F-P ("Al-P")
Table 1. Chemical characteristics of the soil samples. Means with the confidence limits at the 95 per cent level, \( w = \) range.

<table>
<thead>
<tr>
<th>Number of samples</th>
<th>pH</th>
<th>% D.M.</th>
<th>Oxalate extractable (mmol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>Heavy clays</td>
<td>5.0±0.2</td>
<td>5.2±1.0</td>
<td>95±22</td>
</tr>
<tr>
<td></td>
<td>4.2-6.0</td>
<td>1.0-9.0</td>
<td>45-255</td>
</tr>
<tr>
<td>Coarser clays</td>
<td>5.2±0.2</td>
<td>4.4±0.7</td>
<td>63±7</td>
</tr>
<tr>
<td></td>
<td>4.3-6.6</td>
<td>0.5-17.4</td>
<td>32-161</td>
</tr>
<tr>
<td>Non-clay soils</td>
<td>5.2±0.2</td>
<td>3.5±0.1</td>
<td>60±10</td>
</tr>
<tr>
<td></td>
<td>3.8-6.3</td>
<td>0.2-7.7</td>
<td>17-141</td>
</tr>
</tbody>
</table>

Table 2. Water soluble P and P fractions (mg/kg) in the soil samples. Means with the confidence limits at the 95 per cent level, \( w = \) range.

<table>
<thead>
<tr>
<th>Water soluble</th>
<th>NH(_4)Cl</th>
<th>P extracted sequentially by NH(_4)F</th>
<th>NaOH</th>
<th>H(_2)SO(_4)</th>
<th>reduct. solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy clays</td>
<td>4.8±2.2</td>
<td>2.0±0.4</td>
<td>93±49</td>
<td>264±47</td>
<td>132±43</td>
</tr>
<tr>
<td></td>
<td>0.2-20.0</td>
<td>1.0-4.5</td>
<td>14±490</td>
<td>132-427</td>
<td>39-423</td>
</tr>
<tr>
<td>Coarser clays</td>
<td>12.8±4.6</td>
<td>6.4±2.4</td>
<td>112±25</td>
<td>220±33</td>
<td>214±25</td>
</tr>
<tr>
<td></td>
<td>0.2-78.2</td>
<td>0.8-38.6</td>
<td>10-478</td>
<td>36-586</td>
<td>63-423</td>
</tr>
<tr>
<td>Non-clay soils</td>
<td>13.3±7.2</td>
<td>6.7±3.6</td>
<td>129±35</td>
<td>204±36</td>
<td>231±30</td>
</tr>
<tr>
<td></td>
<td>0.3-117.8</td>
<td>0.8-60.0</td>
<td>13-498</td>
<td>65-487</td>
<td>91-411</td>
</tr>
</tbody>
</table>

Water soluble P seemed to be associated with the total fractionated P (\( r=0.75^{**}, n=104 \)). However, this correlation gives no information about factors primarily regulating the level of P soluble in water. The positive relationship is probably due to the fact that the main portion of total P is composed of fractions supposed to represent secondary phosphates (\( \text{NH}_4\text{Cl-P}, \text{NH}_4\text{F-P}, \text{NaOH-P} \) and reductant soluble P). Table 3 shows that, excluding the heavy clay soils, the water soluble resources were quite poorly related to the H\(_2\)SO\(_4\)-P assumed to represent primary apatite-P. They were most closely connected with the \( \text{NH}_4\text{Cl} \) extractable fraction and quite well with the \( \text{NH}_4\text{F} \) soluble one. They correlated distinctively more poorly with the \( \text{NaOH} \)-P, and not at all with the reductant soluble fraction.

The other soil properties studied seemed to have no direct effect on the extractability of P into water. Only an increase in the soil pH tended to exceed that of NaOH-P ("Fe-P"). In the heavy clay soils the ratio of NH\(_4\)F-P to NaOH-P tended to be lower than in the coarser ones.

There was one heavy clay sample containing many times more oxalate soluble Al than the other samples of the group. This exceptional soil sample was mostly excluded from the statistical analyses.
Table 3. Total linear correlation coefficients for the relation between water soluble P and soil characteristics.

