DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JYVÄSKYLÄ
RESEARCH REPORT No. 47

RETENTION OF MOLYBDENUM(VI), VANADIUM(V) AND TUNGSTEN(VI) BY KAOLIN AND THREE FINNISH MINERAL SOILS

BY
ANNELI MIKKONEN

Academic Dissertation
for the Degree of
Doctor of Philosophy

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I dedicate this work to Heikki.

PREFACE

This work was carried out in the Department of Chemistry, University of Jyväskylä from 1987-1994.

I am deeply grateful to my supervisor, Associate Professor Jouni Tummavuori for his patience and continuous encouragement and for his support in this work.

Professor Johannes J. Cruywagen, University of Stellenbosch, South Africa, kindly helped me find some order in the mysterious world of molybdates, vanadates and tungstates. I wish to express my sincere thanks to him.

I also thank Dr. Juha Vilhunen at the Technology Centre of Neste Oy for recording some X-ray diffraction patterns, and Håkan Jansson, M.Sc.(Soil and Forest Sciences) at the Agricultural Research Centre of Finland for determinations of some soil characteristics.

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Finally, I owe my greatest debt of gratitude to my son, Heikki Pirinen. His childhood has been spent in the shadow of this thesis. He has endured all my ups and downs in this study with patient understanding and love.

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Jyväskylä, on December 6th, 1994

Anneli Mikkonen

ABSTRACT

Adsorption of aqueous species of Mo(VI) and V(V) from 10^{-4} M and 10^{-5} M and W(VI) from 10^{-4} M sodium salt solutions by kaolin and three Finnish mineral soils was measured at room temperature using a solid:solution ratio 1:100 (w:v), pH range 2.3-7.5 (pH 2.8-7.5 for W) and an equilibration time of 72 h. Potassium chloride (0.02 M) was used as ionic strength adjustor.

In desorption experiments, 0.80 g of soil or kaolin was extracted with 50 ml of 0.02 M KCl. A shaking time of 17 h was used.

Kaolin $H_2Al_2Si_2O_8 \bullet H_2O$ (Kaolin.pond Ph.Eur.III 180 μm) was provided by the Helsinki University Pharmacy. Cation exchange capacity and pH of kaolin were determined, as well as the powder X-ray diffraction pattern recorded. The test soils, a clay and two finesand samples with organic matter content less than 5 %, were provided by the Agricultural Research Centre, Jokioinen. The characteristics of soils necessary for explaining adsorption properties are given, and the possibility of the reduction of V(V) in contact with these soils is discussed.

Results are given in the form of adsorption and desorption envelopes (adsorption or desorption vs. pH). For molybdate, protonation constants determined from a 10^{-4} M Na_2MoO_4 solution in 0.02 M KCl were used in explaining adsorption and desorption of different ionic species initially present in solution. Retention of V(V) was interpreted using protonation constants taken from the literature. The aqueous chemistry of W(VI) proved to be so inadequately known that it was not possible to explain retention of W(VI) by identifying different ionic species initially present in solution.

Time-dependence of the adsorption of V(V), Mo(VI) and W(VI) at the natural pH of each soil, as well that of Mo(VI) from solutions with initial pH values 2.0 and 3.0 was followed for 70 h. Amounts of phosphorus released at the natural pH of each soil, in addition to those of Ca, Mg, Mn, P, Al, and Fe released in acidic conditions were measured. All elemental analyses were performed by plasma emission spectrometry.

The possibility of utilizing ^{17}O and ^{51}V NMR spectrometry in identifying mono- and polyionic species in aqueous solutions is discussed.

LIST OF ORIGINAL PAPERS

This thesis is based on the following publications:

1. Mikkonen, A. and Tummavuori, J., Retention of vanadium(V), molybdenum(VI) and tungsten(VI) by kaolin. *Acta Agriculturae Scandinavica, Section B, Soil and Plant Science 43* (1993) 11-15.
   https://doi.org/10.1080/09064719309410225
2. Mikkonen, A. and Tummavuori, J., Retention of molybdenum(VI) by three Finnish mineral soils. *Acta Agriculturae Scandinavica, Section B, Soil and Plant Science 43* (1993) 206-212.
   https://doi.org/10.1080/09064719309411243
3. Mikkonen, A. and Tummavuori, J., Retention of tungsten(VI) by three Finnish mineral soils. *Acta Agriculturae Scandinavica, Section B, Soil and Plant Science 43* (1993) 213-217.
   https://doi.org/10.1080/09064719309411244
4. Mikkonen, A. and Tummavuori, J., Retention of vanadium(V) by three Finnish mineral soils. *European Journal of Soil Science*. In press.
   https://doi.org/10.1111/j.1365-2389.1994.tb00520.x
5. Mikkonen, A. and Tummavuori, J., Desorption of phosphate from three Finnish mineral soil samples during adsorption of vanadate, molybdate and tungstate. *Agricultural Science in Finland* 3 (1994) 481-486.
   https://doi.org/10.23986/afsci.72720

CONTENTS

Erratum

Page	Is	Should be
List of original papers Paper 3	European Journal of Soil Science. In press.	European Journal of Soil Science 45 (1994) 361-368.
Page 31 line 3	structure $H_4O_5^-$	structure $H_4VO_5^-$
Page 48 ref. 159	the $(NH_4)_2C_2C_4$-extractable	the $(NH_4)_2C_2O_4$-extractable
Page 49 line 10	0.275 M $NAHC_2O_4$	0.275 M $NaHC_2O_4$
Page 67 lines 18,19	the contact between soil and a very acidic solution and soil	the contact between soil and a very acidic solution
Page 72 line 8	$\mu g\ g^-$ to $mg\ l^{-1}$	$\mu g\ g^{-1}$ to $mg\ l^{-1}$
Page 80 ref. 4 ref. 5	4. Eur. J. Soil Sci. 1994. In press. 5. Agric. Sci. Finl. 1994. In press.	4. Eur. J. Soil Sci. 45 (1994) 361. 5. Agric. Sci. Finl. 45 (1994) 481.

1. INTRODUCTION

Retention, or sorption, by soils and other adsorbents refers to the selective uptake and storage by the solid phase of solute species originally present in solution. The forms of sorption (not necessarily mutually exclusive) most commonly encountered in connection with solute transport in soil are adsorption, chemisorption, and ion exchange. In the adsorption process, solutes adhere to the surface of the solid. This form of sorption tends to be weaker and less specific than when sorption occurs through a true chemical reaction as in chemisorption. In the ion exchange process, charged solutes exchange with ions on the solid.[6]

In agricultural soils, nutrients can be present either as anions, cations, or neutral molecules, and their retention by soils has attracted researchers for several decades.[7] Of the anions, retention of phosphate has been most widely examined, but much work has been done with other anions also.[8-10] Comprehensive studies on adsorption of molybdate were initiated by Jones.[11] In the 1960s and 1970s, retention of molybdate both by soils and different synthetic materials was intensively studied, but many questions still remained unanswered.[12-21]

When discussing adsorption of Mo(VI) species thoroughly, one needs detailed information on molybdenum species present in the solution, in contact with the adsorbent. Unfortunately, at the time when most of the studies on adsorption of molybdate by soils were performed, there was a lack of information on aqueous Mo(VI) chemistry, and the results of experiments were often interpreted using overly simplified assumptions. Great progress was achieved in the solution chemistry of Mo in the 1980s, and today equilibria in aqueous Mo solutions are rather well-known.[22-24]

The overall aim of this study was to learn more about soil chemistry and soil-solution interaction. The specific objectives were:

1. To measure adsorption of molybdate by three Finnish soils (clay and two finesand samples) from two dilute Na_2MoO_4 solutions in order to produce adsorption envelopes. The selected concentrations were 10^{-4} M and 10^{-5} M, because measurements at these concentrations were convenient to perform with the ICP equipment available, and the solution chemistry of Mo(VI) is rather simple in dilute solutions.

2. To measure desorption of adsorbed molybdate.

3. To perform corresponding adsorption and desorption measurements using vanadate and tungstate solutions with molar concentrations corresponding to those of Mo(VI) solutions. These elements were included, because their aqueous chemistry has much in common with Mo.[25] In addition, it has been frequently proposed that V and W could substitute for Mo in nitrogen fixation in plants,[26,27] and from that point of view, it is important to know how these elements behave in contact with soil.

4. To measure retention of molybdate, vanadate and tungstate by purified kaolin, by using both singly added anions and a mixture of Mo+V+W. The results of this experiment could at least partly explain the role of the clay fraction of soil, and show if adsorption of a singly added anion is similar to that from a mixture of anions.

5. To measure the release of Ca, Mg, Mn, and P from soils during adsorption of molybdate, vanadate and tungstate, first, to see how much these raise the ionic strength of the aqueous phase, and second, to see if an artificial addition of rather large amounts of Mo, V or W could cause statistically significant differences in the release of these nutrients. It is known from the literature that there is interaction between cations and anions in soils, especially in connection with anion adsorption where an adsorbed anion creates new cation exchanging groups.[28]

Release of phosphorus was interesting because P plays an important role as an anionic major nutrient. Calcium and magnesium are cationic major nutrients. Manganese, a cationic minor nutrient, is present in agricultural soils in amounts high enough to be comfortably determined even from 1-g samples. The Fe and Al contents of soils needed to be determined also, both to explain the role of their hydrous oxides and to see how Al and Fe are dissolved under acidic conditions.

