

Desorption of phosphate from three Finnish mineral soil samples during adsorption of vanadate, molybdate and tungstate

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Adsorption of V(V) and Mo(VI) from 10^{-4} M and 10^{-5} M solutions and W(VI) from a 10^{-4} M solution (in 0.02 M KCl) by three Finnish mineral soils was studied in two series of experiments.

In the first experiment, the adsorption of V, Mo and W by soil and the desorption of P were measured at the soils' natural pH after an equilibration time of 3, 5, 22, 29, 46 and 70 h. Adsorption of molybdate occurred mainly within the three first hours, whereas adsorption of vanadate and tungstate were slower processes. During the first few hours, the presence of molybdate seemed to increase the desorption of phosphate most effectively, but after a longer equilibration period, the differences between additions of V, Mo, and W became smaller.

In the second experiment, the adsorption process was followed as a function of the acidity of the suspension (pH 2.3–7.5; for W pH 2.8–7.5). Adsorption of V(V), Mo(VI) or W(VI) resulted in a statistically significant increase in the amounts of P desorbed from all three soils over the pH range studied.

The aqueous chemistry of V(V), Mo(VI) and W(VI) is briefly discussed.

Key words: clay, finesand, anions, polyanions, specific adsorption

Introduction

In studying adsorption of anions by different materials, soils, without doubt, are the most complicated adsorbents. Even in simplified adsorption and desorption experiments carried out in laboratory conditions, processes such as cation and anion exchange, dissolution of fertilizer particles or soil constituents, and precipitation can be expected (LINDSAY 1979, BARBER 1984). When different anions are present in soil solution or in the solution in contact with adsorbent, competitive adsorption may occur (MURALI and AYLMOORE 1983, ROY et al. 1986a,b, GOLDBERG and TRAINA

1987, ROY et al. 1989, BARROW 1989, MIKKONEN and TUMMAVUORI 1993a). Addition of a specifically adsorbed ion may affect desorption of other ions already adsorbed (GORLACH et al. 1969, BARROW 1974).

When studying retention of V(V), Mo(VI) and W(VI) by three Finnish soils from sodium oxy-salt solutions (MIKKONEN and TUMMAVUORI 1993 b,c,d), we followed how quickly adsorption of V, Mo and W occurs at the natural soil pH and how much P is released to the aqueous phase. In addition, we measured the amounts of P present in the aqueous phase at the end of the 72-hour equilibration period to see if the desorption of phos-

phate is affected by the addition of rather high amounts of these anions.

The reasons for using 10^{-4} M and 10^{-5} M solutions of added anions was that batch analyses were comfortable to perform at these concentrations and there were no polyanionic species present in molybdate solutions. Molybdate is the most important of these three analytes.

At pH 2–8, in dilute ($\leq 10^{-4}$ mol/l) solutions, Mo(VI) is present as monomeric species $\text{Mo}(\text{OH})_6$, HMoO_4^- , and MoO_4^{2-} , the last one being predominant at pH > 4.5. At concentrations $> 10^{-4}$ mol/l, polyanions, such as $\text{Mo}_7\text{O}_{24}^{6-}$ and its protonated forms, may be present at pH ≤ 5 . In V(V) solutions, at pH ≤ 5 , polyionic decavanadate species $\text{HV}_{10}\text{O}_{28}^{5-}$ and $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ exist even in a low concentration such as 10^{-4} mol/l. In 10^{-5} M solutions, only H_3VO_4 , H_2VO_4^- and small amounts of HVO_4^{2-} are present at pH 2–8. The solution chemistry of tungsten is even more unknown. As yet, the equilibria and ionic forms in $\leq 10^{-3}$ M W(VI) solutions are not precisely known (POPE 1983, MAK-SIMOVSKAYA and BURTSEVA 1985, CRUYWAGEN and VAN DER MERWE 1987).

