Comparison of a bioassay and three chemical methods for determination of plant-available P in cultivated soils of Finland

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Abstract. Phosphorus was extracted from 32 field soil samples with water (P_w), with 0.5 M NH_4-acetate-0.5 M acetic acid at pH 4.65 (P_{AAAc}) and by a method in which freshly precipitated iron hydroxide is used as the sink for P desorbing from the soil (P_i method). P_i is supposed to be the quantity of reversibly adsorbed P in the soil. The results of the three chemical methods were compared with the ones obtained in a bioassay in which four yields of ryegrass were grown in 0.2 dm^3 of soil. The grass took up P effectively and the P reserves of the soils were probably the growth limiting factor. The quantities of P taken up corresponded to 5—21 % (median 10 %) of soil inorganic P. The uptake of P by the grass was approximately twice the quantity of P_i (median 25.9 mg/dm^3) and several times higher than the quantities of P_w (median 6.3 mg/dm^3) and P_{AAAc} (median 6.4 mg/dm^3). The results of all three chemical methods predicted P uptake by ryegrass accurately, the correlation coefficients (r) ranging from 0.88*** to 0.93***. However, in soils low in P (P_{AAAc} < median), P uptake correlated more closely with P_i (r = 0.87***) than with P_w (r = 0.57*) or P_{AAAc} (r = 0.64**). The phosphorus taken up by ryegrass and extracted by the chemical methods probably originated in the same type of P reserves of the soil. The extractions with water or AAAc seem to be sufficient for ranking Finnish soils according to their reserves of plant-available P. If a more quantitative measure of the size of desorbable reserves of P is needed, the determination of P_i may be of use.

Introduction

Assessment of reserves of plant-available P by soil analysis is important for crop production as well as from the environmental point of view. Even though soil testing methods used as the basis for fertilizer recommendations need eventually be calibrated against results from field experiments, pot experiments are practical for preliminary screening of various methods. Extraction methods like water and resin extraction, which do not destroy the microstructure of the soil, have in pot experiments been more in agreement with

P uptake by plants than have methods in which strongly dissolving extractants are used (SIBBESEN 1983). Also in Finnish soils, water and resin extractions have proved successful in predicting the uptake of soil P by plants in pot experiments (AURA 1978, SIPPOLA & JAAKKOLA 1980).

A new method (P_i), which is claimed to give the quantity of reversibly adsorbed P, has recently been introduced (ZEE et al. 1987, MENON et al. 1989). In this method, the P desorbing from the soil is trapped by strips of filter paper which are impregnated with freshly precipitated iron hydroxide. Owing to the high affinity of phosphate for iron hydroxide, the concentration of P in the liquid phase during the extraction is extremely low, which promotes desorption of P from the soil. When this method was tested with soil samples from Finland (YLI-HALLA 1989), the mean (31.2 mg/dm³) of P_i was three times higher than the mean of water-extractable P. The objective of the present investigation was to study the ability of the new P_i method to predict P uptake by ryegrass in a pot experiment as compared to extraction with water or acid NH_4-acetate which is the standard method for soil testing in Finland. In addition, some remarks on the relationship between P uptake and the fractions of inorganic P in the soil were made.

Materials and methods

The soil material consisted of 32 samples taken from plough layers (A_p horizon) of cultivated fields in different parts of Finland. There were 11 clay soils, 18 coarse mineral soils and three organogenic soils. All mineral soil samples except one were used in the previous study (YLI-HALLA 1989) on reversibly adsorbed P. Phosphorus extractable with water (P_w) was determined according to the method of HARTIKAINEN (1982). Phosphorus was also extracted with 0.5 M NH_4-acetate — 0.5 M acetic acid at pH 4.65 (P_{AAAc}) (VUORINEN and MÄKITIE 1955) which is the method used in soil testing in Finland. Reversibly adsorbed P (P_i) was determined according to the method of van der ZEE et al. (1987) in which freshly precipitated Fe hydroxide is used as the sink for P desorbing from the soil while using 0.01 M $CaCl_2$ as the supporting electrolyte. The method has been discussed in more detail previously (ZEE et al. 1987, MENON et al. 1989, YLI-HALLA 1989). Other soil analyses performed, including the Chang and Jackson fractionation of inorganic P, have also been reported earlier (YLI-HALLA 1989). Chemical and physical characteristics of the current soil material are presented in Table 1.