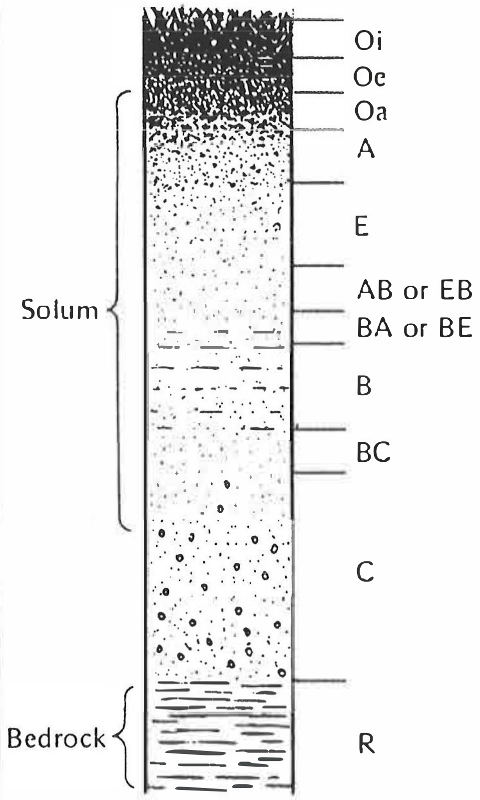
In addition to temperature,[29] both ionic strength and the cation species of the support medium can affect the rate at which equilibrium is attained in adsorption experiments.[30] During adsorption, 0.02 M KCl was used to control the ionic strength of Mo/V/W solutions, and it also provided the presence of Cl^-, a nonspecifically adsorbed anion, and K^+, an exchangeable cation. The V/Mo/W solutions contained Na^+ ions also, which are regarded as weakly-bound exchangeable cations.[28] In extracting the adsorbed Mo, V or W, 0.02 M KCl was used to characterize the easily-soluble fraction of the adsorbates.

The equilibria in dilute Mo solutions with low ionic strength were still unknown[31] when this study began. That is why it was necessary to determine the protonation constants of molybdate in 0.02 M KCl by EMF methods. For vanadate, literature values for protonation constants[25,32] were used. In the case of tungstate, information on equilibria in dilute solutions is lacking.[33-35]

Because non-soil scientists are generally unfamiliar with agricultural soils, the properties of soils important in anion adsorption especially are presented briefly in chapter 2. Chapter 3 explains the aqueous chemistry of Mo, V, and W, as it was understood at the end of 1994. Chapter 4 gives a short introduction to anion and molecular retention, as well as a review of studies on retention (adsorption and displacement) of Mo by different soils and synthetic materials.

2. SOIL CHEMISTRY

2.1. General



O_i	Organic, slightly decomposed
O_e	Organic, moderately decomposed
O_a	Organic, highly decomposed
A	Mineral, mixed with humus, dark coloured
E	Horizon of maximum eluviation of silicate clays, Al, Fe oxides, etc.
AB or **EB**	Transition to B, more like A or E than B
BA or **BE**	Transition to A or E, more like B than A or E
B	Most clearly expressed portion of B horizon
BC	Transition to C, more like B than C
C	Zone of least weathering, accumulation of Ca, Mg carbonates, cementation, sometimes high bulk density
R	Underlying consolidated rock

FIGURE 1. Theoretical mineral soil profile, showing the major horizons that may be present in a well-drained soil in the temperate humid region.

Soil, a multicomponent system, consists of solid, liquid, and gaseous phases, and living organisms.[2] The soil profile (Fig.1) can be divided into O, A, B, E, and C horizons, characterized by the different effects of soil-developing processes. The O group, the organic horizons that form above the mineral soil, occur commonly in forested areas and are absent in grassland regions. The A horizon has an accumulation of organic matter as a result of plant growth, and its quartz content is higher than in other horizons. The E horizon generally has a lighter colour than the A horizon. The B horizon has an accumulation of clay, iron and aluminium due to weathering of the A horizon. Weathering rate is influenced, for example, by temperature, rainfall, slope, drainage, rate of water infiltration, minerals present, and plant growth. The A and B horizons contain material, altered from the original, whereas the C horizon contains the unaltered, original material, from which the soil is presumed to have developed. Any particular profile may exhibit only some of these horizons, and the relative depths vary. In addition, however, more detailed subhorizons than indicated in Figure 1 may be found in a profile.[36,37]

With tillage, fertilization, and cropping of the soil, the A horizon changes to A_p. The A_p horizon is usually more fertile than B or C, because of nutrient recycling by plants during soil development plus fertilizer and lime additions. A plant's root system may extend into all three horizons. Soil particles may be either rock fragments or combinations of inorganic and organic materials, cemented together in a porous structure. The nature of the soil aggregates determines the porosity of the soil through which the roots grow. Plants cannot grow, if the pores are smaller than root tips.[37]

2.2. Soil particle size

Soil minerals can be subdivided into fractions on the basis of particle size (Table 1). Sand and silt particles may be similar mineralogically and differ only in particle size and relative abundance of particular minerals within the particle. Most clay particles differ mineralogically from the sand and silt, though they generally have developed from weathering of silt and sand particles. The surface area of cubical or spherical particles may be calculated from the relation

$$\text{surface area} = 2.31/d_p, \tag{1}$$

where d_p is the particle diameter. However, clay particles are plate-shaped and have a much larger surface area per g.[37]

TABLE 1. Soil particle size and surface area.[37]
Surface area of clay has been calculated so that clay plates of swelling clay have a thickness of $1 \bullet 10^{-7}$ cm and plates of nonswelling clay have a thickness of $2 \bullet 10^{-6}$ cm.

Particle classification	Particle diameter mm	Particles per g	Surface area cm^2 g^{-1}
very coarse sand	2-1	112	15.4
coarse sand	1-0.5	895	30.8
medium sand	0.5-0.25	$7.1 \bullet 10^{3}$	61.6
fine sand	0.25-0.1	$7.0 \bullet 10^{4}$	132
very fine sand	0.1-0.05	$8.9 \bullet 10^{6}$	308
silt	0.05-0.002	$2 \bullet 10^{7}$	888
clay (swelling)	<0.002	$4 \bullet 10^{11}$	$8 \bullet 10^{6}$
clay (nonswelling)	<0.002	$4 \bullet 10^{11}$	$4 \bullet 10^{5}$

2.3. Soil mineralogical composition

2.3.1 Crystalline soil minerals

In most soils, the sand and silt fractions consist largely of primary minerals, formed at elevated temperature and inherited unchanged from igneous and metamorphic rocks.[7] The most abundant primary minerals in soils are quartz SiO_2 and the feldspars

$MAlSi_3O_8$, where M represents combinations of the cations Na^+, K^+, and Ca^{2+}. Micas (e.g. muscovite $K_2Al_2Si_6Al_4O_{20}(OH)_4$, biotite $K_2Al_2Si_6(Fe^{2+},Mg)_6O_{20}(OH)_4$) and olivine $(MgFe)_2SiO_4$ as well as pyroxenes and amphiboles (CaMgFe silicates) are also commonly present but in smaller quantities than quartz or the feldspars.[7]

Common secondary minerals in soils, formed by low-temperature reactions and either inherited from sedimentary rocks or formed directly by weathering, include the carbonate and sulfur minerals, the layer silicates, and various oxides.[7] Calcium and magnesium carbonates, the limestones, may vary from almost pure $CaCO_3$, calcite, to equal-molar amounts of $CaCO_3$ and $MgCO_3$, dolomite. They persist in soils only with pH above approximately 7.0. Sulfates commonly occur as $CaSO_4$.[37] Pyrite FeS_2, frequently associated with shales and coal seams, may form in soils under reducing conditions.[7]

Table 2 lists naturally occurring crystalline hydroxides, oxyhydroxides and oxides of Fe, Al, Mn, Ti, and Si. These can be identified by analytical techniques such as X-ray diffraction. Iron oxides are found in most soils and are responsible for the red, orange, yellow and brown colours that are widely used to distinguish soils and soil horizons.[38]

2.3.2 Clays

Clay minerals consist of sheetlike crystalline minerals as well as silica and amorphous minerals. Because of their sheetlike structure, clays provide the majority of the particle surface area found in soil. Clays are made up of layers of Si tetrahedra and Al octahedra in either a 1:1 or 2:1 arrangement. The 1:1 arrangement has one octahedral and one tetrahedral layer. The 2:1 arrangement has a tetrahedral layer on each side of an octahedral layer, which is sandwiched in the middle (Fig. 2).[7]

In clay minerals, Al^{3+} (ionic radius 50-57 pm) can proxy for Si^{4+} (39-41 pm) in the tetrahedral layer. The octahedral layer can also have Mg^{2+} (65-78 pm), Fe^{2+}(75-83 pm), Zn^{2+}(74-83 pm), and Li^+(60-78 pm) proxying for Al^{3+} in the octahedral position (Table 3).[37,38]

TABLE 2. Naturally occurring hydroxides, oxyhydroxides and oxides of Al, Fe, Mn, Ti, and Si; those common in soils are italicized.
Greek letters are used to denote different polymorphs of the same chemical constitution. The γ-forms have structures based on cubic close packing of anions, whereas the α-forms are based on hexagonally close-packed anions.[38]

Mineral name	Formula
IRON	
Goethite	α-FeOOH
Lepidocrocite	γ-FeOOH
Akaganeite	β-FeOOH
Hematite	α-Fe_2O_3
Ilmenite	$FeTiO_3$
Maghemite	γ-Fe_2O_3
Magnetite	Fe_3O_4
Ferrihydrite	$Fe_5HO_8 \bullet 4H_2O$
ALUMINIUM	
Diaspore	α-AlOOH
Boehmite	γ-AlOOH
Corundum	α-Al_2O_3
Gibbsite	$Al(OH)_3$
Nordstrandite	$Al(OH)_3$
Bayerite	$Al(OH)_3$
MANGANESE	
Pyrolusite	
Birnessite	
Lithiophorite	
Hollandite	
Todorokite	
SILICON	
Quartz	SiO_2
Cristobalite	SiO_2
Tridymite	SiO_2
Opaline silica	SiO_2
TITANIUM	
Rutile	
Brookite	
Anatase	

In some clays, sheets are bonded together so that they do not swell; for example, potassium bonds clay sheets of illite together. The potassium ion is similar in size (ionic radius 133 pm)[38] to the natural cavity that exists in the surface of the tetrahedral layer. Vermiculite has a layer of hydrated magnesium ions between the clay sheets, permitting only limited swelling of this species as well. Nonexpanding minerals exhibit only an external surface, but expanding minerals have both an internal and external surface.