In addition to the isopolyanions mentioned above, it is possible that V(V), Mo(VI), and W(VI) form heteropolyanions with each other or with many other elements present in aqueous solutions. Examples of such heteropolyanions that might also occur in soil suspensions are molybdophosphates $(\text{H}^+)_p(\text{MoO}_4^{2-})_5(\text{HPO}_4^{2-})_2$, $p = 8, 9, 10$ (PETTERSSON et al. 1985) and tetra-decavanadophosphate $\text{HPV}_{14}\text{O}_{42}^{8-}$ (HARRISON and HOWARTH 1985). Both of these have been shown to exist in laboratory conditions, using high ionic strength and 10^{-3} – 10^{-2} M solutions. At present, it is still uncertain if these kinds of species exist in very dilute solutions.

Material and methods

Test soils were a clay (soil 1) and two finesand samples (soils 2 and 3). Soil 2 had the coarsest texture. Selected characteristics of the soils are given in Table 1. The ammonium oxalate-oxalic

acid (pH 3.3) extractable amounts of Mo and W, and $\text{HClO}_4 + \text{HNO}_3$ -extractable amounts of V are given in our previous papers (MIKKONEN and TUMMAVUORI 1993b,c,d).

The soils were air-dried and hand-crushed to pass through a 2-mm sieve. When measuring adsorption of V, Mo and W as a function of time, aliquots of 100.0 ml of 10^{-4} M NaVO_3 , Na_2MoO_4 , or Na_2WO_4 , all in 0.02 M KCl, were mixed to the 1.00-g samples of soils (two replicates) in 250-ml beakers, covered with Parafilm and allowed to equilibrate for 3, 5, 22, 29, 46, and 70 h at room temperature. Before filtration, the pH values of the suspensions were measured. From these filtrates, V, Mo or W as well as P concentrations were measured by Perkin-Elmer ICP 2000.

For experiments, where adsorption was studied as a function of pH, subsamples of 1.00 g were placed into 250-beakers and aliquots of 100.0 ml of 0.02 M KCl, 10^{-4} or 10^{-5} M Na_2MoO_4 , 10^{-4} M Na_2WO_4 , or 10^{-4} or 10^{-5} M NaVO_3 , all in 0.02 M KCl were added. KCl was used to keep the ionic strength constant. pH adjustments to obtain final pH 2.3–7.5 were made by adding dilute HCl or NaOH. The beakers were covered with Parafilm, shaken manually for 2–3 min, and left to equilibrate at room temperature for 72 h. The final pH values of the suspensions were recorded prior to the filtration using a standard combination electrode. During the pH measurements, the samples were stirred using a magnetic rod. The samples were then filtered through Whatman 40 filter paper, and the concentrations of the analytes in the filtrates were measured by a Perkin-Elmer ICP 5000 spectrophotometer. The concentrations were volume-corrected because of the H^+/OH^- addition. From each soil, arbitrarily-selected filtrates were also analysed using the standard addition method, so that the accuracy of the ICP measurements was checked both for the blank samples and for the samples into which V, Mo or W was added. The added 100.0-ml aliquots of 10^{-4} M V, Mo or W solution contained 509.4 μg of V, 959.4 μg of Mo and 1838.5 μg of W, respectively.

Table 1. Selected characteristics of the soil samples.

	soil 1	soil 2	soil 3
colour and texture	dark grey clay	brown coarser finesand	grey-brown finer finesand
*particle-size fraction, %			
particle diameter < 0.002 mm	77.0	28.2	27.7
0.002–0.02 mm	10.0	16.7	17.7
0.02–0.06 mm	5.1	8.8	26.8
0.06–0.2 mm	2.7	24.5	24.1
0.2–2 mm	5.2	21.8	3.7
> 2 mm	0	0	0
*pH (CaCl ₂); 1:2.5	7.3	6.1	5.6
pH (KCl); 1g:100 ml	7.1	6.1	6.0
*bulk density kg/l	0.95	1.14	1.02
*AO-OA extractable Fe (g per liter of soil);			
16-h extraction	6.6 ± 0.2	5.1 ± 0.2	4.6 ± 0.3
2-h extraction	6.1 ± 0.2	3.9 ± 0.4	2.7 ± 0.1
*AO-OA extractable Al (g per liter of soil);			
16-h extraction	2.3 ± 0.1	1.6 ± 0.1	2.2 ± 0.1
2-h extraction	2.3 ± 0.1	1.5 ± 0.1	1.7 ± 0.1
*organic C %	4.2	2.3	4.6
*extractable P mg per liter of soil	37.2	25.3	18.8