For the pot experiment, two 200 ml portions of each soil were measured, fertilized and

Table 1. Physical and chemical properties of the experimental soils.

Soil characteristics	Mean	Median	Range	Standard deviation
Clay, %	29	25	2—71	19
Organic C, %	5.9	3.2	1.9—30	7.7
pH ($CaCl_2$)	5.1	5.0	4.0—6.9	0.6
Fe*, mmol/dm³	64.2	61.0	30.0—136	23.3
Al*, mmol/dm³	70.2	52.0	26.0—240	46.2
NH_4F-P ("Al-P"), mg/dm³	123	76	13—401	105
NaOH-P ("Fe-P"), mg/dm³	171	151	33—419	86
H_2SO_4-P ("Ca-P"), mg/dm³	178	161	41—531	106
P_{AAAc}, mg/dm³	11.2	6.4	1.7—51.5	12.0
P_w, mg/dm³	10.4	6.3	2.3—39.0	9.8
P_i, mg/dm³	33.0	26.0	7.6—64.2 (149)**	16.5

* extracted with 0.05 M NH_4-oxalate at 3.3
** The value in parentheses refers to a finesand soil deviating from the rest of the material

poured into 0.5 dm³ plastic boxes. Forty seeds of Italian ryegrass (*Lolium multiforum,* Lam.) were sown, and the pots were covered with 250 g of acid-washed quartz sand. Deionized water was used for watering. The following quantities of nutrients (mg/dm³ of soil) were initially mixed with the soil: N 142 as NH_4NO_3, K 100 as KCl, Mg 52 as $MgSO_4 \cdot 7H_2O$, Ca 126 as $CaSO_4 \cdot 2H_2O$, S 175 mainly as $CaSO_4 \cdot 2H_2O$ and $MgSO_4 \cdot 7H_2O$, Mo 1 as $Na_2MoO_4 \cdot 2H_2O$, B 0.5 as H_3BO_3, Zn 3 as $ZnSO_4 \cdot 7H_2O$, Cu 3 as $CuSO_4 \cdot 5H_2O$, Mn 4 as $MnSO_4 \cdot 4H_2O$ and Fe 2 as $FeSO_4 \cdot 7H_2O$. For the three successive crops, N (200 mg/dm³) as NH_4NO_3 and K (100 mg/dm³) as KCl were applied onto the surface of the pots. The growing periods for the four crops were 34 d, 30 d, 22 d and 27 d, respectively. The plant material was dried at 60°C. In order to reduce the number of plant analyses, the first two and the last two yields were combined. The plant material was analyzed for P by a vanadomolybdate method (SAARI and PAASO 1980). At the end of the experiment, the pH($CaCl_2$) of the soils taken from the pots was determined.

Results

Due to the small volume of the soil in the pots and the high rate of N fertilization, the growth of the grass was very intensive; the quantity of dry matter produced (Table 2) corresponded to 50—95 tons/ha, provided the plough layer contains 2 million dm³ of soil. In general, the P content of the plant material was low (Table 3). The plant material produced in 17 soils had a P concentration

Table 2. The size of the four consecutive dry matter yields (I, II, III, IV) produced by ryegrass in the pot experiment.

Yield	Mean g/dm³	Median g/dm³	Range g/dm³
I	7.1	7.6	2.8—10.1
II	11.8	12.2	6.9—14.3
III	8.9	9.3	3.9—14.2
IV	9.3	10.1	3.5—12.5
Total yield	38.1	39.5	17.1—47.5

equal to or less than 1.0 g/kg in the last two yields, suggesting P deficiency. On the other hand, in one finesand soil the concentration of P in the plant material was maintained at the normal level of 2.9—3.0 g/kg throughout the experiment; the quantity of P_i was as high as 149 mg/dm³, i.e. more than double the second highest result, revealing the large reserves of plant-available P in that specific soil. Quantities of P taken up by the four yields were several times larger than those of P_{AAAc} or P_w and nearly twice as large as the quantity of P_i. Phosphorus uptake corresponded to 5—21 % (median 10 %) of the sum of inorganic P fractions ("Al-P" + "Fe-P" + "Ca-P") in the soil.