Soil clays are usually less well-ordered and smaller in size than the pure minerals and often overlap neighbouring particles or sheets. Interleafings and interstratifications of various layer silicates are common, and the mineralogy of soil clays is rarely simple or uniform.[7]

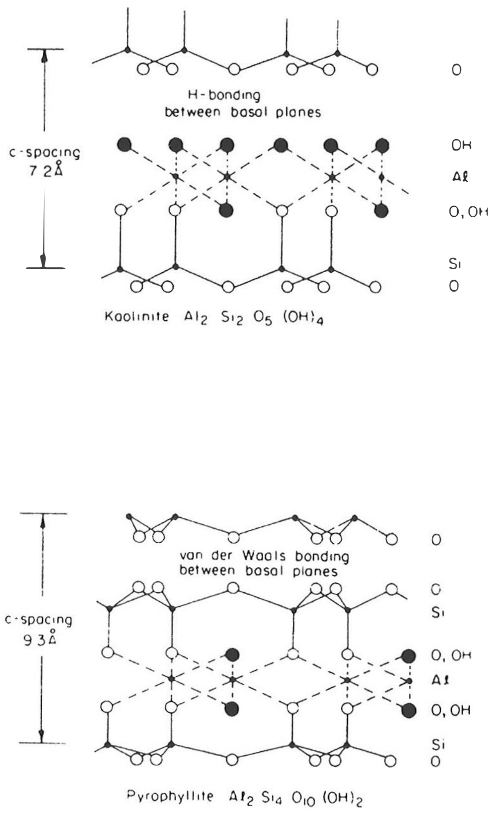


FIGURE 2. Structure of a 1:1 and 2:1 clay mineral.[7]

TABLE 3. Structure of common clay minerals [7,26,37,39-42]

CEC = cation exchange capacity.

Clay	Dominant Isomorphous Substitution	Additional Substitution	Surface Area $m^2\ g^{-1}$	CEC me per 100 g
1:1 Structure				
*Kaolinite $Al_4(OH)_8(Si_4O_{10})$	none	none	7-30	1-15
*Halloysite $Al_4(OH)_8(Si_4O_{10})$	none	none	30	1-15
2:1 Structure (swelling)				
*Pyrophyllite $Al_2(OH)_2(Si_4O_{10})$	none	none	?	1-15
*Montmorillonite $Al_2(OH)_2(Si_4O_{10})\bullet xH_2O$	Mg for Al	Al for Si, Fe for Al	600-800	80-150
*Beidellite $Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	Al for Si	?	?	70-100
2:1 Structure (limited swelling)				
*Vermiculite $Mg_3(OH)_2Si_4O_{10}\bullet xH_2O$	Al for Si	Hydrated Mg between layers	600-800	140-200
2:1 Structure (nonswelling)				
*Illite $K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	Al for Si	Mg for Al	65-100	40-70
*Chlorite $Mg_5Al(OH)_8(AlSi_3O_{10})$	Al for Si	Brucite sheets between layers	70-150	30-40

2.3.3 Amorphous soil minerals

Many soils contain minerals that do not have a definite crystal structure. Hence, these minerals are described according to their chemical composition and the reactivity, including solubility, of their surfaces. Small amounts of amorphous minerals may be found in most soils, often as coatings on crystalline minerals, and thus the significance of amorphous soil minerals can be greater than suggested by the fractional amount present.[37] Noncrystalline clay-sized minerals in the soil include Al and Fe oxides and hydroxides as well as allophane. Some of these minerals are also present in crystalline form. Ferrihydrite, amorphous ferric hydroxide, consists of spherical particles, 10-20 nm diameter, with a large surface area (100-300 $m^2\ g^{-1}$). Amorphous Al hydroxide is unstable and crystallizes to pseudoboehmite and bayerite.[43] Allophane, a hydrous aluminosilicate, is a dominant mineral in soils developed from volcanic material. Allophanes may also be formed, for example, from basic igneous rocks by intense tropical weathering or from acid rocks by podsolization.[38] Allophane particles are probably spherical, with a diameter of about 5 nm and a structure consisting of a glass-like aluminosilicate core with an outer surface of aluminium surrounded by an octahedral arrangement of water and OH^- ions.[43] Allophane was long-considered to be synonymous with amorphous, clay-sized aluminosilicates in soils and sediments. More recently, attempts have been made to restrict the definition to noncrystalline materials that typically have a SiO_2/Al_2O_3 molar ratio between 1.0 and 2.0.[44]

Imogolite always occurs more or less intimately associated with allophane. It has a tubular structure with ten unit cells forming a ring. The imogolite structure has an empirical unit formula of $(HO)_3Al_2O_3SiOH$, with two formula units occurring in each unit cell. The formula may also be written as $SiO_2{\bullet}Al_2O_3{\bullet}2H_2O$.[38]

2.4 Organic matter

Soils contain organic matter in amounts varying from 0.1% in desert soils to over 50% (w/w) in Histisols (organic soils). Classification of soils according to the content of organic matter is given in Table 4.[45] The chemical composition of organic matter is approximately 50 % C, 5 % N, 0.5 % P, 0.5 % S, 39 % O, and 5 % H (w/w), but these values can fluctuate from soil to soil. The organic matter is amorphous, varies widely in composition, and can be divided into nonhumic and humic substances. The nonhumic consists of carbohydrates, proteins, amino acids, fats, waxes, alkanes, and low-molecular-weight organic acids, and are attacked readily by microorganisms. Humic substances decompose slowly. The main functional groups in humic matter are carboxyl, phenolic hydroxyl, alcoholic hydroxyl, and carbonyls. The carboxyl and some of the phenolic hydroxyls provide sites for cation exchange. In addition to the adsorption of cations in a readily exchangeable form, organic matter can adsorb multivalent cations as coordination complexes, thus making them insoluble and poorly exchangeable. Organic matter present in soil solution may also form coordination complexes with metal cations.[37]

TABLE 4. Classification of soils according to the organic matter content.[45]

Content of Organic Matter in the Soil	Humus Content
< 3	low
3-5.9	medium
6-11.9	rich
12-19.9	very rich
20-40	mould
> 40	peat soil

2.5 Soil solution

The formation of horizons in soil profiles results principally from the mass flow of water. Diffusion is the main process for the movement of gases into and out of the soil. Mass flow and diffusion may act in opposite directions. The rate of movement of salts through soil under irrigation or rainfall depends on the rate of the water flow, and is generally faster than the movement due to diffusion. In unstirred liquids, diffusion is caused by the random thermal motion of the molecules and ions of the solvent and solutes. As a result of this motion, which occurs in all directions, any irregularities in the concentration of a solution or a mixture of gases eventually disappear.[46]

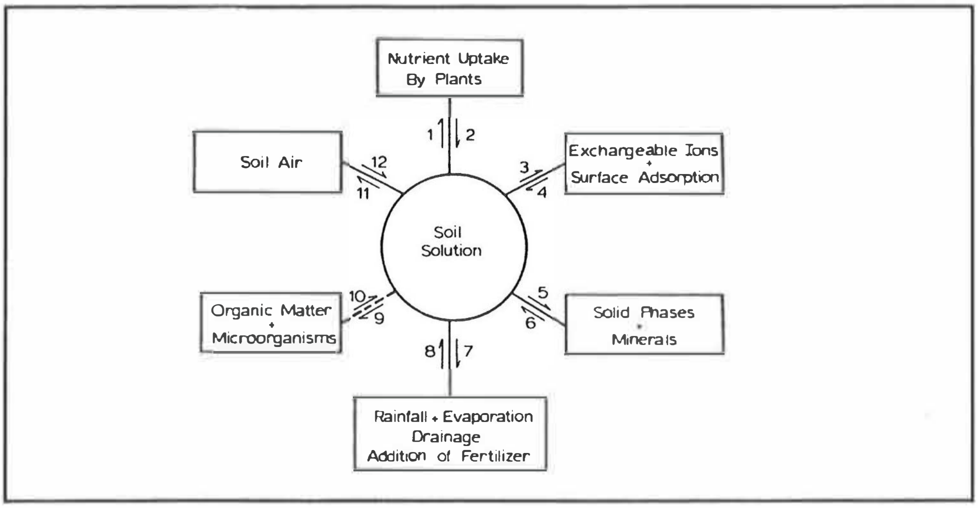


FIGURE 3. The dynamic equilibria that occur in soils.[40]

Plants absorb nutrients from the soil solution, the thin aqueous film surrounding soil particles. (Figure 3, Reaction 1). Small quantities of plant constituents may also be released back into the soil solution (Reaction 2). Ions in the soil solution are buffered by those adsorbed onto soil surfaces or held by exchange sites (Reactions 3 and 4). If the soil solution becomes supersaturated with respect to any mineral, that mineral can precipitate (Reaction 5) until equilibrium is attained. Similarly, if the soil solution becomes undersaturated with respect to any mineral present in the soil, that mineral can dissolve until equilibrium is attained (Reaction 6). Rainfall adds water that dilutes the soil solution (Reaction 8). Excess water may drain from the soil profile and carry with it salts and other dissolved constituents (Reaction 7). Fertilizers of various kinds are frequently added to soils. These may dissolve (Reaction 8), form new reaction products (Reaction 5), or be distributed in other ways in soil. Living organisms remove constituents from the soil solution and incorporate them into their body tissues (Reaction 9). Nutrients are released during the decomposition of organic matter or upon the death of organisms (Reaction 10). True equilibrium relationships are generally not achieved in reactions 9 and 10. Gases in the soil air also tend to attain equilibrium with the soil solution. Gases may either be released to the soil air (Reaction 11) or dissolved in the soil solution (reaction 12). In soils, plants and microorganisms generally utilize O_2 as an electron acceptor and release CO_2 from metabolic processes. Diffusion gradients are established between the gas phase in the finer pore spaces of the soils and the atmosphere above. In waterlogged soils the exchange of $CO_2(g)$ and $O_2(g)$ is greatly restricted because diffusion rates in water are approximately 10^{-4} those in air. As O_2 in the soil is depleted, reduction takes place in the soil. Even in unsaturated soils, there are often zones of fine-textured materials where reducing conditions may prevail.[40]