* = A determination made at the Agricultural Research Centre of Finland, Jokioinen.
 AO-OA = ammonium oxalate-oxalic acid extraction solution, pH 3.3

Results and discussion

Adsorption of V, Mo and W begins within the first three hours, but adsorption of vanadate occurs more slowly than adsorption of molybdate or tungstate (Fig. 1a–c). The pH remained rather constant in all samples.

Figures 1a–1c show that during the 70-h equilibration period, 33–55 % (170–280 µg/g) of added V, 3–10 % (30–100 µg/g) of added Mo and 21–33 % (400–600 µg/g) of added W (Fig. 1c) were retained. Vanadate is retained most strongly in neutral conditions, but the order becomes different when the suspensions are acidic (MIKKONEN and TUMMAVUORI 1993b,c,d).

If we take a 30-cm layer of soil and use a bulk density of 1.00 kg/l, the soils could retain at least 510–840 kg/ha of V, 90–300 kg/ha of Mo, and

1200–1800 kg/ha of W, respectively. These are, of course, only estimates, because the adsorption capacity was not determined using a series of more concentrated solutions.

In addition that phosphate can displace e.g. adsorbed molybdate, phosphate can be displaced by high amounts of other specifically adsorbed anions. Within the first few hours, the presence of molybdate seems to increase the desorption of phosphate most, but after a longer equilibration period, the differences in displacing ability of V, Mo, and W become smaller (Fig. 2a–c).

The desorption of P from the blank samples in 72 h and the changes in the desorption because of the addition of Mo (at the 10⁻⁴ mol/l level) as a function of pH are presented in Fig. 3. The differences in the shape of the curves of soils 2 and 3 at pH > 6 compared with that of soil 1 are

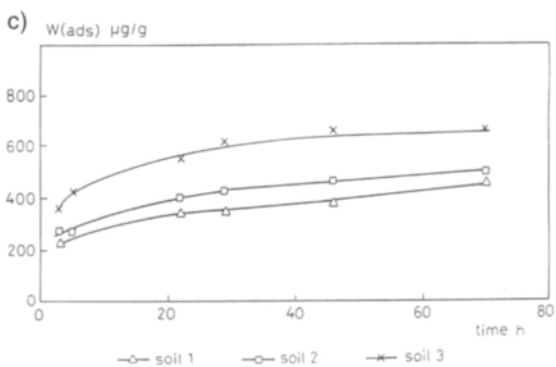
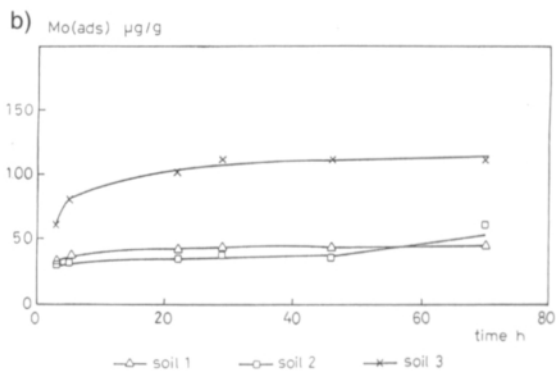
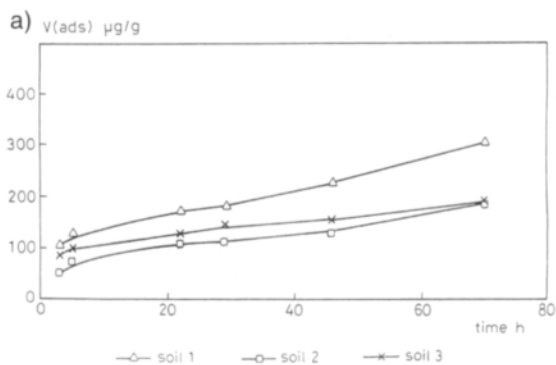