Linear correlation coefficients (r) between dry matter yields, P uptake and soil characteristics were calculated. In these calculations, the finesand soil extremely rich in P was excluded due to its drastic deviation from the bulk of the material. The correlation coefficients calculated separately for different yields or for the sums of the yields were of equal magnitude. Therefore, only the correlation coefficients for the total yield and total P uptake are presented (Table 4). P uptake by the grass correlated more closely with P_w, P_{AAAc}

Table 3. P concentration of the plant material and the uptake of P by the crop in the pot experiment. The results of a finesand soil very rich in P are given in parentheses.

Yield	P concentration, g/kg			P uptake, mg/dm³		
	Mean	Median	Range	Mean	Median	Range
I + II	1.4	1.2	0.8—2.9 (3.0)	27.9	22.5	6.0—72.0 (75.5)
III + IV	1.2	1.0	0.7—2.0 (2.9)	22.4	17.8	7.0—50.5 (77.5)
All yields				49.4	40.3	15.0—123 (151)

Table 4. Linear correlation coefficients (r) between dry matter yields and the different indicators of soil P status.

Indicator of soil P status	Dry matter yield	P uptake
P_w	0.54**	0.92***
P_{AAAc}	0.46**	0.88***
P_i	0.61***	0.93***
"Al-P"	0.15$^{n.s.}$	0.38*
"Fe-P"	0.40*	0.33$^{n.s.}$
"Ca-P"	0.64***	0.66***
"Al-P"/Al	0.39*	0.79***
"Fe-P"/Fe	0.40*	0.47**

and P_i than did the dry matter yields. The quantities of P taken up correlated statistically very significantly with the results of all three chemical methods (Fig. 1). In pot experiments very poor in P (usually $P_w < 4$ mg/kg), the P_i method has been superior to water extraction in predicting P uptake by soybean and maize (van der Zee, personal communication). Therefore, also in the current material the soils of $P_{AAAc} < 6.4$ mg/dm (i.e. below the median) were studied separately. Among these soils, the results of the P_i method predicted the uptake of P by ryegrass more accurately than did the P_w and P_{AAAc} methods. The last two methods tended to overestimate the P status of coarse mineral soils and to underestimate that of clay soils. The linear correlation coefficients (r) between P uptake and P_i, P_w and P_{AAAc} for these soils (n = 16) were as follows:

	r
P_i	0.87***
P_w	0.57*
P_{AAAc}	0.64**

Among the fractions of inorganic P, "Ca-P" correlated most closely with dry matter yields and P uptake by plants (n = 31) (Table 4). A reason for this may lie in the acidification of soil in the pots. The decrease of pH during the experiment ranged from 0.1 to 0.9 pH units, mean 0.5 pH units. Calcium phosphates are acid-soluble and this fraction may partly have dissolved and contributed to P uptake by the grass in the pot experiment. The absolute quantities of "Al-P" and "Fe-P" did
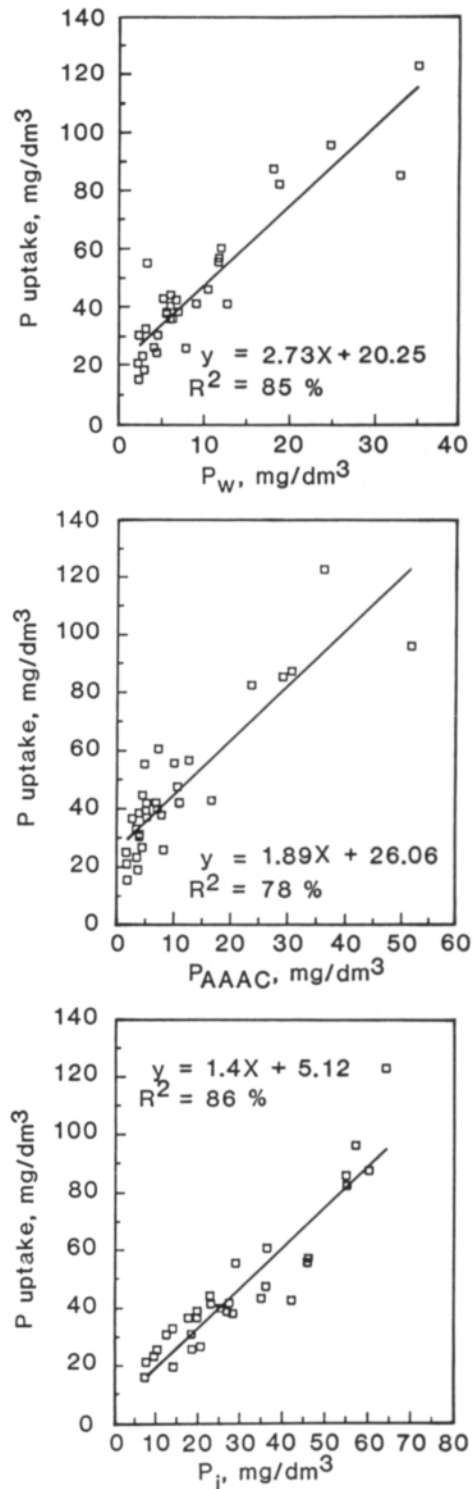