2.6 The charge of soil

The permanent charge of soil results from the negative charge because of isomorphous substitution either in the tetrahedral or octahedral sheet of the clay mineral. The positive charge developed at low pH and the excess negative charge developed at high pH are collectively known as pH-dependent charge.[7]

The zero point of the charge is the pH at which the net surface charge from all sources is zero.[47]

The primary source of the pH-dependent charge is considered to be the gain or loss of H^+ from functional groups on the surfaces of soil solids. The soil solids containing functional groups capable of developing a pH-dependent charge are layer silicates, oxides and hydrous oxides, including allophane, and organic matter. Most soils have a net negative charge because of the negative charges on layer silicates and organic matter, but some highly weathered soils dominated by allophane and hydrous oxides may actually have a net positive charge at low pH. Variations in the pH-dependent charge of layer silicates are more likely associated with reversible protonation and deprotonation of exposed Al(OH) groups. Only 5 to 10 % of the negative charge on 2:1 layer silicates is pH-dependent, whereas 50 % or more of the charge developed on 1:1 minerals can be pH-dependent. Organic material and the Fe, Al, Ti, and Mn oxide minerals possess no permanent charge.[7] Because soils containing large amounts of Fe and Al oxides have a strongly pH-dependent charge and highly variable cation exchange capacity values, their cation exchange capacity must be measured at a particular soil pH, usually 7.0 or 8.0. Measurements at pH 8.0 and 3.0 can be used to separate the cation-exchange capacity into that due to the pH-dependent charge and that due to the permanent charge.[37] Exchangeable cations are loosely defined as those removed by neutral salt solutions. Soluble cations and salts are removed by water alone.[7]

2.7 The soil/root interface

The tip of, for example, a young wheat root may be around 10 μm in diameter. The largest pores containing water in soil which has drained after rain, i.e. which is at field capacity, are about 20-50 μm in diameter. The young root is normally covered by a layer of mucilaginous material containing much pectin. The mucigel is a true gel, allowing water and ions to pass rather freely.[48]

At the root/soil interface water, nutrient ions, and oxygen must move into the root, and CO_2 must move out. The absorption of nutrient cations and anions is normally an exchange for hydroxonium and HCO_3^- ions respectively, as most nutrient absorption is 'active', although some occurs as the 'passive' entry of an anion and cation in the inward flow of the soil solution. In soil solution the nutrient concentration is often of the order 10^{-3} M, and in the plant sap they range up to 10^{-1} M.[48] The contact area between the active parts of plant roots and the surface of soil particles, and along with that the contact with soil solution is very limited, not exceeding a few percent of the total soil surface. The nutrient uptake, therefore, induces diffusion processes.[49] Absorption of nutrients is presented in detail in ref. 37.

2.8. Molybdenum, vanadium and tungsten in soils and plants

Molybdenum occurs in soils in the following forms: 1) water-soluble, present in the soil solution, 2) adsorbed by soil colloids, 3) held in the crystal lattice of minerals, and 4) present in organic matter.[50,51] The most common Mo mineral is MoS_2 (molybdenite). Occasionally MoO_3 (molybdite) and Mo_3O_8 (ilsemannite) are found as alteration products of MoS_2. The more familiar secondary molybdate minerals are $CaMoO_4$ (powellite), $PbMoO_4$ (wulfenite), and $Fe_2(MoO_4)_3 \bullet nH_2O$ (ferrimolybdite). Of less importance are $Cu_3(MoO_4)_2(OH)_2$ (lindgrenite), $H_6CaFe(PO_4)(MoO_4)_4 \bullet 6H_2O$ (melkovite), $CaFe_2(As_2Mo_5O_{24}) \bullet 14H_2O$ (betpakdalite), and possibly $CoMoO_4 \bullet nH_2O$ (pateraite).[52] Microorganisms are important in liberating Mo from its mineral hosts.[53] The precipitation of common Mo minerals in soils appears to be limited only to severely contaminated soils. In the absence of Pb minerals controlling the Pb^{2+} solubility in soils, the solubility of Mo can be raised until powellite or ferrimolybdite starts to precipitate. Since Ca and Fe are abundantly present in soils, the solubilities of $CaMoO_4$ and $Fe_2(MoO_4) \bullet nH_2O$ provide natural upper limits for the Mo solubility in soils.[52] The range of total Mo content in Finnish unfertilized till, for example, is 0.7-1.8 $\mu g\ g^{-1}$.[54]

Plants need C, H, O, N, P, K, Ca, Mg, and S as major nutrients, and at least Fe, Mn, Cu, Zn, Mo, B, and Cl as micronutrients. Sodium, Si and Co are beneficial to some plants. Selenium is essential to animals and humans.[55] In 1930 Bortels[56] recognized the biological importance of Mo and showed that Mo was beneficial in N_2 fixation by *Azotobacter Croococcum*. In 1939 Arnon and Stout[57] noticed that deficiency symptoms in tomatoes could be controlled by the addition of Mo in the nutrient solution. Mo is a component of at least five distinct enzymes, namely nitrogenase, nitrate reductase, xanthine oxidase, aldehyde oxidase, and sulfite oxidase that catalyze diverse and unrelated reactions. Nitrate reductase, nitrogenase, and sulfite oxidase are found in plants. Nitrate reductase reduces NO_3^- to NO_2^-.[58] It is found in most plant species as well as in fungi and bacteria.[51]

Nitrogenase is an enzyme complex composed of two distinct components that combine to reduce N_2 to NH_3, or acetylene to ethylene. Nitrogenases have been isolated from a variety of different sources, e.g. *Azotobacter vinelandii* and *Azotobacter chroococcum*.[51,59]

Molybdenum is readily translocated in plants, and its deficiency symptoms generally appear on the whole plant. Symptoms include a general yellowing and stunting of the plant,[50,51] and interveinal mottling and cupping of the older leaves followed by necrotic spots at leaf tips and margins.[51,60] Today, the Mo-deficiency symptoms of more than 40 higher plants have been identified. [61]

The annual Mo need in agricultural soils is 150 g - 1 kg per hectare. Fertilizers usually contain Mo as $Na_2MoO_4 \cdot 2H_2O$ or $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. Soil, seed and foliar applications are possible.[36,45,51,62] Agricultural soils should contain 0.06-0.2 mg dm^{-3} of plant-available Mo.[45]

Poorly drained soils accumulate so much available MoO_4^{2-} that the plants grown on them prove toxic to animals. The Mo supplied by root interception (i.e. Mo intercepted by the growth of the root through the soil)[37] and diffusion is influenced by the level of available Mo in the soil, whereas the Mo moved to the root by mass-flow is related to the level of Mo in the water that moves to the root.[63-65] General symptoms of Mo toxicity on cultivars are yellowing or browning of leaves, depressed root growth and depressed tillering. Cereals are sensitive crops.[26] Application of P increases Mo absorption by plants, whereas S reduces Mo uptake.[26,51] Mo-Mn antagonism resulting from soil acidity influences the availability of these elements. Liming can correct both

Mo deficiency and Mn toxicity. Mo-Fe interactions in Fe-rich soils can induce Fe deficiency, or accentuate Mn-induced Fe chlorosis.[26,66,67]

Under naturally occurring conditions, a true Mo deficiency has never been reported in man or farm animals. High levels of Mo in forages can induce Cu deficiencies in animals.[51,68] This disorder, referred to as molybdenosis, teart disease or peat scours, occasionally results in death. Severe molybdenosis in cattle may occur under natural grazing conditions, whereas horses and pigs are much less likely to contract the disease. The dietary concentration of Mo required to produce Mo toxicity varies according to the Cu and the SO_4^{2-} concentration and the Mo/Cu/SO_4^{2-} ratio in the diet. Mo toxicity symptoms can be corrected by Cu supplementation.[69]

The average V content of soils worldwide is 90 $\mu g\ g^{-1}$. Fine soil fractions may contain large amounts of V, exceeding that of the parent material.[26] Patronite (a complex sulfide), carnotite $K(UO_2)VO_4 \bullet 3/2H_2O$, vanadinite $Pb_5(VO_4)_3Cl$, colusite, montroseite, and roscoelite are the most common of the about 60 known vanadium-bearing minerals.[70,71] In Finnish till, the HNO_3-soluble V concentration ranges between 15 and 70 $\mu g\ g^{-1}$.[54]

The necessity and possible toxicity of V to plants is briefly reviewed in Paper **4**. In animals V, no matter how administered, is unquestionably poisonous in all but small doses.[70,72] Certain invertebrates are, however, able to accumulate vanadium in their blood without poisoning symptoms.[39]

Concentrations of W usually found in rocks range from 0.10 to 2 $\mu g\ g^{-1}$, but concentrations as high as 211-1480 $\mu g\ g^{-1}$ around a W deposit in Britain have been reported.[26,73] In Finnish till the W content is 0.6-2.2 $\mu g\ g^{-1}$.[54] Tungsten is found almost exclusively in the form of tungstates, the main ones being wolframite (solid solution and/or mixture of the isomorphous substances $FeWO_4$ and $MnWO_4$), scheelite $CaWO_4$, and stolzite $PbWO_4$.[71] $MnWO_4$ is called hübnerite, and $FeWO_4$ ferberite.[74]

