

Evaluation of water and ammonium acetate tests as indices for available P in limed soils

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Abstract. The water and acid acetate extractions as predictors of the P uptake by plants were compared in a two-year pot experiment and a simultaneous incubation test. The accuracy of these methods was dissimilarly affected by individual cultivation measures, such as the addition of nutrient salts and liming. In contrast to acetate-extractable P, the water-soluble P proved to be sensitive to the salt addition reducing the water extraction test values markedly. On the other hand, in limed soils the water-soluble P seemed to be more closely related to the P uptake by plants than the acetate-extractable P which tended to overestimate available reserves.

Index words: water-soluble P, acetate-soluble P, soil testing, liming

Introduction

For economic and environmental reasons, it is important that judicious amounts of fertilizers be applied to correct a shortage of nutrients. A sound basis for determining the necessary amounts of P fertilizers, however, has long been a subject of controversy. P test methods often explain the variation in yield response to P fertilization only poorly (HOLFORD 1983, HOLFORD and CULLIS 1985, LABHSETWAR and SOLTANPOUR 1985).

There are also indications that no single extractant will be superior to the others under very different soils and soil conditions (HOLFORD 1983, MACKAY et al. 1984). This suggests that the accuracy of various P tests may

be dissimilarly affected by previous cultivation measures, such as liming and addition of nutrient salts. To test this hypothesis, the plant P uptake and water extraction data of two fine sand soils (HARTIKAINEN 1983a and b, 1984) were collected and used for comparison with the P extraction results of the acid ammonium acetate method used for routine soil testing in Finland.

Material and methods

a) Pot and incubation experiment

A two-year pot experiment with turnip rape (*Brassica campestris* v. *oleifera* f. *annua*) was

Table 1. Characteristics of experimental soil samples.

| | Soil 1 | Soil 2 |
|-------------------------|--------|--------|
| Clay % | 22.4 | 22.5 |
| Org. C % of D.M | 3.0 | 6.4 |
| pH (CaCl ₂) | 4.8 | 4.8 |
| Total inorg. P mg/kg | 721 | 893 |

carried out with two acid surface soil samples whose properties are given in Table 1. The methods of soil and plant analyses as well as the fertilization treatments are described in detail in previous papers (HARTIKAINEN 1983a and b). In brief, in the *pot experiment* (four replicates) 4.5 kg of moist soil (= 3.9 kg of air-dried muddy fine sand soil (1) and 3.6 kg of fine sand soil (2)) were treated with calcitic limestone (6, 12 or 24 g), dolomitic limestone (24 g) or basic slag (blast furnace slag, 24 g). The control samples received no liming agents. The nutrients added were: 1 000 mg N as NH₄NO₃, 200 mg Mg as MgCl₂ · 6 H₂O, 10 mg B as H₃BO₃, 15 mg Cu as CuSO₄ · 5 H₂O, 10 mg Mn as MnSO₄ · H₂O, 10 mg Zn as ZnSO₄ · 7 H₂O, 5 mg Mo as NaMoO₄ · H₂O. Half of the soil samples were fertilized with 400 mg of P (as K₂HPO₄) and the pots without P fertilization received an equivalent quantity of K as KCl.

An analogous *incubation experiment* was carried out simultaneously in a greenhouse. The quantities of soil, liming agents and nutrient salts added to plastic pots were 1/10 of those used in the pot experiment.

b) Soil P tests

Water-soluble P (P_w): Air-dried samples were extracted with H₂O at a soil-solution ratio of 1:60 (w/v). The suspensions were shaken for 1 h, allowed to stand for 24 h and reshaken for 10 min. After centrifugation (3 000 g) the supernatant solutions were filtered through a 0.2 µm membrane filter and analyzed for PO₄-P by a molybdenum blue-ascorbic acid method (ANON. 1969).

NH₄OAc-soluble P (P_{AAc}): Air-dried soil samples were shaken for 1 h with acid acetate solution (0.5 M CH₃COOH + 0.5 M CH₃COONH₄, pH 4.65) at a soil-solution ratio of 1:10 (w/v). The suspensions were filtered through a blue ribbon filter paper, and the filtrates were analyzed for PO₄-P by the molybdenum blue-stannous chloride method of KAILA (1955).

