

## Chloride and sulphate solutions as extractants for soil P III Effect of increasing sulphate concentration on P desorption

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**Abstract.** The effect of increasing sulphate concentration on P desorption was studied in 102 mineral soil samples with: a) solutions of a constant ionic strength  $I=0.1$  adjusted with KCl and b) 0.1 M and 0.033 M sulphate solutions of different ionic strengths. Further, the efficiency of chloride and sulphate solutions of equal anion concentration (0.1 M) was compared.

At a constant ionic strength, P desorption was enhanced as the sulphate concentration of the extractant increased. Even despite a much higher ionic strength the extraction power of the  $K_2SO_4$  solution was greater than that of the KCl solution of the same anion concentration. Comparison of the 0.1 M and 0.033 M  $K_2SO_4$  solutions revealed in 53 soil samples the extractability of P to be depressed by an increase in sulphate concentration (and ionic strength). In 49 samples, on the contrary, the 0.1 M  $K_2SO_4$  solution extracted equal or greater P amounts than did the 0.033 M  $K_2SO_4$ . It was observed that the lower the P coverage on the oxide surfaces in the soil was, the more obviously the promoting effect of increasing sulphate concentration overruled the depression induced by increasing ionic strength, and the more superior the  $K_2SO_4$  solution was as compared to the KCl solution.

### Introduction

Indifferent anions depress the desorption of P from soil to solution (RYDEN and SYERS 1975). The ionic strength created by sulphate is, however, found not to decrease the desorption as much as the same ionic strength created by chloride (HARTIKAINEN and YLI-HALLA 1982 a).

WIKLANDER and ANDERSSON (1974) have demonstrated the mobilization of P under field conditions to be promoted in autumn when the ionic strength is diminished. Their analyses of soil solution showed that in spring, after fertilization, the concentration of cations and anions at field capacity was 91–97 mmol/l, at wilting point as high as 211–307 mmol/l. Fertilization caused a high concentration of  $Cl^-$  ions, the ratio of  $Cl^-$  to  $SO_4^{2-}$  being about 10:1.

In Finland, a common fertilization practice is to add potassium to the soil as KCl. For instance, the fertilizers sold during the period of July 1979 to

June 1980 corresponded to the addition of Cl 44 kg/ha on an average, whereas that of S (mainly as  $K_2SO_4$  and superphosphate) was only 13 kg/ha. Thus, the chloride-sulphate ratio can be expected to be high at least in the beginning of the growth season which is usually dry and no leaching occurs.

In earlier papers (HARTIKAINEN and YLI-HALLA 1982 a and b) dealing with the extractability of soil P, the ionic strength of the extractants was composed solely of  $K_2SO_4$  or KCl. The purpose of the present additional study was to elucidate the effect of different sulphate concentrations as well as chloride-sulphate ratio in the extractants on P desorption from soil. Further, chloride and sulphate solutions of equal anionic concentrations were briefly compared.

## Materials and methods

The soil material, 102 mineral soil samples, was the same described in the previous papers by HARTIKAINEN and YLI-HALLA (1982 a and b).

Soil P was extracted with solutions of different concentrations of sulphate. The extractants, equal in ionic strength ( $I=0.1$ ), were marked with roman numerals according to the increasing sulphate portions, and they had the following concentrations of salts:

solution	$K_2SO_4$ conc.	KCl conc.
I	—	0.100 M
II	0.011 M	0.067 M
III	0.022 M	0.033 M
IV	0.033 M	—

The effect of a very high sulphate concentration was studied by extracting the soils with a 0.1 M  $K_2SO_4$  solution corresponding to the ionic strength of 0.3.

The soil-solution ratio was 1:60 (w/v) and desorption time 18 hours. The soil suspensions were centrifuged and filtered through a membrane filter of 0.2  $\mu$ m pore size. The pH of the clear extractants was measured and the solutions were analyzed for P by a molybdenum blue method (ANON. 1969) and for Ca by an atomic absorption spectrophotometer (acetylene-nitrous oxide flame).