The geochemical behaviour of W plus its essentiality and toxicity to plants is discussed in Paper **3**. Tungsten probably does not constitute an important environmental hazard to animals and man.[75]

Industrial processing of certain mineral ores (ore smelters, cement, and phosphate rock plants) increase the deposition of V residues in soils. Combustion of fossil fuels is a serious source of contaminating soils with V.[76,77] Crude oils especially from Venezuela and Canada contain vanadium.[39] Processes that run the risk of contaminating ecosystems with W are purification of ores for industrial use and application of sewage sludge on agricultural land.[26] In sewage sludge samples from different wastewater-treatment plants in Iowa, for example, the concentrations of W varied from 0.5 to 62 mg kg^{-1}.[78] The range of Mo concentration in sewage sludges from the United States and Canada is reported to be 2-1000 ppm.[79] Vanadium concentrations in sewage sludge ash is reported at 55-105 ppm in USA.[80] In Finland, concentration of V, Mo and W in sewage sludges seems to be low, because problems with hazardous wastes have not been reported.[81]

3. AQUEOUS CHEMISTRY OF Mo(VI), V(V), AND W(VI)

3.1 General

In aqueous solutions, vanadates, molybdates, tungstates, and, to a smaller extent, niobates, tantalates, and chromates, undergo complex hydrolysis-polymerization reactions upon acidification. The major solute species generated by such reactions, the so-called isopolyanions, may be represented by the general formulas $M_qO_y^-$, and their formation can be expressed by the equation

$$p\ H^+ + q\ MO_4^{r-} = [H_xM_qO_y]^{n-} + (4q\text{-}y)\ H_2O, \qquad (2)$$

where $p = 8q\text{-}2y+x$.[25,82]

In the presence of other ions, it is also possible that heteropolyanions $X_iM_rO_y^{z-}$ ($i \leq r$) are formed, where M is Mo, V or W, less frequently Nb or Ta, or mixtures of these elements, in their highest (d^0, d^1) oxidation states.[25]

In the polymerization of vanadate, molybdate and tungstate, the coordination number of the metal increases from four to six. There are two essential requirements an atom has to fulfill in order to be able to form discrete isopoly or heteropolyoxoanions: the octahedral cationic radius has to be 65-80 pm, and the atom must have ability to act as a good acceptor of oxygen pπ-electrons. No such restrictions are placed on the heteroatom, and more than 65 elements from all groups of the Periodic Table except rare gases can act as heteroatoms.[25] Little is known about the polyanion chemistry of chromium(VI), it seems, because of the smaller size of Cr^{6+} (58 pm) relative to V^{5+}(68 pm), Mo^{6+}(73 pm), and W^{6+}(74 pm), which leads to a maximum oxygen coordination of four.[83] A few isopoly and heteropoly chromates, e.g. $Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$ are known, but they are all based on corner-shared CrO_4 tetrahedra. The solution chemistry of these species is limited or nonexistent as they readily undergo hydrolysis to CrO_4^{2-} and $HCrO_4^-$.[25]

Most polymolybdates and polytungstates contain octahedrally coordinated Mo^{6+} and W^{6+} but with the metal atoms displaced from the centers of the octahedra towards a corner or an edge. The short M-O bonds are directed towards the exterior of the polyanion, forming a layer of surface oxygens which are strongly polarized towards the interior of the anion by $p\pi$-$d\pi$ interactions. Such terminal (non-bridging) oxygen atoms are essentially non-basic and discourage extensive protonation and further polymerization of the polyanion.[25,84,85]

X-ray crystallography has played a major role in elucidating the solid state chemistry of polyoxometalates. In the identification and structural characterization of species in solution, more than one complex may be present, and complexes may undergo rapid or slow exchange or exhibit fluxional behaviour. The solute species may bear no structural relationship to those crystallized from solutions. The most widely used experimental methods for the characterization of polyoxometalate solutions are equilibrium analysis (EMF methods), polarography and voltammetry, salt cryoscopy, diffusion and dialysis, ultracentrifugation, X-ray scattering, electronic spectroscopy, vibrational spectroscopy, nuclear magnetic resonance, and electron spin resonance.[25]

The equilibria between polyanions and mononuclear species in Mo(VI) solutions can be obtained in some minutes, but the reactions between polyionic and monoionic species in V(V) and W(VI) solutions may be slow.[39] However, Souchay et al.[86] report that, in W(VI) solutions, condensation into polyanions occurs very quickly (completed after 10^{-2} sec. in 10^{-4} M solutions).

The literature on the aqueous chemistry of Mo(VI) is voluminous. Not so many studies on equilibria in aqueous V(V) and W(VI) solutions exist. In the next sections, a general review is given on aqueous Mo(VI), V(V), and W(VI) species. References 23, 25, and 31-33 are recommended for finding protonation constants. Structures of selected aqueous isopolyanions are presented, for example, in refs. 39 and 71.

3.2 Aqueous Mo(VI) species

In addition to the MoO_4^{2-} ion, the existence of $HMoO_3^+$, $H_2Mo_2O_6^{2+}$, $H_3Mo_2O_6^{3+}$, $H_2MoO_3^{2+}$, $Mo(OH)_5(H_2O)^+$, $Mo(OH)_4(H_2O)_2^{2+}$, $Mo_2O(OH)_9H_2O^+$, $Mo_2O(OH)_8$-$(H_2O)_2^{2+}$, $Mo_2O(OH)_7(H_2O)^{3+}$, MoO_3, H_2MoO_4, $HMoO_4^-$, $HMo_2O_8^{3-}$, $HMo_2O_7^-$, $[Mo_4O_{10}(OH)_6]^{2-}$, $Mo_4O_{14}^{4-}$, $Mo_6O_{20}^{4-}$, $Mo_6O_{21}^{6-}$ and its protonated forms, $Mo_7O_{24}^{6-}$ and its protonated forms, $Mo_8O_{26}^{4-}$, $Mo_8O_{27}^{6-}$ and its protonated forms, $Mo_{10}O_{34}^{8-}$, $H_6Mo_{12}O_{44}^{10-}$ and its protonated forms, $[Mo_{18}O_{56}(H_2O)_{10}]^{4-}$, as well as $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ in aqueous solutions has been suggested.[87-113]

The determining factors in the distribution of ionic species (Fig. 4) are Mo concentration, pH, ionic medium, and temperature. In solutions of high ionic strength, polyions are formed more reluctantly than in dilute salt solutions.[22,110 p. 76] The vast literature on molybdates has been covered in a recent review.[114]

The formula of molybdic acid, H_2MoO_4, is usually written as $Mo(OH)_6$ for convenience to indicate six coordination. From the structural point of view, the formula $MoO_3(H_2O)_3$ seems more likely.[31,109] An increase in the coordination number of Mo(VI) takes place in the second protonation step of the MoO_4^{2-} ion.[104] For brevity, a species with an overall formation constant β_{pq} is denoted by the stoichiometric coefficients defining its composition, for example (1,1) and (8,7) for $HMoO_4^-$ and $Mo_7O_{24}^{6-}$, respectively.

3.3. Aqueous V(V) species

A distribution diagram for aqueous ionic V(V) species is presented in Figure 5. In addition to these species, the existence of $V_4O_{13}^{6-}$, $V_3O_9^{3-}$, $HV_6O_{17}^{3-}$, $V_6O_{17}^{4-}$, $V_5O_{16}^{7-}$, $V_6O_{18}^{6-}$, and $H_{12}V_{13}O_{40}^{3-}$ has been reported.[115-119] Today, one interesting point of view is that a Swedish research group[120,121] found no indication of an uncharged H_3VO_4

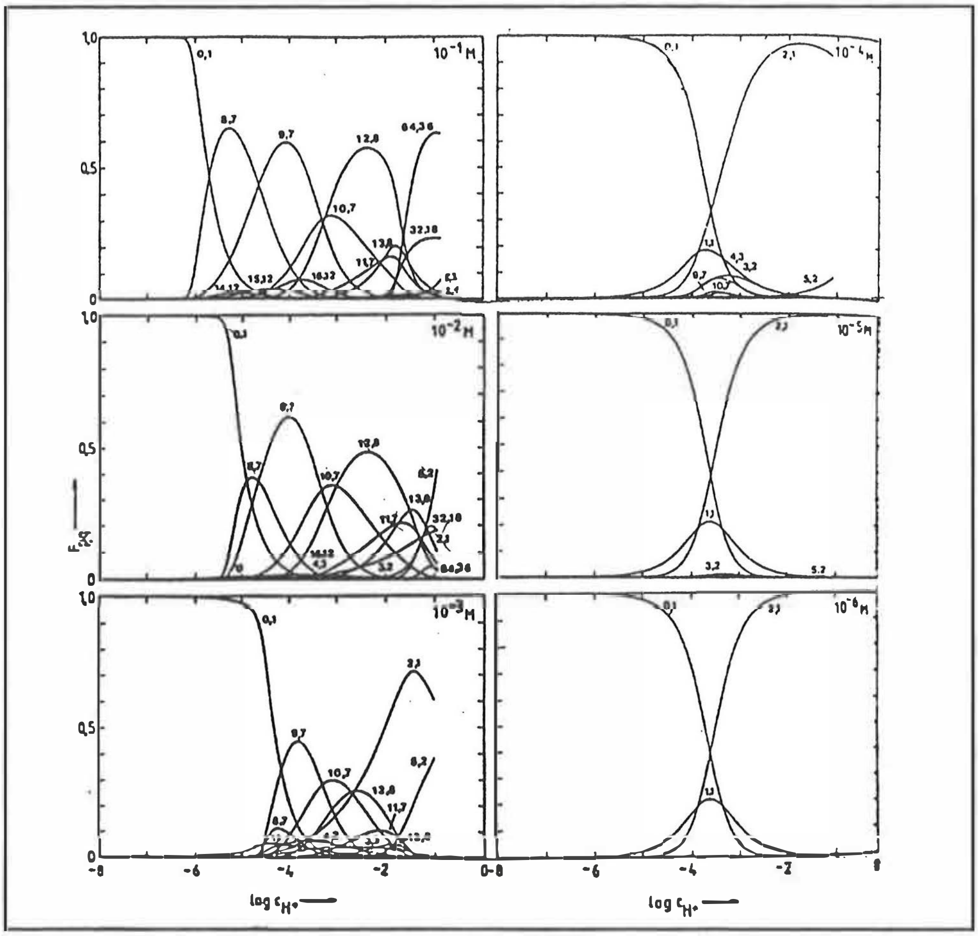


FIGURE 4. An example of the distribution of Mo(VI) species in 1.0 M NaCl, 25 °C.[110 p.142]

monomer at a vanadium concentration of 0.3 mM either in 0.6 M NaCl or in 3 M $NaClO_4$. In addition, a recent report[122] suggests that in an aqueous solution, the vanadate ion has the five-coordinate structure $H_4O_5^-$. These two aspects need to be carefully considered in the near future.