<table>
<thead>
<tr>
<th></th>
<th>Heavy clays (18)</th>
<th>Coarser clays (51)</th>
<th>Non-clay soils (34)</th>
<th>All samples (103)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>0.48*</td>
<td>0.34*</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>NH₄Cl-P</td>
<td>0.68**</td>
<td>0.96***</td>
<td>0.97***</td>
<td>0.96***</td>
</tr>
<tr>
<td>NH₄F-P</td>
<td>0.62**</td>
<td>0.75***</td>
<td>0.80***</td>
<td>0.77***</td>
</tr>
<tr>
<td>NaOH-P</td>
<td>ns</td>
<td>0.59***</td>
<td>0.53**</td>
<td>0.48***</td>
</tr>
<tr>
<td>H₂SO₄-P</td>
<td>0.60**</td>
<td>0.53***</td>
<td>0.38*</td>
<td>0.47***</td>
</tr>
</tbody>
</table>

ns = not significant

somewhat to enhance the solubility in the heavy clay soils (r=0.50*, n=19). When the effect of organic carbon was eliminated, the correlation rose to r=0.58*. In the other soil groups, the relationship between organic carbon and soil acidity was not very distinct, and the values of the partial correlation coefficients remained low.

Some dependence did, however, exist between certain P fractions and chemical soil properties. In the coarser clay soils, NH₄Cl-P was positively, but weakly correlated with pH (r=0.44**, n=51). The H₂SO₄ soluble reserves seemed to be the greater the higher the soil pH was, but the values of the correlation coefficients remained quite low. This relationship between H₂SO₄-P and pH probably explains to some degree the correlation found between the water soluble P and H₂SO₄-P; by excluding the effect of pH, the correlation in the heavy clay soils was lowered from r=0.60** to 0.48* and in the coarser clay soils from r=0.53*** to 0.47***.

The NH₄F-P was not connected with oxalate extractable Al, whereas the oxalate soluble Fe seemed to some extent to explain the variation in the NaOH-P in the heavy and coarser clay soils (60 % and 56 %, respectively), but not in the non-clay soils. On the contrary, the ratio of NH₄F-P to NaOH-P correlated moderately with the ratio of Al to Fe, the value of r being 0.78*** (0.97***, n=19) in the heavy clay soils, 0.75*** in the coarser clays, 0.47** in the non-clay soils and 0.60*** in all samples. The ratio NH₄F-P/NaOH-P was not significantly related to the soil pH. In the heavy clay soils it tended to become greater with an increase in the content of organic carbon (r=0.58**).

An interesting finding observed was the tendency the reductant soluble P fraction being slightly related to oxalate extractable Fe (r=0.53*, n=19) in the heavy clay soils, and to oxalate extractable Mn in the coarser clays and non-clay soils (r=0.63*** and 0.75***, respectively). The difference between the values of r for the last two soil groups was not statistically significant as tested by the z-transformation test (SNEDECOR and COCHRAN 1972), and the coefficients hardly changed when the effect of Fe was excluded.

Because the distribution of secondary P in NH₄F and NaOH soluble forms seemed to be markedly controlled by the ratio Al/Fe, the partial correlation coefficients for the relationship between water soluble P and a particular
fraction were calculated by eliminating the effect of corresponding sorptive component. The values of \( r \), given in the following, were higher than the total correlation coefficients (cf. Table 3):

<table>
<thead>
<tr>
<th></th>
<th>( \text{NH}<em>4\text{F}-\text{P}</em>{\text{Al}} )</th>
<th>( \text{NaOH}-\text{P}_{\text{Fe}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy clays</td>
<td>0.81***</td>
<td>0.63**</td>
</tr>
<tr>
<td>Coarser clays</td>
<td>0.87***</td>
<td>0.77***</td>
</tr>
<tr>
<td>Non-clay soils</td>
<td>0.91***</td>
<td>0.57***</td>
</tr>
<tr>
<td>All samples</td>
<td>0.86***</td>
<td>0.68***</td>
</tr>
</tbody>
</table>

The amorphous Al and Fe oxides and the phosphates bound by them seem to be of great importance in controlling the level of easily soluble P in soils. Therefore the dependence of water extractable P on the molar ratios \( \text{NH}_4\text{F}-\text{P}/\text{Al} \) and \( \text{NaOH}-\text{P}/\text{Fe} \) was calculated. As these molar ratios seemed to correlate with each other, the corresponding partial correlation coefficients, too, were calculated (Table 4). The results imply that water soluble P is primarily controlled by the ratio \( \text{NH}_4\text{F}-\text{P}/\text{Al} \). This factor was found to explain 77% of the variation in the \( \text{NH}_4\text{Cl}-\text{P} \).

Table 4. Total and partial correlation coefficients for the relation between the water soluble P (1), molar ratio \( \text{NH}_4\text{F}-\text{P}/\text{Al} \) (2), and molar ratio \( \text{NaOH}-\text{P}/\text{Fe} \) (3).