The two previous papers by HARTIKAINEN and YLI-HALLA (1982 a and b) were aimed at finding out soil properties which control the effectiveness of various salt solutions as extractants for soil P. Therefore the soil sample material was divided into three categories according to the order of efficiency of different solutions to desorb P. In the present study, where attention was focused on the effect of sulphate concentration, this grouping seemed to give no advantage. Thus, the conventional division according to soil texture was used.

## Results

The effect of anion concentration on P desorption was studied by extracting the soil samples with  $K_2SO_4$  and KCl solutions of the equal anionic concentration 0.1 M. The amounts of P desorbed (mg/kg) from various soil textural classes are presented, with the confidence limits at the 95 % level, in the following tabulation:

	KCl (I=0.1)	K <sub>2</sub> SO <sub>4</sub> (I=0.3)
Heavy clays (n=17)	1.89±0.79	3.70±1.34
Coarser clays (n=51)	8.04±3.26	10.30±3.69
Non-clay soils (n=34)	9.46±5.13	11.70±5.88

The results show the average desorption by the K<sub>2</sub>SO<sub>4</sub> solution to have been somewhat greater. These solutions were, however, unequal in the concentration of potassium. Thus, in order to elucidate more accurately the effect of varying sulphate concentrations on P desorption, it was necessary to eliminate the influence of cation exchange reactions. Therefore the ionic strength was adjusted to the constant level of I=0.1.

Table 1 shows that, in spite of different anion and cation compositions, the salt solutions of the same ionic strength exchanged equal quantities of Ca. P desorption, on the contrary, was enhanced as the sulphate concentration in the extractants increased (Table 2). This appeared in all the soil groups, but very distinctly in the heavy clay soils. The increase in P desorption at each step of the sulphate concentration was statistically significant at the confidence level of 99.9 %. Only in the heavy clay soils, where the quantities dissolved were low and thus somewhat unreliable, the difference between the quantities dissolved by the solutions I and II remained statistically insignificant. In a given soil, an increase in the P desorption at every concentration step was of the same magnitude.

As can be seen in Table 3, the extractants differed to some extent in their acidity: the higher the sulphate concentration, the higher the pH value. The data show that generally the pH of the extract did not markedly deviate from that of the initial salt solution. However, in the heavy clay soils the leachate tended to be a little more acid than the extracting solution.

Table 1. Ca (mg/kg) exchanged by solutions of different SO<sub>4</sub><sup>2-</sup> concentrations at ionic strength I=0.1. Means with confidence limits at 95 % level.

	Ca exchanged by sulphate solutions of			
	0 M	0.011 M	0.022 M	0.033 M
Heavy clays	2250±393	2211±328	2216±324	2203±355
Coarser clays	1715±156	1720±155	1716±153	1720±156
Non-clay soils	1298±178	1319±184	1315±185	1272±195

Table 2. P (mg/kg) extracted with solutions of different SO<sub>4</sub><sup>2-</sup> concentrations at ionic strength I=0.1. Means with confidence limits at 95 % level.

	P extracted with sulphate solutions of			
	0 M	0.011 M	0.022 M	0.033 M
Heavy clays	1.9±0.8	2.2±1.2	2.7±1.4	3.0±1.4
Coarser clays	8.0±3.3	8.7±3.4	9.6±3.6	10.7±3.9
Non-clay soils	9.5±5.1	10.0±5.4	10.7±5.6	12.5±6.1

Table 3. pH of the extracts. Means with confidence limits at 95 % level.

	pH of the extracts obtained by sulphate solutions of			
	0 M (pH 5.25)	0.011 M (pH 5.30)	0.022 M (pH 5.35)	0.033 M (pH 5.45)
Heavy clays	5.02±0.22	5.04±0.23	5.11±0.22	5.20±0.22
Coarser clays	5.20±0.14	5.23±0.15	5.31±0.15	5.40±0.14
Non-clay soils	5.13±0.21	5.29±0.21	5.35±0.20	5.34±0.19

