Chloride and sulphate solutions as extractants for soil P

II Dependence of the relative extraction power of chloride and sulphate solutions on some soil properties

HELINÄ HARTIKAINEN and MARKKU YLI-HALLA

Department of Agricultural Chemistry, University of Helsinki, 00710 Helsinki 71

Abstract. The relative P extraction power of KCl and K_2SO solutions of the same ionic strength was investigated in 102 mineral soil samples. By using the ratio of chloride soluble P to sulphate soluble P ("Cl-P"/"SO_4-P") instead of absolute differences it was possible to find out a more accurate relationship between soil properties and varying extraction efficiency of salt solutions.

In the soils of low P intensity, the extractability ratio of P ("Cl-P"/"SO_4-P") seemed to decrease with an increase in the molar ratio of NH_4F soluble P (CHANG and JACKSON's method) to oxalate extractable Al, which indicates the improvement of the relative replacement power of sulphate. Conversely, in the samples of high or medium P intensity an increase in NH_4F-P/Al had an opposite effect: the ratio "Cl-P"/$\sqrt{"SO_4\text{-}P"}$ rather than "Cl-P"/"SO_4-P" was raised, suggesting a marked depression in the efficiency of sulphate. The superiority of sulphate, as compared to chloride, tended to be reduced also with increasing soil pH; the decrease seemed to be the greater the poorer the P status of the soil was.

A theory explaining the variation in the relative extraction power of chloride and sulphate solutions was presented and the possible contributory influence of point of zero charge (pzc) was discussed.

Introduction

Chloride and sulphate anions are known to differ in their tendency to be sorbed by the soil. When comparing their solutions as extractants for soil P or supporting media for P adsorption, the choice of electrolyte concentration has been based on the molarity (MATTSON et al. 1950) or normality (KURTZ et al. 1946, LEHR and WESEMAEL 1952) of the salts, or on the same cationic concentration of the solutions (STÅHLBERG 1980). However, according to HARTIKAINEN and YLI-HALLA (1982), the activity rather than the concentration of the ion seems to be of importance in the exchange reactions. In their study, the solutions were compared at the same ionic strength, and neither the concentration of cations nor that of anions were equivalent.

In the first part of this study (HARTIKAINEN and YLI-HALLA 1982) more P was found to be replaced by sulphate than by chloride and the desorption

was depressed with increasing ionic strength. The differences between the quantities of P extracted by KCl and K_2SO_4 solutions seemed to be markedly affected by the level of water soluble P and, thus, did not reliably describe the actual desorption ability of the salts in various soils. The purpose of the present study was to investigate the influence of soil properties on the relative extractability power of chloride and sulphate anions as well as to get further information about sulphate solutions as extractants for soil P, a method recently presented by STÅHLBERG (1980). In addition, the results may give intimations of the effect of drainage, fertilization and liming on the reactions of P in certain coastal soils extremely rich in native sulphur.

Materials and methods

The relative ability of chloride and sulphate to replace soil P was studied by extracting 102 mineral soil samples with KCl and K_2SO_4 solutions at ionic strengths of 0.025 and 0.1. The properties of the soil samples as well as the extraction method are presented in a previous paper (HARTIKAINEN and YLI-HALLA 1982).

In the first part of this study, the soil samples were divided into three categories differing in the sequence of extractability of soil P in water and salt solutions. This classification is used also in the present paper. In the group W>S>Cl, consisting of 53 soil samples, P was most effectively desorbed by water and most ineffectively by chloride solutions. The group S>Cl>W consists of 12 samples from which P was most abundantly dissolved by sulphate solutions and least by water. In the group S>W>Cl, being composed of 37 soil samples, water extracted less P than did sulphate solutions but more than chloride solutions.

Results

The relative desorption power of chloride and sulphate solutions in different soils was studied by calculating the ratio of KCl soluble P to K_2SO_4 soluble P at the same ionic strength. This quotient was termed the extractability ratio of P. The lower it is the more effective extractant a sulphate solution is, as compared to the corresponding chloride solution or, *vice versa*, the higher it is the better a chloride solution is able to compete with sulphate solution. The means (with the confidence limits at the 95 per cent level) and the range of ratios in the various groups are shown in Table 1.