<table>
<thead>
<tr>
<th></th>
<th>( r_{12} )</th>
<th>( r_{13} )</th>
<th>( r_{12,3} )</th>
<th>( r_{13,2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy clays</td>
<td>0.89***</td>
<td>0.63***</td>
<td>0.82***</td>
<td>ns</td>
</tr>
<tr>
<td>Coarser clays</td>
<td>0.93***</td>
<td>0.77***</td>
<td>0.82***</td>
<td>ns</td>
</tr>
<tr>
<td>Non-clay soils</td>
<td>0.95***</td>
<td>0.54***</td>
<td>0.93***</td>
<td>ns</td>
</tr>
<tr>
<td>All samples</td>
<td>0.93***</td>
<td>0.66***</td>
<td>0.88***</td>
<td>ns</td>
</tr>
</tbody>
</table>

ns = not significant

Further, the relationship between water soluble P and soil characteristics was investigated by the regression analysis. The coefficient of multiple determination \( R^2 \) for the equation with the variables soil pH as well as the ratios \( \text{NH}_4\text{F}-\text{P}/\text{Al} \) and \( \text{NaOH}-\text{P}/\text{Fe} \) was calculated, but \( \text{NH}_4\text{F}-\text{P}/\text{Al} \) was the only statistically significant variable. Soil pH explained merely 0.4 % (P=0.05) and \( \text{NaOH}-\text{P}/\text{Fe} \) not at all the variation in water extractable P. Thus, in 103 samples the relationship between water soluble P as mmol/kg (y) and the ratio of \( \text{NH}_4\text{F} \) soluble P to oxalate extractable Al as mmol/kg (x) was found to conform to the following regression equation (the soil-solution ratio 1:60):

\[
y = -0.209 + 9.792 \, x_1, \quad R^2=0.87, \quad S = 0.201, \quad s_b = 0.009
\]

If the \( \text{NH}_4\text{F}-\text{P} \) and Al dissolved in oxalate solution were used as independent variables, the value of the coefficient of multiple determination \( R^2 \) would have lowered to 0.75.
Discussion

The quantities of water soluble P varied very largely; from about 0.4 kg to 235 kg per one hectare, surface layer 0–20 cm corresponding to bulk density 1 kg/dm$^3$. The soil sample extremely rich in water soluble P was a very heavily limed muddy fine sand. Generally, more P was extracted from the non-clay soils than the clay soils. This can be expected, because Finnish soils are found to retain P the more effectively the finer the soil material is (KAILA 1965, HARTIKAINEN 1979). The greater retention ability of fine textured soils is primarily due to their higher content of active sorption components. Also in the present material the heavy clay soils contained more abundantly oxalate extractable Al and Fe than the soils in the other groups.

The nature of P bonding seemed to be of major importance in controlling the extractability of soil P into water. It was found that, the later phase of the extraction sequence a given fraction represented, the more weakly it seemed to be associated with the water soluble resources. The NH$_4$Cl-P correlated most closely because it is obviously included in water soluble reserves. Thus, it reflects the soil P status alike with the water extractable P. SHARPLEY et al. (1977), for instance, found that the mean concentration of dissolved inorganic phosphate in each of several surface runoff events from established pasture was closely correlated with the amounts of inorganic P extracted by 0.1 M NaCl from the top soil prior to the event.

The results of the correlation analyses illustrate the role of the NH$_4$F soluble fraction in determining the concentration of phosphate in the soil solution. However, as expected on the basis of a previous study (HARTIKAINEN 1979), the supplying power of this fraction seems to be controlled by the amount of corresponding sorption component. Hence, the water soluble P was most closely related to the molar ratio NH$_4$F-P/Al.

But, in spite of the striking correlation ($r=0.93^{***}$, n=103), the role of this ratio as well as that of the NH$_4$F-fraction should not be overestimated. First, it should be taken into consideration that this index does not include other anions (silicate, organic anions, etc.) competing with phosphate for sorptive surface, and so it does not describe actual conditions in soils. Second, at a certain "saturation degree", one soil sample may contain smaller amounts of free active sorption components than another with higher absolute content of sorption agents. In the present material, for instance, the heavy clay soil sample exceptionally rich in oxalate soluble Al had the second highest molar ratio within the group, but the second lowest quantity of water soluble P. Third, it is obvious that, in addition to NH$_4$F-P supposed to be bound by Al, also the NaOH-P likely bound by Fe is of significance. Partly this results from the fact that there is no specific reagent to distinguish specifically these P forms (e.g. BROMFIELD 1970, KURMIES 1972), but other factors, too, are involved.

It is true that phosphate oxygen forms a stronger bond with Fe than with Al (cf. AURA 1980). The significance of Al bound phosphate is established by many investigators (MacKENZIE 1962, DUNBAR and BAKER 1965, MURR-MANN and PEECH 1969). However, according to HINGSTON et al. (1974) it is
possible with progressing desorption the bonding pattern of remaining phosphate to change and more stable surface complexes to form. Thus, it can be assumed that in proportion, as phosphate is desorbed from the surface of Al oxides, the bonding strength of the remaining phosphate increases and converges that of phosphate bound by Fe oxides. As a result, at a certain stage also Fe bound phosphate is able to participate in desorption reactions. Consequently, this stage is reached the sooner the more phosphate is sorbed on Fe oxides. This theory involves the decisive role of sorptive agents and the relationship between P intensity and capacity in soils.