In order to get some further information about the efficiency of concentrated sulphate solutions as extractants, the P quantities dissolved by 0.1 M  $K_2SO_4$  ( $I=0.3$ , above tabulation) and 0.033 M  $K_2SO_4$  ( $I=0.1$ , Table 2) were compared. The data reveal that the solution of higher sulphate concentration tended to enhance desorption in heavy clay soils and to depress it in other textural classes. A closer examination showed, however, that in 49 out of 102 samples the marked increase in ionic strength had either no effect whatsoever or a promoting effect on the extractability of P. The result suggests the depressive effect of increasing ionic strength to have been counteracted by some factors. These soil samples were relatively poor in secondary phosphates as compared to their content of sorption components. The differences between P amounts dissolved by 0.1 M and 0.033 M  $K_2SO_4$  were found to correlate closely with the molar ratio of  $NH_4F$ -P and oxalate soluble Al, the value of  $r$  being  $-0.86^{***}$  ( $n=102$ ). The correlation coefficient with the molar ratio of NaOH-P/Fe was much lower ( $r=-0.53^{***}$ ).

## Discussion

Earlier tests of HARTIKAINEN and YLI-HALLA (1982 a and b) showed a  $K_2SO_4$  solution to be more effective as extractant for P than a KCl solution of the same ionic strength. In both solutions, a moderate increase in ionic strength reduced P desorption from soils rich in secondary phosphates but did not affect that from soils of lower P coverage on oxide surfaces. In the present study, the comparison of KCl and  $K_2SO_4$  solutions equal in anion concentration (0.1 M) gave further evidence of the superiority of the sulphate solution: in spite of much higher ionic strength, more P was extracted from all the soil groups. The result suggests that the effect of the greater extraction power exceeded the depressive effect of the increased ionic strength.

The cation species and concentration are known to affect P desorption (HELYAR et al. 1976, BARROW and SHAW 1979). Therefore the effect of sulphate concentration was investigated also at a constant ionic strength ( $I=0.1$ ). All the solutions of different ratios of  $Cl^-/SO_4^{2-}$  exchanged equal quantities of  $Ca^{2+}$ , whereas P desorption was enhanced as the sulphate concentration was raised.

The pH of the extraction solution somewhat increased with increasing sulphate concentration but hardly affected the extraction ability of sulphate solution. Sulphate is assumed to be sorbed as  $\text{HSO}_4^-$  anion to the oxide surface (HINGSTON et al. 1972). If this occurred, the protonation of sulphate would raise the pH of the solution. The increase in pH can be expected to be the greater, the higher the sulphate concentration is, because all the salt solutions obviously exchanged equal quantities of  $\text{H}^+$  ions to the solution. However, especially in the heavy clay soils, the mean pH of the leachate was lower than that of the extractant and the decrease was of the same magnitude at every sulphate concentration step.

The facts discussed above allow to conclude that the difference between P amounts extracted by 0.1 M and 0.033 M  $\text{K}_2\text{SO}_4$  solutions is a net effect of three forces. Firstly, increasing ionic strength depresses desorption. Secondly, increasing sulphate concentration enhances desorption. Thirdly, the cationic composition in leachates is not equal, which causes an additional effect, too. Apparently, the resultant being positive or negative is dependent on soil properties.

It is interesting to notice that in soils of high P coverage on oxide surfaces the net result of these reactions is a reduction in P extractability. In these soils, sulphate seems to behave like any indifferent anion when its concentration is raised. If a direct ligand exchange between sulphate and phosphate occurred, an increase in the sulphate concentration of the extractant would inevitably, according to the law of mass action, promote P desorption. However, the observation made was just the reverse, which suggests the depressive effect of increasing ionic strength to be dominating. On the other hand, in soils poor in phosphates, especially on the Al oxide surfaces, P desorption is enhanced by an increase in sulphate concentration. In these soils, the extraction power of sulphate seems to be able to overrule the ionic strength action.