Results and discussion

The extractability of soil P and its changes due to incubation for 4 mo with nutrient salts and various liming agents are given in Table 2. In soil 1, the water-soluble P in the unin-cubated control sample about equalled that of the acetate-soluble P, but in soil 2 it was markedly higher. In both soils, the addition of nutrient salts (excepting phosphate) caused a substantial reduction in P_w but no change in P_{AAc}.

An increase in ionic strength has, however, been proved to result in an enhanced P sorpt-

Table 2. pH and soil P (mg kg⁻¹) extracted by acetate and water in unincubated and incubated samples.*

| Treatment | Soil 1 | | | Soil 2 | | |
|------------------|------------------|-------------------|-------------------|------------------|--------------------|-------------------|
| | pH | P _{AAc} | P _w | pH | P _{AAc} | P _w |
| Unincubated | 4.8 ^b | 12.0 ^a | 10.7 ^c | 4.8 ^b | 30.3 ^{ab} | 42.1 ^c |
| Incub., no lime | 4.2 ^a | 12.2 ^a | 5.4 ^a | 4.4 ^a | 29.8 ^a | 28.9 ^b |
| » calcite 0.6 | 4.9 ^b | 12.5 ^a | 5.6 ^a | 4.9 ^c | 31.5 ^{ab} | 28.2 ^b |
| » » 1.2 | 5.6 ^d | 14.0 ^b | 6.3 ^{ab} | 5.3 ^c | 32.2 ^{bc} | 25.2 ^a |
| » » 2.4 | 6.3 ^f | 19.7 ^c | 7.3 ^b | 5.9 ^e | 38.5 ^d | 23.6 ^a |
| » dolomite 2.4 | 6.0 ^e | 15.2 ^b | 6.8 ^b | 5.5 ^f | 33.3 ^c | 24.8 ^a |
| » basic slag 2.4 | 5.1 ^c | 11.8 ^a | 5.5 ^a | 5.0 ^d | 30.5 ^{ab} | 25.6 ^a |

* Each column was tested separately. The means followed by a common letter do not differ at P = 0.05.

ion and in a decreased desorption or desorption rate (LEHR and WESEMAEL 1952, RYDEN and SYERS 1975, BARROW and SHAW 1979). Under field conditions, a practical consequence of the ionic strength effect is that the mobilization of P is promoted in autumn, when the ionic strength is diminished (WIKLANDER and ANDERSSON 1974, KUO and JEL-LUM 1987). ERIKSSON (1940) noticed that the KCl fertilization may even decrease yield by depressing the solubility of soil P. Thus, the extraction results suggest that the water-soluble P gives a more accurate estimate of short-term available reserves than the acetate-extractable P.

Table 2 demonstrates that the P tests responded dissimilarly also to an increase in pH. Excluding the basic slag and the lowest dosage of calcite, the liming treatments distinctly enhanced the extractability of soil P into the acid NH_4OAc . This effect was quite proportional to the increase in pH, even though relatively more pronounced in soil 1 than in soil 2. As for the water-soluble P, on the contrary, the soils reacted differently to decreasing acidity: in soil 1 it tended to increase and in soil 2 to decrease. However, consistently with P_{AAc} , the liming-induced

changes in P_w remained statistically insignificant in the lowest calcite treatment, and in soil 1 also in the basic slag treatment. In fact, the close positive correlation found for P extracted from all the incubated samples by water and acetate solution ($r = 0.94^{***}$, $n = 12$) was seeming and did not hold true for soil 2 ($r = -0.76$).

The total removals of soil P by two harvests in the pot experiment are given in Table 3. Owing to a great variation between the replicates, the differences between treatments often remained statistically insignificant. There is, however, a tendency that the liming agents augmented the utilization of P reserves in soil 1, whereas in soil 2 the highest dosages of calcite and dolomite depressed it.