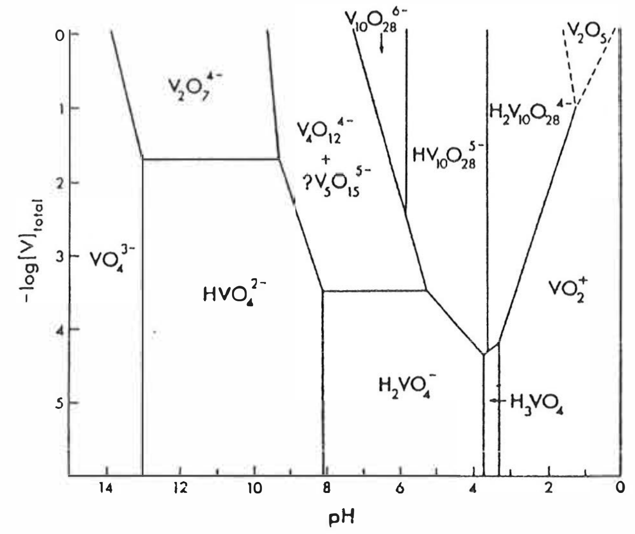


FIGURE 5. Distribution of aqueous V(V) ionic species. [25]

3.4 Aqueous W(VI) species

Early studies on tungsten(VI) equilibria in aqueous solutions are reviewed in references 25, 33 and 86. An analysis of aqueous polytungstate equilibria is complicated by the extreme range of rates observed (Fig. 6). Some apparently stable isopolytungstates may in fact be kinetic intermediates. On acidification, paratungstate B loses one W atom to give an anion with no symmetry, which is identified as the solution form of ψ-metatungstate. This in turn is protonated, before transmuting to the known species tungstate-Y.[25,35] In addition to these species, the presence of $W_6O_{20}(OH)_2^{6-}$ and the protonated form $HW_7O_{24}^{5-}$ of paratungstate A have been reported.[33] W(VI) equilibria in dilute W solutions ($< 10^{-3}$ mol l^{-1}) and in concentrated W(VI) solutions with low ionic strength are still unknown.

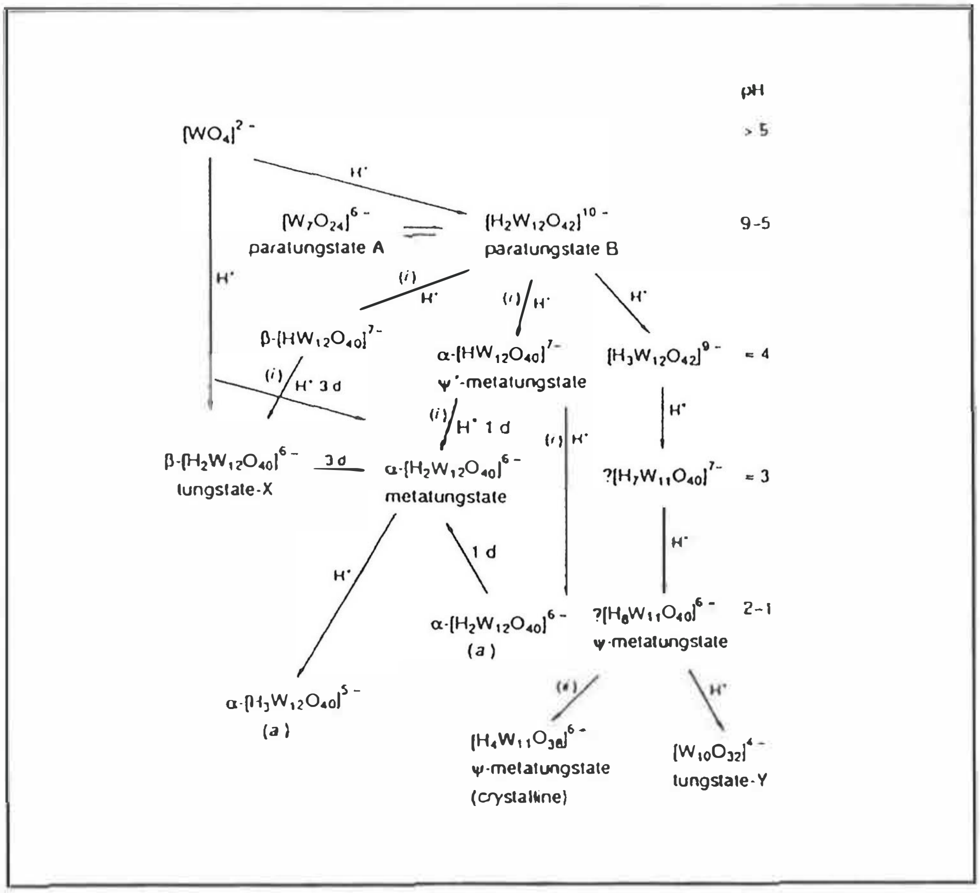


FIGURE 6. Scheme for relationships between aqueous W(VI) ionic species.[35]

3.5 Heteropolyanions

Today, NMR techniques (^{17}O, ^{95}Mo, ^{51}V, ^{183}W, ^{31}P, etc.) are frequently used in identifying both isopoly and heteropoly species present in aqueous solutions. Because of the low natural abundance (0.04 %) of ^{17}O, the use of ^{17}O NMR without isotopic enrichment is restricted to rather concentrated solutions. ^{51}V NMR is suitable for measurements in dilute (10^{-5} M) solutions also.

Heteropolyanions are a subject of intensive study among NMR chemists. Table 5 gives examples of some heteropolyanions of vanadium present in aqueous solutions.

From the point of view of the present work, it is helpful to be familiar with some other heteropolyanions also. In mixtures containing molybdate and phosphate, with $pH \geq 5.5$ or $Mo/P < 2.5$, a series of pentamolybdodiphosphate complexes, e.g., $(H^+)_p(MoO_4^{2-})_5$-$(HPO_4^{2-})_2$, $p = 8,9,10$ are formed. For $Mo/P \geq 4$ and $pH \approx 4.3$, two molybdophosphates with different Mo/P quotients are formed, the dominating species being that with the higher Mo/P ratio.[113,123] The existence of $Mo_6W_6O_{41}^{10-}$, $Mo_3W_{15}O_{60}H_3^{9-}$ and $H_2MoW_{11}O_{40}^{6-}$ has also been reported but needs confirmation.[25,124]

Great progress can be expected in the field of aqueous heteropolyanions within the next few years.

TABLE 5. Some aqueous heteropolyanions of V(V).
(*) Concentrations; ionic medium; temperature; pH; analysis methods.

Reference	**Reported Species**	**Analytical Conditions(*)**
125	$VMo_5O_{19}^{3-}$, $V_2Mo_4O_{19}^{4-}$, $HV_2Mo_4O_{19}^{3-}$, $V_9MoO_{28}^{5-}$, $HV_9MoO_{28}^{4-}$, $V_xMo_{13-x}O_{40}^{-x-3}$ x–2-3, $V_2Mo_6O_{26}^{6-}$	[V]=0.4-100 mM, V/Mo=3:1-1:6 H_2O, 20 °C, pH 2-7, ^{51}V NMR, ^{17}O NMR, ^{95}Mo NMR
126	$MoV_9O_{28}^{5-}$, $Mo_2V_8O_{28}^{4-}$	[V]=10-1000 mM, [Mo]=5-50 mM 0.6 M NaCl, 20 °C, 99 °C, pH 1-7, potentiometry, ^{51}V NMR, ^{17}O NMR, ^{95}Mo NMR
127	cis-$Mo_4V_2O_{19}^{4-}$, cis-$HMo_4V_2O_{19}^{3-}$, $Mo_5VO_{19}^{3-}$, $Mo_4V_5O_{27}^{5-}$, $HMo_4V_5O_{27}^{4}$, β-$Mo_7VO_{26}^{5-}$, α-$HMo_7VO_{26}^{4-}$, α-$HMo_6V_2O_{26}^{5-}$, $Mo_4VO_{17}^{5-}$, $HMo_8V_2O_{32}^{5-}$, $MoV_9O_{28}^{5-}$, $HMoV_9O_{28}^{4-}$, $Mo_2V_8O_{28}^{4-}$, $HMo_{10}V_2O_{38}^{5-}$, $Mo_9V_3O_{38}^{7-}$, $HMo_9V_3O_{38}^{6-}$, $HMo_9VO_{32}^{4-}$, $HMo_8V_2O_{32}^{5-}$, β-$H_2Mo_6V_2O_{26}^{4-}$, $VMo_{10}V_2O_{40}^{5-}$	[V]=10-100 mM [Mo]=40-1000mM 0.6 M NaCl, 25 °C, pH 1.4-7, potentiometry, ^{51}V NMR, ^{17}O NMR
128	$HPV_{14}O_{42}^{8-}$	[$Na_8HPV_{14}O_{42}$•$9H_2O$] = 1-60 mM 2 M $NaClO_4$, 25 °C, pH 2-7, ^{31}P NMR, ^{51}V NMR
129,130	$W_5VO_{19}^{3-}$, cis-$W_4V_2O_{19}^{4-}$, $HW_4V_2O_{19}^{3-}$, fac-$W_3V_3O_{19}^{5-}$ $VW_{10}V_2O_{40}^{5-}$	[V]=10-20 mM H_2O, 30 °C, pH 2.5-8.5, ^{51}V NMR
130	$WV_9O_{28}^{5-}$, mer-$W_3V_3O_{19}^{5-}$	[V]=50 and 80 mM, [W]=20 and 50 mM H_2O, 99 °C, pH 4.97, 6.51 ^{51}V NMR