Similarly, the superiority of  $\text{K}_2\text{SO}_4$  solution as compared to KCl solution depends on the way comparison is made. In the soils of low P coverage, the difference between P quantities dissolved in  $\text{K}_2\text{SO}_4$  and KCl solutions of the same anion concentration gives the impression of a  $\text{K}_2\text{SO}_4$  solution to be even more superior than if the comparison is made on equal ionic strength basis. On the other hand, in the soils of high P coverage the comparison at equal anion concentration lessens the apparent effectiveness of the  $\text{K}_2\text{SO}_4$  solution. Thus, when comparing the solutions at anion concentration basis, the difference in the extraction ability seems to be more decisively dependent on soil properties.

The dissimilar response of the soil samples to increasing sulphate concentration can be explained by the conclusions reached by HARTIKAINEN and YLI-HALLA (1982 a and b). Hence, in soil samples of high P coverage there are only sparsely  $\text{H}_2\text{O}$  ligands exchangeable by sulphate. Consequently, sulphate is not able to make the charge near the oxide surface more negative and to displace phosphate by increasing the repulsion. Further, owing to the minor anion exchange, the ionic strength of an outer solution is hardly affected. On the other hand, in the soils of low P coverage, ligand exchange

between H<sub>2</sub>O groups and sulphate may be possible, leading to changes in the charge properties near the oxide surface.

The results of the present study are in accord with the evidence of some pot experiments: sulphate promotes the P uptake by plants (e.g. SALONEN et al. 1968, MANCHANDA et al. 1982). Further studies are needed, however, to prove whether these findings are consequences of increased phosphate concentration in soil solution.

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## Kloridi- ja sulfaattiliuokset maan fosforin uuttajina III Kasvavan sulfaattikonsentraation vaikutus P:n uuttumiseen

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Sulfaattikonsentraation vaikutusta fosforin uuttumiseen selvitettiin 102 kivennäismaanäytteen aineistolla. Näytteitä uutettiin neljällä  $K_2SO_4$ -liuoksella, joissa sulfaattikonsentraatio vaihteli 0–0.033 M ja joiden ionivahvuus oli säädetty 0.1:ksi KCl-lioksella. Lisäksi selvitettiin fosforin uuttumista 0.1 M ja 0.033 M  $K_2SO_4$ -liuoksiin, joiden ionivahvuutta ei säädetty. KCl:n ja  $K_2SO_4$ :n uuttotehoa verrattiin käyttämällä liuoksia, joissa anionikonsentraatio oli 0.1 M, mutta liuosten ionivahvuudet olivat erisuuruiset.

Ionivahvuuden ollessa vakio maanäytteistä uuttui fosforia sitä enemmän mitä korkeampi oli uuttoliuoksen sulfaattikonsentraatio. Puhtailla 0.033 M ja 0.1 M  $K_2SO_4$ -liuoksilla saadut tulokset osoittivat, että vahvempi sulfaattiliuos uutti fosforia 53 näytteestä vähemmän ja 49 näytteestä joko enemmän tai yhtä paljon kuin laimeampi liuos.

Tuloksista voitiin päätellä ionivahvuuden kasvun vähentävän ja sulfaattikonsentraation kasvun lisäävän P:n uuttumista. Liuoksen ionivahvuuden ja sulfaattikonsentraation samanlaisen kasvamisen nettovaikutus fosforin uuttumiseen riippuu maan ominaisuuksista. Ionivahvuuden suurenemisen aiheuttama desorption väheneminen näyttää olevan sitä vallitsevampi, mitä korkeampi on maan Al-oksidipolymeerien fosforinkyllästysaste. Näytteissä, joissa  $NH_4F$ -liukoisen fosforin suhde oksalaattiuuttoiseen aluminiumiin oli pieni, sulfaattikonsentraation kasvu lisäsi desorptiota enemmän kuin ionivahvuuden kasvu sitä vähensi. Vaikka 0.1 M KCl-liuoksen ionivahvuus oli kolmasosa 0.1 M  $K_2SO_4$ -liuoksen ionivahvuudesta, sulfaattiliuos oli tehokkaampi P:n uuttaja. Erot uuttumisen määrässä olivat sitä suuremmat, mitä alhaisempi maanäytteen fosforinkyllästysaste oli.