Fig. 1. Relationships between the quantities of P extracted with different methods (P_w, P_{AAAc}, P_i) and P uptake by ryegrass in a pot experiment.

not correlate statistically significantly or correlated only weakly with P uptake by the grass. But the molar ratio "Al-P"/Al, reflecting the P coverage of poorly crystalline Al compounds in the soil, correlated positively with P uptake.

Discussion

The current P concentrations of the grass were low, with quite a few extreme values, as compared to the results by KÄHÄRI and NISSINEN (1978) on field-grown timothy. In that study, the bulk of P concentrations in 2 015 timothy samples was in the range of 2.0—3.0 g/kg, which is approximately twice the concentration commonly found in the present study. Low P concentrations in the grass as well as the positive correlation between the yield and the indices of soil P status suggest that P supply to the plants has been the growth-limiting factor in the pot experiment. When plants take up P from soil, the most easily soluble reserves are depleted first, and gradually the less soluble fractions are utilized. These sparingly soluble P reserves maintain a lower P concentration in the soil solution. Consequently, after the P concentration of the soil solution decreases below the critical level, P nutrition of the plants is reduced and growth is depressed. Owing to the apparent P deficiency experienced by the grass, it can be assumed that the reserves of plant-available P were practically used up in the course of the pot experiment. The quantities of P taken up in the experiment cannot, however, be regarded as the estimates of the reserves of P available to plants in practical farming. In a pot experiment, the dense root system with its exudates and the acidification of the soils in the pots have probably caused dissolution of phosphates which would be virtually insoluble in the field. Furthermore, utilization of soil P to the extent measured in the pot experiment would probably result in a seriously limited P supply to the plants and in a loss of the potential yield. Yet, the results may give an estimate for the maximum quantity of P which, in aerobic conditions, can be dissolved from the soil by plants at extreme P starvation. The study showed that the plants were able to utilize only a small fraction of soil P. This suggests that the bulk of soil P is probably of no practical significance in P nutrition of plants.

The bioassay and the chemical methods (P_w, P_{AAAc} and P_i) probably extracted P from the same reserves, since the results of all three chemical methods correlated highly with P uptake in the pot experiment, as far as the whole soil material was concerned. According to earlier results, the P coverage of poorly crystalline Al compounds in the soil (i.e. molar ratio "Al-P"/Al) seems to control the level of P_w (HARTIKAINEN 1982) as well as that of P_{AAAc} and P_i (YLI-HALLA 1989). The results also agree with the view obtained in pot experiments by NOVAIS and KAMPRATH (1978) that "Fe-P" is of lesser importance than is "Al-P", as far as the P supply of the soil to plants is concerned. The quantities of P_w, P_{AAAc} and P_i also correlated closely (r = 0.81*** − 0.84***) with each other (YLI-HALLA 1989) in a soil material which consisted principally of the same samples as were used in the present study. Therefore, the high correlation between the results of the bioassay and all three chemical methods is understandable.