Fig. 1. Time-dependence of adsorption from a 10^{-4} M solution. a) V, b) Mo, c) W. Error limits $\leq 5\%$.

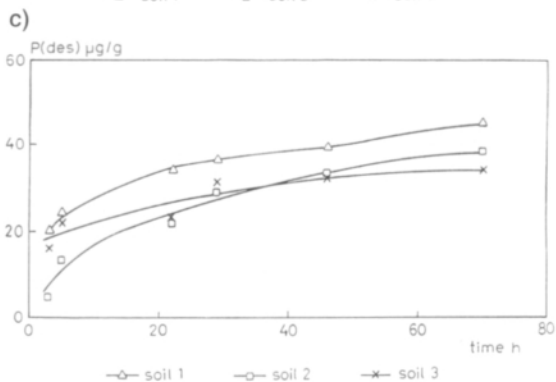
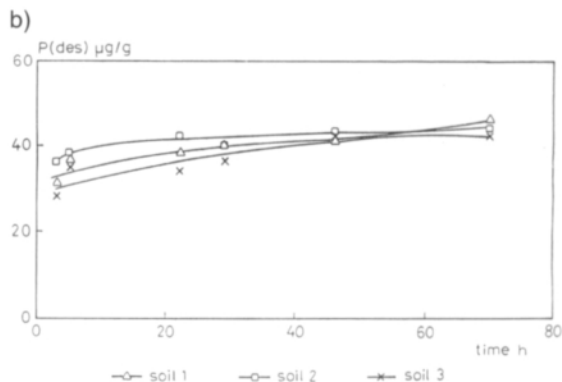
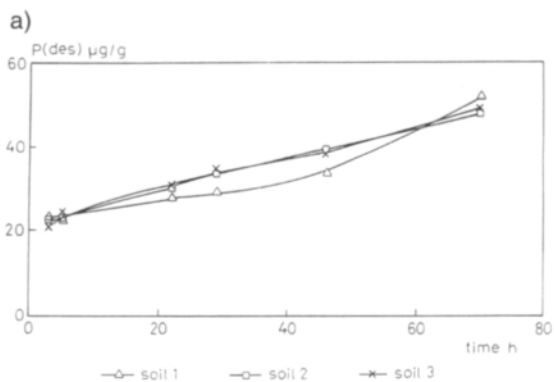


Fig. 2. Time-dependence of desorption of P during adsorption of a) V, b) Mo, c) W. Error limits $\leq 8\%$.

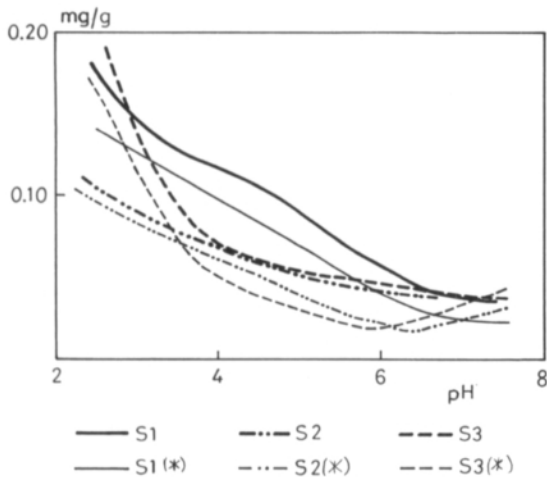


Fig. 3. Mobility of P from the blank samples and changes caused by the addition of 10^{-4} M molybdate. S1 = soil 1, S2 = soil 2, S3 = soil 3; (*) denotes blank samples.

attributable to the addition of OH^- ions that displaced some of the adsorbed phosphate ions. Because the natural pH of soil 1 was 7.3, no addition of OH^- ions was necessary for obtaining final high pH values of 6–7. In the most acidic suspensions, phosphorus bound to oxide surfaces or present in apatitic form or in the organic matter may also begin to dissolve, in addition to the other forms of P in soil.