4. ANION AND MOLECULAR RETENTION

The anion and molecular retention capacity of most agricultural soils is much smaller than the cation retention capacity. Common soil anions include nitrate (NO_3^-), orthophosphate ($H_2PO_4^-/HPO_4^{2-}$), sulphate (SO_4^{2-}), carbonate (HCO_3^-/CO_3^{2-}), chloride (Cl^-), selenite (SeO_3^{2-}), molybdate (MoO_4^{2-}), polyphosphates, and anions of organic acids. Some harmful metals may exist as anions, too (e.g. CrO_4^{2-} and $HAsO_4^{2-}$). Boron and silicon exist and probably are taken up by plants as undissociated acids H_3BO_3 and $Si(OH)_4$. Borax $Na_2B_4O_7 \bullet 10H_2O$ from fertilizers dissociates to monomers in dilute solutions.[7,37,131]

4.1 Nonspecific anion reactions

Nonspecifically adsorbed anions are only retained electrostatically. Soils contain a variety of solids which develop both negative and positive charges. An anion approaching a charged surface is subject to either attraction by positively charged sites on the surface or repulsion by negative charges.[7]

The anions Cl^-, NO_3^-, SO_4^{2-}, ClO_4^- and probably Br^- are generally considered to be nonspecifically adsorbed, though only the first three of these are of usual concern. Sulphate can be regarded as both a specifically and nonspecifically adsorbed anion.[131]

The mechanism of nonspecific adsorption can be expressed as follows. In an aqueous suspension the terminal metal atoms on the surface of an oxide, for example, complete their coordination shells with OH groups and water molecules. The OH groups and water in the first coordination shell are in the inner Helmholtz plane (i.H.p.) with reference to the metal atoms in the solid. When the ions in solution do not have a specific affinity for the metal atoms on the surface, e.g. $NaNO_3$, the surface will adsorb H^+ and OH^- according to Fig. 7.[9]

The capacity of soils to adsorb anions nonspecifically increases with increasing acidity; this capacity is great in kaolinitic soils, which have a significant pH-dependent charge. Nonspecific anion adsorption occurs only when the surface carries a net positive charge. At all pH values, divalent anions are adsorbed to a greater extent than monovalent anions. For soils containing a considerable pH-dependent charge, nonspecific anion adsorption is negligible at $pH > 7$. Chloride is often used as an indicator of NO_3^- mobility in soils, because it is not subject to the complicated biological reactions characteristic of NO_3^-.[7]

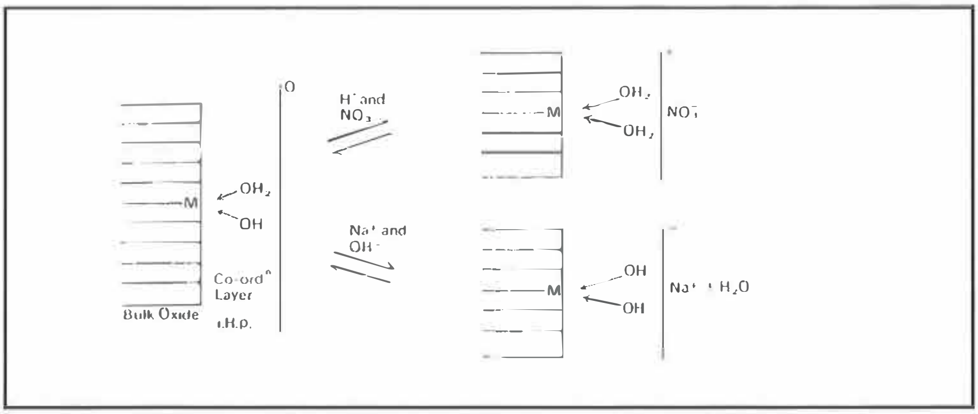


FIGURE 7. Nonspecific anion adsorption.[9]

Ions commonly exhibiting anion repulsion are Cl^-, NO_3^-, and SO_4^{2-}. Anion repulsion is a manifestation of unequal ion distribution in the diffuse double layer surrounding charged colloid surfaces. It increases with anion charge and concentration. Other affecting factors include the changeable cation species, pH, the presence of other anions, and the nature and charge of the colloid surface. In soils with a pH-dependent charge, lowering the pH decreases the net negative charge of the system and anion repulsion. Anion repulsion decreases when anions can be adsorbed by positively charged sites on soil colloids.[7]

4.2 Specific anion reactions

Fe or Al oxide-dominated soils, for example, have an adsorption capacity for some anions that is much greater than predicted from the quantity of adsorbed anions needed to neutralize the surface positive charge alone. The reactive sites for anion adsorption are the singly coordinated Al•OH and Fe•OH groups. The metal ions on the surface layer behave as Lewis acids and exchange the general ligand OH^- against another Lewis base.[132] In soils these groups are present at the edges of clay minerals as well as on the surfaces of hydrous oxides. The two- or three-coordinated OH sites do not usually take part in ligand exchange reactions in pure systems, although they can form hydrogen bonds. The Lewis acid sites $Al{\bullet}OH_2$ and $Fe{\bullet}OH_2$ also occur on the edges of minerals. At low pH, the sites that adsorb protons are probably the one-coordinated Al•OH and Fe•OH groups, which give $Al{\bullet}OH_2^+$ and $Fe{\bullet}OH_2^+$. On some oxides and oxyhydroxides FeO groups may also be exposed at the surface, and they may become protonated ($FeOH^+$) at low pH. In the presence of OH^- ions, a proton may be lost from the $M{\bullet}H_2O$ sites to give $M{\bullet}OH^-$ at the surface.[43]

In imogolite, anion adsorption probably can occur on the external surface as well as on sites at the ends of the tubes, where broken bonds occur. Other sites within the tubes contain Al•OH and Si•OH groups, and it is unlikely that anion adsorption occurs in this region.[133,134]

When specific adsorption of an anion of a fully dissociated acid takes place, an equivalent amount of the nonspecifically adsorbed anion is displaced from the outer Helmholtz plane or the diffuse layer, hence there is no change in the H^+:OH^- ratio and the surface does not develop a net negative charge. Fluoride ion is strongly adsorbed by several soil minerals. F^- adsorption conforms to the ligand exchange theory and is probably favoured because F^- and OH^- ions are very similar in size. In acid soils at equal anion concentrations, F^- adsorption predominates over that of other common anions, and F^- is an effective desorbing agent for previously adsorbed anions. (Fig. 8)[9]

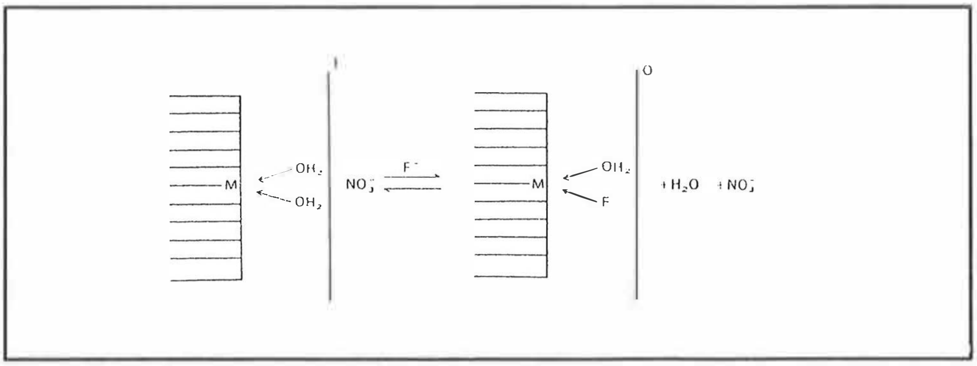


FIGURE 8. Specific adsorption of an anion of a fully dissociated acid.[9]

A species need not be initially charged to be retained by soils. Molecules in the soil solution may be converted to charged species and then be adsorbed as cations or anions, or may remain nonionic and be adsorbed as a consequence of polarity that produces a localized charge within the molecule. Weak acids are a class of nonionic compounds that dissociate in solution to form anions and hydrogen ions. When soil $pH > pK_a$, the weak acid anions are adsorbed.[7] Nonionic molecules that do not protonate or deprotonate to become charged species can still be adsorbed on soil by hydrogen bonding and van der Waals attraction.[7]

The dissociation of the acid during adsorption produces an increase in the H^+:OH^- ratio on the surface due to the reaction of a surface OH^- with an acid proton. Further dissociation of coordinated H_2O may lead to an increase in the negative charge (Cf. Fig. 9).[9]