The P_i method was introduced for tropical soils, partly due to the fact that the soils studied by van Zee (personal communication) were in most cases too low in soluble P to allow a precise determination of P_w. In Finnish soils the level of P_w in most cultivated soils is high enough to be measured without any analytical difficulty. Nevertheless, P uptake by the grass from the poorer half of the present soil material was more accurately predicted by the P_i method as compared to the other two chemical methods. Owing to the small number of soils (n = 16) on which this conclusion was drawn, it can be regarded as a tentative result only. However, there are certain differ-

ences in the nature of the extraction methods used in this study which may partly explain this observation. Primarily P_{AAAc} and also P_w are measures of soil P intensity (i.e. P concentration of soil solution) and do not express the size of the capacity factor (i.e. the absolute quantity of plant-available P). Instead, the P_i is supposed to be the actual amount of reversibly adsorbed P (ZEE et al. 1987) and it is probably more closely related to the capacity factor. In the present experiment in which the reserves of plant-available P were used very effectively, especially in the soils poor in P, the high positive correlation between P uptake by plants and an index closely connected with the capacity factor can be comprehended. Yet, in field trials performed in Finland (SIP-

POLA & SAARELA 1986) in which the supply of P to plants is not as critical for growth as was the case in the current pot experiment, P_{AAAc} and P_w rather successfully predicted yield responses to P fertilization. Therefore, determination of P_w or P_{AAAc} seems to be satisfactory in ranking soils to form a basis for P fertilization recommendations. If a more quantitative measure for the size of these reserves is needed than are P_w and P_{AAAc}, the determination of P_i should be considered. Even though somewhat laborious, the P_i method may prove useful, for example, when studying the capacity of erosion material to load water courses with P and for the determination of residual effect or fixation rate of P fertilization.

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SELOSTUS

Kolme uuttomenetelmää raiheinän
fosforinoton kuvastajina

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Viljelysmaiden muokkauskerroksesta eri puolilta Suomea kerätyistä 32 maanäytteestä uutettiin fosforia deionisoidulla vedellä (P_w) ja viljavuusanalyysissä käytettävällä happamalla ammoniumasetaattiliuoksella (P_{AAAc}). Lisäksi fosforia uutettiin menetelmällä, jossa liuokseen tuleva fosfori kerättiin rautahydroksidilla käsiteltyihin suodatinpaperisuikaleisiin. Tässä menetelmässä (P_i) liuoksen fosforipitoisuus pysyi koko ajan alhaisena, mikä edistää fosforin liukenemista. Samoissa maanäytteissä kasvatettiin neljä satoa Italian raiheinää, jonka fosforipitoisuus määritettiin. Raiheinä otti 5—21 % maanäytteiden epäorgaanisesta fosforista. Raiheinän ottamat fosforimäärät olivat n. kaksinkertaiset P_i-menetelmän tuloksiin verrattuna (mediaani 25.9 mg/dm³) ja monta kertaa suuremmat kuin P_w (mediaani 6.3 mg/dm³) tai P_{AAAc} (mediaani 6.4 mg/dm³). Kaikkien kolmen menetelmän antamat tulokset olivat kiinteässä vuorosuhteessa (korrelaatiokerroin r 0.88***:sta 0.93***:een) kasvien ottamien fosforimäärien kanssa. Kuitenkin niukasti fosforia sisältävissä maissa P_i-menetelmän tulosten perusteella voitiin kasvien P-ottoa ennustaa hieman tarkemmin kuin kahden muun menetelmän tulosten avulla. P_w ja P_{AAAc} ovat hyviä menetelmiä luokiteltaessa maita esim. P-lannoitussuosituksia varten. Näiden menetelmien tulokset kuvastavat fosforin intensiteettiä maassa. Työläämpi P_i-menetelmä voi sen sijaan antaa arvokasta tietoa kapasiteettitekijän suuruudesta eli siitä, kuinka paljon liukoista fosforia maassa kaikenkaikkiaan on.