Comparison of the results of the pot and incubation experiments (Tables 2 and 3) reveals the P removal by shoot yields to be inconsistent with the P test values of the incubated samples. For instance, in soil 2 the highest dosage of calcite increased soil P_{AAc} (by 29 %) but reduced the P utilization (by 15 %). The P uptake seemed to be more accurately predicted by P_w being congruently reduced (by 18 %). In soil 1, on the contrary, this treatment promoted the utilization of soil P (by 48 %) and increased P_{AAc} markedly more (by 62 %) than P_w (by 35 %). The long-term available P in limed soils seems to be underestimated in the water extraction test, where the effect of liming on the solubility of P obviously was masked to some extent by a high nutrient salt concentration.

The soil P_{AAc} remaining after cultivation (Table 3) was the greater the higher the liming intensity was, but it seemed not to be related to the P quantities removed by the shoots. On the other hand, in soil 1 the residual soil P_w was not markedly affected by liming and an enhanced P uptake, whereas in soil 2 it was lowest in the samples where also the P uptake had been lowest.

The recovery of fertilizer P by the NH_4OAc and water extractions (Table 4) shows that most of the added P (104 and 114 mg kg^{-1} to soil 1 and 2, respectively) was retained. The

Table 3. The uptake of soil P (mg kg^{-1}), and residual soil P (mg kg^{-1}) and soil pH after cultivation.*

| | Uptake | Residual | | pH |
|---------------|--------------------|-------------------|--------------------|------------------|
| | | P_{AAc} | P_w | |
| Soil 1 | | | | |
| Unlimed | 22.8 ^a | 9.8 ^b | 5.9 ^{bc} | 4.2 ^a |
| Calcite 6 | 33.1 ^b | 8.4 ^a | 5.1 ^a | 4.9 ^b |
| » 12 | 29.0 ^{ab} | 9.3 ^{ab} | 5.6 ^{ab} | 5.5 ^d |
| » 24 | 33.8 ^b | 15.5 ^d | 5.9 ^{bc} | 6.5 ^f |
| Dolomite 24 | 29.5 ^{ab} | 11.4 ^c | 6.2 ^c | 6.0 ^e |
| Basic slag 24 | 36.3 ^b | 9.3 ^{ab} | 5.5 ^{ab} | 5.1 ^c |
| Soil 2 | | | | |
| Unlimed | 58.6 ^a | 23.8 ^a | 27.5 ^c | 4.5 ^a |
| Calcite 6 | 60.7 ^a | 23.8 ^a | 24.1 ^{cd} | 5.1 ^b |
| » 12 | 57.0 ^a | 24.2 ^a | 23.1 ^{bc} | 5.5 ^d |
| » 24 | 49.7 ^a | 31.1 ^c | 20.5 ^a | 6.1 ^f |
| Dolomite 24 | 49.8 ^a | 26.4 ^b | 22.4 ^b | 5.8 ^e |
| Basic slag 24 | 59.4 ^a | 23.5 ^a | 25.0 ^d | 5.2 ^c |

* Each column was tested separately.

Table 4. The recovery of fertilizer P (mg kg⁻¹) by NH₄OAc and water extraction in the incubation test and the apparent uptake of added P (mg kg⁻¹) in the corresponding pot experiment.

| Liming g/pot | Soil 1 | | | Soil 2 | | |
|--------------------|------------------|----------------|--------|------------------|----------------|--------|
| | P _{AAc} | P _w | Uptake | P _{AAc} | P _w | Uptake |
| No lime | 5.0 | 8.3 | 35.0 | 6.7 | 17.1 | 24.5 |
| Calcite 0.6 (6) | 7.3 | 8.8 | 29.4 | 6.8 | 15.3 | 25.1 |
| Calcite 1.2 (12) | 8.5 | 8.2 | 42.1 | 9.3 | 15.1 | 22.5 |
| Calcite 2.4 (24) | 12.0 | 8.6 | 30.3 | 14.7 | 13.6 | 23.2 |
| Dolomite 2.4 (24) | 8.0 | 8.0 | 25.4 | 10.9 | 12.4 | 30.0 |
| Bas. slag 2.4 (24) | 7.1 | 8.6 | 17.7 | 7.7 | 14.5 | 16.8 |

lime-derived changes in the extractability of fertilizer P showed similar trends found for soil P. The higher the soil pH, the more NH₄OAc was able to recover the applied P, which is in accordance with results of an earlier study on a large Finnish soil sample material (PAASIKALLIO and HÄKKINEN 1977). The results indicate the extraction power of NH₄OAc to be highly dependent on soil pH. Similar observations have been made by GRIFFIN (1971) for a modified Morgan test (NH₄OAc, pH 4.8). The recovery of fertilizer P by water extraction, on the contrary, seemed not to be as markedly dependent on liming intensity. This implies that the solubility of soil and fertilizer P into water was equitably promoted by liming.