As can be seen, the relative extraction ability of sulphate, as compared to that of chloride, was not constant; it ranged very widely in all soil groups. The relationship between the extractability ratio of P and the intensity parameter as well as other soil properties were investigated by the correlation analysis. It was found that in the soil groups W>S>Cl and S>W>Cl these ratios were quite poorly related to water soluble P, the correlation coefficients being r =

Table 1. Means and range of extractability ratios of P in various soil groups.

Soil group	I = 0.025		I = 0.1	
	Mean	Range	Mean	Range
W > S > Cl	0.76±0.03	0.54−0.94	0.70±0.03	0.49−0.90
S > W > Cl	0.73±0.05	0.43−0.90	0.71±0.03	0.51−0.89
S > Cl > W	0.74±0.09	0.51−0.95	0.73±0.08	0.56−0.94

Table 2. Correlation coefficients for the relationship between extractability ratio "Cl-P"/$\sqrt{}$"SO_4-P" and soil properties.

	Soil group					
	W > S > Cl		S > W > Cl		S > Cl > W	
	I = 0.025	I = 0.1	I = 0.025	I = 0.1	I = 0.025	I = 0.1
pH	0.37**	0.36**	0.69***	0.71***	−0.35[n.s.]	−0.18[n.s.]
org.C	−0.16[n.s.]	−0.15[n.s.]	0.07[n.s.]	0.04[n.s.]	0.45[n.s.]	0.40[n.s.]
H_2O-P	0.96***	0.97***	0.97***	0.97***	0.62*	0.59*
NH_4F-P	0.79***	0.79***	0.65***	0.65***	0.21[n.s.]	0.11[n.s.]
NaOH-P	0.36**	0.41**	0.44**	0.41*	0.37[n.s.]	0.41[n.s.]
Al	−0.37**	−0.44***	−0.31[n.s.]	−0.31[n.s.]	0.18[n.s.]	−0.00[n.s.]
Fe	−0.25[n.s.]	−0.32*	−0.32[n.s.]	−0.33*	−0.17[n.s.]	0.05[n.s.]
NH_4F-P/Al	0.91***	0.94***	0.88***	0.89***	0.33[n.s.]	0.32[n.s.]
NaOH-P/Fe	0.73***	0.80***	0.67***	0.65***	0.40[n.s.]	0.38[n.s.]

n.s. = not significant

0.41** and r = 0.52*** at ionic strength of 0.025, and r = 0.55*** and r = 0.61*** at that of 0.1, respectively.

In the soil group S>Cl>W, too, the values of the correlation coefficients were low but of the opposite sign: r = −0.38[n.s.] and r = −0.66* at ionic strengths of 0.025 and 0.1 respectively.

In the soil groups W>S>Cl and S>W>Cl, only a vague association existed between the extractability ratios and various soil properties. Some soil characteristics rather seemed to be connected with the ratio of chloride soluble P to the square root of sulphate soluble P (Table 2). In the group S>Cl>W, on the contrary, no values of the correlation coefficients calculated for the corresponding relationship deviated statistically significantly from zero. In this category the soil properties studied seemed to be correlated simply to the ratio "Cl-P"/"SO_4-P" as shown in the following tabulation:

	r	
	I=0.025	I=0.1
pH	−0.01[n.s.]	0.45[n.s.]
org. C	−0.58[n.s.]	−0.86***
H_2O-P	−0.38[n.s.]	−0.66*
NH_4F-P	−0.37[n.s.]	−0.77**
NaOH-P	−0.47[n.s.]	−0.61*
Al	−0.26[n.s.]	−0.82**
Fe	−0.41[n.s.]	−0.16[n.s.]
NH_4F-P/Al	−0.53[n.s.]	−0.80**
NaOH-P/Fe	−0.43[n.s.]	−0.62*

It should be mentioned that in all soil groups also the correlation coefficients for the relationships between the soil properties and the ratio "SO_4-P"/"Cl-P" as well as the ratio $\sqrt{"SO_4\text{-}P"}$ /"Cl-P" were calculated, but the values of r usually remained much lower. The ratio of "SO_4-P" or $\sqrt{"SO_4\text{-}P"}$ to "Cl-P" did not differentiate the samples as well as did the inverse values.