In statistical analyses, the results at pH 2.3–7.5 (pH 2.8–7.5 for W) after every V/Mo/W treatment were used as one group of test points. A paired t-test confirmed that the sieved soils were homogenous enough for accurate analytical work. When pairs of test points after each V/Mo/W application were divided into two subgroups and the means of the latter compared, the means were identical only when the pH of the test pairs was within 0.05 pH units.

ANOVA was used for statistically testing the effect of adding competing anions on the desorption of P (Table 2). The statistical tests showed that addition of a foreign heavy metal (V, Mo, W) as sodium oxosalt increased the release of P from all soils. A correlation between adsorbed Mo, V, or W, and desorbed P, however, existed only in the case of W (Table 3). This correlation

Table 2. P-release from untreated soils and differences in means of desorbed P from soil samples with a Mo, V, or W application compared to means of amounts desorbed from blank samples.

Set of samples	the statistical significance of the differences		
	soil 1	soil 2	soil 3
blank mean $\mu\text{g/g}$	47.5	47.3	62.3
10^{-4} M Mo	***	***	***
10^{-5} M Mo	NS	*	*
10^{-4} M W	***	***	**
10^{-4} M V	***	***	*
10^{-5} M V	***	***	*

* = $P(> 0.05)$

** = $P(> 0.01)$

*** = $P(> 0.001)$

NS = not significant

is linear at pH 3–6. Both at low solubility of P at pH 6–7 and at high solubility of P from soil 3 at pH < 3, the W-P correlation deviates from a straight line.

In creating adsorption isotherms and adsorption envelopes, solution chemistry, properties of the adsorbent, and the analytical conditions should all be taken into account. Today, scientists should carefully investigate especially the possibility of vanadium's forming heteropolyanions. ^{51}V NMR studies, for example, are in progress (MIKKONEN and KOLEHMAINEN 1994). As soon as better results are obtained in laboratory experiments, the behaviour of Mo, V, and W in soils could be more thoroughly discussed.

Table 3. Correlation between retained W (in $\mu\text{g/g}$) and desorbed P (in $\mu\text{g/g}$) at pH 3–6.

Soil	Number of samples	Coefficient of correlation	Slope
soil 1	26	0.9629	0.097 ± 0.005
soil 2	27	0.9702	0.079 ± 0.004
soil 3	26	0.9588	0.065 ± 0.004

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SELOSTUS

Fosforin desorptio kolmesta suomalaisesta mineraalimaasta vanadaatin, molybdaatin ja volframaatin adsorption aikana

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Tutkittaessa molybdaatin, vanadaatin ja volframaatin adsorptiota kolmeen suomalaiseen mineraalimaanäytteeseen 10^{-4} tai 10^{-5} M liuoksesta mitattiin myös adsorption aikana liuosfaasiin siirtyneen fosforin määriä. Adsorption etenemistä ja fosfaatin desorptiota seurattiin ajan funktiona kunkin maan luonnollisessa pH:ssa. Toisessa kokeessa mitattiin desorboitunut fosfori, kun tutkittiin vanadaatin, mo-

lybdaatin ja volframaatin adsorptiota 72 tunnin aikana pH-alueella 2,3–7,5. Tulokset osoittivat, että molybdaatin, volframaatin ja vanadaatin läsnäolo pyrki lisäämään liuosfaasissa olevan fosforin määrää.

Artikkelissa tarkastellaan lyhyesti myös molybdeenin, vanadiinin ja volframin ionimuotoja vesiliuoksissa.