The apparent utilization of fertilizer P by yields (included in Table 4) was calculated as the difference between the P quantities taken up from soil samples with and without P treatment. In soil 1, initially poorer in P_{AAc} and P_w than soil 2, the utilization of added P was more effective. On the other hand, utilization seemed to be somewhat reduced by liming, which may be at least partly attributable to an enhanced withdrawal of soil reserves, especially in the basic slag treatment (c.f. Table 3). However, when comparing the results of the incubation and pot experiments in Table 4, one can conclude that the acetate extraction may overestimate the efficiency of lime in enhancing the utilization of added P. Although the extractability of fertilizer P into

NH₄OAc was more than doubled by the highest dosage of calcite, the removal of applied P seemed not to be affected, or it was even decreased.

The observations made in the present study suggest that the accuracy of the water and acetate extractions are dissimilarly affected by individual cultivation measures, such as addition of nutrient salts or liming. Although the water-soluble P proved to be sensitive to the salt addition, it seemed, especially in limed soils, to be more closely related to the P uptake by plants than was the acetate-extractable P which tended to overestimate available reserves.

The results are in accordance with the conclusions drawn by SIBBESEN (1983), who reviewed numerous pot experiments with contrasting soils: the soil P status was most accurately estimated by the resin method, followed by the water and bicarbonate extractions. The acetate buffer extraction fell into the group of least accurate methods. Also in an earlier two-year pot experiment with Finnish soils, the water extraction was found to be superior to the acetate extraction in the assessment of soil P status (SIPPOLA and JAAKKOLA 1980). Recently, SIPPOLA and SAARELA (1986) reported similar observations in a large field experiment where the variation in the yield increase due to P fertilization was explained better by the water extraction (68 %) than by the NH₄OAc method (53 %).

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SELOSTUS

Vesi- ja ammoniumasetattiuton soveltuvuus käyttökelpoisten fosforivarojen arviointiin kalkituissa maissa

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Tutkimuksessa vertailtiin kevätrypsin fosforin ottoa lannoitetuista ja kalkituista maista vesiutolla ja happamalla asetaattiuutolla saatuihin fosforiarvoihin. Aineistona käytettiin kaksivuotista astiakoetta ja sitä vastavaa muhituskoetta, joissa kahta hapanta hietamaata oli käsitelty dolomiittikalkilla, masuunikuonalla tai nousevilla kalsiittikalkkimäärillä.

Ravinnesuolojen lisääminen maahan pienensi vesiuttoisen fosforin määrää 30—50 %, mutta ei vaikuttanut asetaattiuuttoisen fosforin määrään. Koska suolapitoisuuden laskiessa (esim. kasvien ravinteiden oton seurauksena) fosforin vapautumisen maanesteeseen tiedetään lisääntyvän, lannoitetuista maista tehty vesiututto saattaa ali-

arvioida fosforireservejä, jotka ajan mittaan voivat tulla kasvien käyttöön. Toisaalta asetaattiuutto näytti yliarvioivan kalkituksen tehokkuutta fosforin käyttökelpoisuuden parantajana. Vesiuttoisen fosforin määrissä tapahtuneet muutokset vastasivat paremmin kalkituksen vaikutusta kevätrypsin fosforin ottoon. Toisessa koemaassa kalkitus pyrki vähentämään kevätrypsin fosforin ottoa (suurin kalsiittimäärä 15 %), vaikka asetaattiuuton perusteella käyttökelpoisuuden olisi pitänyt selvästi parantua (29 %). Tässä maassa vesiuttoinen fosfori kuvasi paremmin käyttökelpoisia varoja, sillä sen määrä väheni kalkituksen intensiteetin noustessa (18 %).