Part of the P released from NaOH soluble fraction under reduced circumstances or in the presence of complexing agent can be resorbed into NH₄F extractable form (HARTIKAINEN 1979). Also in the water treatment the rate of desorption of Fe bound P may be decreased by a possible resorption. If this is true the final desorption would take place through the NH₄F fraction. In any case, it can be concluded in accordance with the conception of ELRASHIDI and LARSEN (1978) that both Al bound and Fe bound P control the phosphate concentration in the soil solution. This assumption is supported also by the unpublished data obtained by the author in a test with soils very rich in easily soluble P. They showed that NH₄F as well as NaOH soluble reserves were attacked by water extraction.

According to the current conception the P in NH₄F and NaOH soluble fractions originates from reserves bound onto the surfaces of hydrated oxides rather than from specific chemical compounds. Therefore these fractions are more able to participate in desorption than the H₂SO₄ and reductant soluble ones, more likely originating from discrete chemical compounds. With progressing weathering the H₂SO₄-P may have only an indirect and extremely slow influence on the water extractable P. In some soils quite a great portion of the total inorganic P was composed of the reductant soluble reserves. The results of the present study give intimations that Mn may, along with Fe, participate in reactions removing P from active P cycle to the form difficult to dissolve and indirectly affect quantities of P soluble in water. In the litterature there is, however, scarce, if any knowledge about the role of Mn in the soil P cycle. Manganese may be of some importance especially in the reactions of sedimentary P.

Because the availability of secondary P seems to be dependent on the amount of sorption components, the suitability of strong reagents able to remove most of the adsorbed P is questionable. Besides, some other factors have shown to limit the reliability of many common extractants. Van der PAAUW (1969), for instance, has reported that the P concentration in the potato tops correlated closely and independently of soil pH with water soluble P, but with P-AL (according EGNER-RIEHM-DOMINGO) only within a narrow pH range. Also in the present investigation there existed only slight, if any, dependence between water soluble P and soil pH. According to common knowledge, the availability of soil P improves with decreasing soil acidity. The significance of pH on desorption is, however, found to lessen as the amount of secondary P in the soil increases (HARTIKAINEN 1981 a). Thus, the importance of pH varies in different soils. Further, on the basis of
earlier studies (KAILA 1965, HARTIKAINEN 1981a) it can be assumed that the nature of P bonding, determining the extractability, is somewhat connected with soil pH.

In the heavy clay soils the ratio of NH\textsubscript{4}F-P to NaOH-P tended to become greater with increasing content of organic carbon in the soil. This may partly be due to the fact that in soil, Al participates less in complexation reactions than Fe (e.g. SCHNITZER and SKINNER 1963). In addition, the complexation reactions have been found to remove P from the NaOH soluble form to the NH\textsubscript{4}F extractable one (HARTIKAINEN 1979, 1981b). But, in accordance with the results of van der PAAUW (1969), the water soluble P was not dependent on the content of organic carbon in soil.

On the basis of what is stated above it can be concluded that water extractable P illustrates the "effective P status" which is determined by the quantity and quality of sorption components, soil pH and the content of organic matter. Thus, these factors indirectly control the magnitude of easily soluble resources by affecting the nature of P bonding which, in turn, seems to be of decisive importance in water extraction.

Water extraction seems to be a suitable method for estimating the immediate P loading into waters caused by eroded soil and for estimating amounts of P possible to be carried out from fields as dissolved in runoff waters. It is obvious, however, that a relatively low surface layer is able to supply the runoff or flood water with P, because the diffusion of P in soil is very slow (LEWIS and QUIRK 1967, KUNISHI and TAYLOR 1975).

The factors found to govern the water soluble P in soils may, to some extent, determine also the P exchange between the lake sediment and overlying water under aerobic conditions. If this assumption is valid, in addition to Fe bound phosphates also Al and P bound by Al are important factors in the P budget of lakes, as concluded earlier by HARTIKAINEN (1979).

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References


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Vesiliukoinen fosfori ja siihen vaikuttavat tekijät suomalaisissa kivennäismaissa

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Vesiuuttoisen fosforin määrä vaihteli 104 pintamaanäytteen aineistossa 0.2 mg:sta 117.8 mg:aan maakiloa kohti. Aitosavista uuttui keskimäärin vähemmän fosforia (4.8 ±2.2 mg/kg) kuin muista savimaista (12.8 ± 4.6 mg/kg) sekä hiesu- ja hietamaista (13.3 ± 7.2 mg/kg).