Further, the relationship between the extractability ratio of P (y) and the soil characteristics was investigated by the regression analysis. In the equations of the groups W>S>Cl and S>W>Cl, y stood for the ratio "Cl-P"/$\sqrt{"SO_4\text{-}P"}$ and in that of the group S>Cl>W, for the ratio "Cl-P"/"SO_4-P". The coefficients of multiple determination R^2 were calculated for the equations with the following variables:

x_1 = molar ratio NH_4F-P/Al ($\cdot\ 10^2$)
x_2 = molar ratio NaOH-P/Fe ($\cdot\ 10^2$)
x_3 = soil pH
x_4 = org. C %

However, in the group W>S>Cl the factor x_1 was the only statistically significant variable. The ratio NaOH-P/Fe explained 8 % and soil pH 5 % of the variation in the extractability ratio and organic carbon none at all ($P=0.05$). In this group of 53 soil samples the value of R^2 was 0.89.

In the group S>W>Cl, also the soil pH was a statistically significant variable. The factors x_2 and x_4 explained merely 1 and 5 % ($P=0.05$) of the variation in y, respectively. In these 37 soil samples the multiple determination coefficient for the equation was $R^2 = 0.84$.

The number of soil samples (12) in the group S>Cl>W is too small to give a reliable relationship between the ratio "Cl-P"/"SO_4-P" and soil properties. Nevertheless, by way of comparison, the regression equation was calculated. The value of the coefficient of multiple determination for the total equation was $R^2 = 0.84$. Although the ratio NaOH-P/Fe and the content of organic carbon explained 19 and 25 % of the variation of y, respectively, they were not statistically significant at $P = 0.10$. When these variables were excluded, the value of R^2 for the equation was 0.73. With the NH_4F-P and oxalate extractable Al as independent variables, the values of R^2 would have been lowered in all soil groups.

The relative importance of the molar ratio NH_4F-P/Al and soil pH affecting the extractability ratios in the equations for the groups S>W>Cl and S>Cl>W may be compared by the following β-coefficients:

	S>W>Cl	S>Cl>W
NH_4F-P/Al	0.733	−0.735
pH	0.261	0.372

Soil pH seems to be a variable relatively more important in the group S>Cl>W than in the group S>W>Cl.

Discussion

In a previous paper, HARTIKAINEN and YLI-HALLA (1982) reported that sulphate solutions extract soil P more abundantly than do chloride solutions of the same ionic strength. In addition, the absolute differences in P quantities dissolved tended to increase with an increase in water soluble P.

Also the results of the present study indicate that the role and significance of anion species in P desorption are dependent on soil characteristics. In all soil groups the extractability ratio of P expressing the relative replacement power of chloride and sulphate solutions varied widely. It seemed to be associated primarily with the molar ratio NH_4F-P/Al, found to control markedly the P intensity in these soils (HARTIKAINEN 1982).

There were, however, some disparities between various soil categories. In the groups W>S>Cl and S>W>Cl, the molar ratio NH_4F-P/Al was positively related to the quotient "Cl-P"/$\sqrt{\text{"SO}_4\text{-P"}}$ and in the group S>Cl>W negatively to the quotient "Cl-P"/"SO_4-P". The result suggests that in the first two groups an increase in P coverage sharply diminishes the superiority of a sulphate solution as compared to chloride solution. In other words, it impairs the specific exchange ability of sulphate.

The depressive effect found is in accordance with the theory presented by HARTIKAINEN and YLI-HALLA (1982). Thus, it may be explained by the fact that with an increase in P coverage on oxide surface the portion of H_2O groups, exchangeable with sulphate according to HINGSTON et al. (1972), decreases. Consequently, it can be concluded that the less H_2O groups are exchanged the less the ionic strength of the solution and the electrical pressure near the soil surface are affected. This, in turn, means that the difference between chloride and sulphate solutions decreases.

Even if the soil group S>Cl>W consisted of no more than 12 samples and, thus, the results obtained can be considered indicative only, some theoretical aspects can be presented. In this group, even the chloride solutions were more effective than water as P extractants, which gives reason to suppose that the chloride anions were possibly adsorbed by the oxide surface. As is generally known, this can take place only below the point of zero charge (pzc) of the oxide. The coordination of anions on oxide surface, in turn, shifts the pzc in a more acidic direction. As discussed earlier (HARTIKAINEN and YLI-HALLA 1982), this category deviated from the others in that the soil samples were extremely poor in secondary P and most samples also in organic carbon. With these properties it may be possible for the pzc to lie at a high pH value. Under these circumstances the greater replacement power of sulphate, as compared to that of chloride, is due to the greater basicity and, thus, the greater adsorption tendency of the sulphate anion (see e.g. AURA 1980). These facts may, at least to some extent, explain the decrease in the ratio "Cl-P"/"SO_4-P" with an increase in NH_4F-P/Al, an indicator of the P coverage as well as P intensity.

The results obtained in the regression analyses gave further evidence of the association between the P intensity parameter (water soluble P) and the relative desorption of soil P in chloride and sulphate solutions. The factors

found to control the extractability ratio in a particular soil group were analogical with the extractability sequence of P therein: the weaker extractant water was in the sequence the greater number of soil factors, in addition to NH_4F-P/Al, seemed to explain the relative desorption ability of the salt solutions.

The regression analyses showed in the groups $S > W > Cl$ and $S > Cl > W$ that an increase in soil pH improved the relative ability of chloride solution to compete with sulphate solution as extractant for soil P. In other words, the superiority of sulphate was depressed with decreasing acidity. This is in contradiction to the theory of the ligand exchange with OH^- ions (CHAO et al. 1965), but in agreement with the proposal presented in a previous paper by HARTIKAINEN and YLI-HALLA (1982). According to this paper, the specific effect of sulphate is due to the exchange reactions with H_2O groups and reactions involved therein. With increasing acidity the portion of H_2O ligands on the oxide surface increases at the expence of OH^- ligands, which may explain the greater activity of sulphate in acid soils.

In the soil group $W > S > Cl$, consisting of samples generally very rich in secondary and water soluble P, the extractability ratio seemed not to be significantly affected by pH. This is logical, because due to the high P coverage degree on the oxide surface there are probably few H_2O ligands also in acid samples capable of improving the extraction ability of sulphate.

In summary, a sulphate solution is a more effective extractant for soil P than a chloride solution of the same ionic strength, but its relative superiority can be concluded to be dependent on soil characteristics. Further, the theory of extraction mechanisms as well as the results obtained suggest that, as compared to water, in acid soils poor in secondary P a sulphate solution improves the extractability, but in soils rich in secondary P it is depressed. Conversely, in most soils the relative extraction ability of a chloride solution is unlikely directly affected by pH; it seems to be in accordance with the level of water soluble P.

The facts discussed above should be kept in mind when developing an extraction method for plant available P in soils. The results indicate that the poorer the P status of the soil is the more the anion composition of a fertilizer affects the mobilization of soil P resources. However, further studies are needed to confirm this hypothesis.

More detailed investigations are also needed about the effect of liming on the fate of P in acid sulphate soils. The results suggest that the mobilization of P may be secondarily improved by the formation of $CaSO_4$, which decreases the ionic strength in the soil solution. Furthermore, it seems possible that when leaching sulphate from soil the simultaneous leaching of P downwards in the profile is dependent on the P status of the soil.

References

AURA, E. 1980. Oxygen as an exchangeable ligand in soil. J. Scient. Agric. Soc. Finl. 52: 34–44.

CHAO, T. T., HARWARD, M. E. & FANG, S. C. 1965. Exchange reactions between hydroxyl and sulfate ions in soils. Soil Sci. 99: 104–108.

HARTIKAINEN, H. 1982. Water soluble phosphorus in Finnish mineral soils and its dependence on soil properties. J. Scient. Agric. Soc. Finl. 54: 89–98.

— & YLI-HALLA, M. 1982. Chloride and sulphate solutions as extractants for soil P. I. The effect of ionic species and ionic strength on P desorption. J. Scient. Agric. Soc. Finl. 54: 287–296.

HINGSTON, F. J., POSNER, A. M. & QUIRK, J. P. 1972. Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. J. Soil Sci. 23: 177–192.

KURTZ, T., DE TURK, E. E. & BRAY, R. 1946. Phosphate adsorption by Illinois soils. Soil Sci. 61: 111–124.

LEHR, J. J. & WESEMAEL, J. C. H. van. 1952. The influence of neutral salts on the solubility of soil phosphate. J. Soil Sci. 3: 125–135.

MATTSON, S., ALVSAKER, E., KOUTLER-ANDERSSON, E., BARKOFF, E. & VAHTRAS, K. 1950. Phosphate relationships of soil and plant. VI. The salt effect on phosphate solubility in pedalfer soils. Ann. Agric. Coll. Sweden 17: 141–160.

STÅHLBERG, S. 1980. A new extraction method for estimation of plant-available P, K and Mg. Acta Agric. Scand. 30: 93–107.

SELOSTUS

Kloridi- ja sulfaattiliuokset maan fosforin uuttajina

II Kloridi- ja sulfaattiliuosten suhteellisen uuttokyvyn riippuvuus maan ominaisuuksista

Helinä Hartikainen ja Markku Yli-Halla

Helsingin yliopiston maanviljelyskemian laitos, 00710 Helsinki 71

Tutkimuksen ensimmäisessä osassa havaittiin K_2SO_4 -liuosten olevan tehokkaampia maan fosforin uuttajia kuin ionivahvuudeltaan vastaavat KCl-liuokset, mutta uuttuneiden P:n määrien väliset erot näyttivät vaihtelevan melkoisesti. Tässä osassa selvitettiin uuttoliuosten tehokkuuden riippuvuutta maan ominaisuuksista.

KCl:iin ja K_2SO_4:iin uuttuneiden määrien suhteen ("Cl-P"/"SO$_4$-P") katsottiin kuvaavan liuosten uuttotehoa toisiinsa verrattuna. Mitä pienempi suhteen arvo on, sitä tehokkaampi sulfaattiliuos on P:n uuttajana kloridiliuokseen verrattuna. Suhteen arvo vaihteli 0.43:sta 0.95:een.

Näytteissä, joissa oli hyvin matala P:n intensiteetti (vähän vesiliukoista P:a), sulfaattiliuosten suhteellinen uuttokyky parani, kun NH$_4$F-uuttoisen P:n (CHANGin ja JACKSONin menetelmä) moolimäärän suhde oksalaattiliukoiseen Al:iin kasvoi. Sen sijaan maissa, joissa oli kohtalaisesti tai runsaasti veteen liukenevaa P:a, sulfaatin suhteellinen uuttoteho näytti jyrkästi alenevan moolisuhteen NH$_4$F-P/Al kasvaessa. Myös maan pH:n kohoaminen vähensi sulfaattiliuosten tehokkuutta.

Sulfaatin suuremman uuttotehon katsottiin aiheutuvan sen kyvystä vaihtaa oksidien pinnoilta H_2O-ligandeja, minkä seurauksena liuoksen ionivahvuus pienenee ja fosfaatin

desorptio lisääntyy. Koska happamuuden vähetessä ja moolisuhteen NH_4F-P/Al kasvaessa H_2O-ligandien osuus oksidipinnalla pienenee, sulfaatti- ja vesiligandien välisen vaihtoreaktion merkitys vähenee, mikä merkitsee kloridi- ja sulfaattiliuosten P:n uuttokyvyn erojen kaventumista.