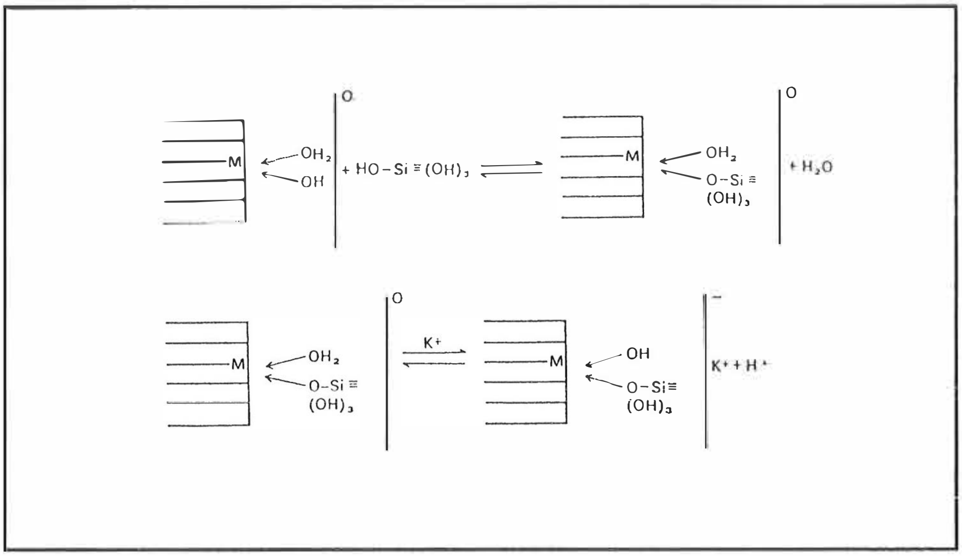


FIGURE 9. Specific adsorption of an anion of an incompletely dissociated acid.[9]

The effect of the ligand exchange is to neutralize positive sites until the surface reaches a new zero point, where no further adsorption of the specifically adsorbed anion takes place. Any change in surface charge as a result of a pH change must be balanced by adsorption or desorption of cations. The general tendency for the adsorption of polyprotic anions to rise as pH is decreased may be associated with proton adsorption, thus providing more sites for anion adsorption. The average charge added to the surface per adsorbed anion, however, is always less than the maximum charge on the anion in solution. The ligand exchange process always leads to the removal of OH^- from the coordination shell (Fig7+8, Fig. 9), while the charging process can lead to the liberation of H^+ from coordinated H_2O (Fig. 9).[9]

4.3 Adsorption isotherms and adsorption envelopes

In an equilibrium situation, more than any other cause, the rate of sorption between the soil solution and the solid phase is much greater than the rate of change in the concentration of solute in the soil solution. In a kinetic situation, an equilibrium sorption isotherm cannot be used because of the fast water flow through soil, for example.[6]

An adsorption isotherm shows the amount of adsorbate (solute) adsorbed by an adsorbent as a function of the equilibrium concentration of the adsorbate.[7] A known amount of adsorbate is added to a system containing a known amount of adsorbent. The amount of adsorbate removed from solution at equilibrium is assumed to be adsorbed. An adsorption envelope gives the relationship between the adsorption plateaux and pH at constant initial concentration in the solution.[9] In measuring both adsorption isotherms and envelopes, equilibrium conditions must prevail and secondary reactions, such as precipitation, must be eliminated or corrected for.[7]

Several models have been developed for explaining adsorption by different adsorbents.[6,132,135-138] The simplest of these is that given by a linear relationship. The isotherm models most often mentioned are the Langmuir[139] and Freundlich[140] equations. Although no adsorption isotherms were used in the present work, some of these models are briefly discussed here, because of their frequent use in anion adsorption experiments.

The Langmuir equation was initially derived for the adsorption of gases by solids. It is based on three assumptions: (1) constant energy of adsorption that is independent of the extent of surface coverage (i.e., a homogenous surface); (2) adsorption on specific sites, with no interaction between adsorbate molecules; and (3) maximum adsorption possible is that of a complete monomolecular layer on all reactive adsorbent surfaces. The Langmuir equation defines a finite limit to adsorption on a given array of sites, which meet the Langmuir model criteria. This capability has been used to estimate the total adsorption capacity of soils for various adsorbates.[7]

The linear form of the Langmuir equation is

$$C/(x/m) = 1/Kb + C/b, \tag{3}$$

where C is the equilibrium concentration of adsorbate in question, x/m is the weight of adsorbate per unit weight of adsorbent, K is a constant related to the binding strength, and b is the maximum amount that can be adsorbed (i.e. a complete monomolecular layer). If adsorption data conform to the Langmuir equation, a plot of $C/x/m$ vs. C yields a straight line with a slope $1/b$ and an intercept $1/Kb$.[7]

The Freundlich equation can be derived theoretically by assuming that the decrease in energy of adsorption with increasing surface coverage is due to surface heterogeneity. It implies that the energy of adsorption decreases logarithmically as the fraction of surface covered increases.

The Freundlich equation is limited in that it does not predict a maximum adsorption capacity.[7] The linear form of the Freundlich equation is

$$\log(x/m) = n^{-1} \log C + \log k, \tag{4}$$

where k and n are empirical constants and the other terms are defined as previously.

One of the newest descriptions for adsorption of anions on surfaces is the model of Barrow,[141] which postulates that there is a reaction between ions in solution and the charged surfaces of the soil particles. The surfaces are assumed to be non-uniform and to differ in their electrical potential. Competition includes both ordinary competition between ions for adsorption sites and the electrostatic interactions that occur because a reaction with one anion makes the surface more negative and, therefore, less favourable for reaction with a second anion. With an appropriate choice of parameters, the model describes sorption both when the anions are added singly and when they are added in competing pairs.

For competition between two anions, the fraction θ of the surface within a given interval that is occupied by the anion under consideration is

$$\theta=[\Sigma a_iK_i\exp(-z_iF\psi_i/RT]/[1+\Sigma a_jK_j\exp(-z_jF\psi_jRT], \qquad (5)$$

where i indicates the ionic species of the anion under consideration that participate in the reaction, j indicates all the species of anions that participate in the reaction, a indicates the activity of the ionic species thought to participate in the reaction, z is the valency including sign, K is the binding constant for the reacting species, ψ is the electric potential of the surface after sorption has occurred, and F, R, and T have their usual meaning.

In creating adsorption models, the trend is to proceed from the simplified models (Langmuir, Freundlich) towards more realistic and more complicated ones. A good review on kinetic sorption models is given in ref. 6. Competitive adsorption, for example, is discussed by Murali and Aylmore[142] and Roy et al.[143,144] Much new information on multicomponent anion adsorption is to be expected in the coming years.

4.4 Adsorption of Mo(VI), V(V) and W(VI) by soils and other adsorbents

Adsorption of Mo(VI) by different adsorbents has been measured by several researchers. It is difficult to compare results of various investigations, because adsorption studies have been carried out using different procedures. Variables in the procedures are, for instance, the adsorbent/solution ratio, temperature, equilibrating time, shaking time, the amount of adsorbate, the concentration of inert salt, pH adjustments, and separation of the supernatant from the solid phase. A review of Mo adsorption experiments, representing an analytical point of view, is given in Tables 5 and 6. Concentrated Mo solutions ($>10^{-4}$ M) have been used in many adsorption experiments. In these cases, the most concentrated solutions already contained polyanions, and the simple adsorption models cannot be applied.

In the determination of Mo, the thiocyanate and dithiol methods[145-147] are the most common and have therefore been mentioned in the tables. Other colorimetric methods have been explained or referred to in the original papers mentioned in Tables 5 and 6. During the last decade, plasma emission spectrometry has found its way into adsorption experiments, too.

Studies on adsorption of tungstate or vanadate by different adsorbents are scarce. Reviews are given in Papers **3** and **4**, respectively. The adsorption of W(VI) by activated carbon was measured using a procedure similar to the one in Mo(VI) adsorption experiments in ref. 152. The procedure for adsorption of V(V) and W(VI) by ferric oxide is given in ref. 14. Adsorption by soils and synthetic materials from very dilute V or W solutions ($\leq 10^{-4}$ M) would provide valuable information.

TABLE 6 (Continued on the next page). Studies on retention of Mo(VI) by different adsorbents. (*) temperature; ionic medium; equilibration time; Mo(VI) concentration; soil:solution ratio; separation method; Mo analysis method

Reference; Adsorbent	Aim of the Study	Procedure (*)
11 Hydrous Al and Fe oxides, clay minerals	adsorption vs. pH; adsorption vs. concentration at pH 4.35±0.15	room temperature; H_2O 1+14+1 h (1+1 h shaking); 0.01-3.2 μg cm^{-3}; 100 mg oxides, 1000 mg clay minerals + 50 cm^3; centrifuging; the dithiol method
12 hydrous Al and Fe oxides, kaolin, bentonite	adsorption vs.pH	20 °C H_2O; 16 h; ~1 μg cm^{-3} (0.01 mmol dm^{-3}), 0.1 μg cm^{-3}; 8 g (oxides), 100 g (clay minerals) + 1000 cm^3; centrifuging; the thiocyanate method
148 hydrous oxides of Fe, Al, and Ti	adsorption vs. concentration at pH 4.45, 5.70, 6.25, 6.75, 7.20 and 7.75; adsorption vs. pH	?; 4 mM ammonium acetate; 3 d; 0.1 μg cm^{-3}; 100-200 mg + 32 cm^3; centrifuging; the thiocyanate method

13 hematite	adsorption vs. concentration at pH 4.0 and 7.75	22 °C, 40 °C; H_2O; 53 h; 0-200 μg cm^{-3}; 0.5 g + 30 cm^3+20 cm^3; equilibrium dialysis; the thiocyanate method
14 ferric oxide powder (α-hematite)	adsorption vs. pH	22 °C, 50 °C, 95 °C; H_2O, 0.1 M NaCl, saturated NaCl; 10 min; 41 μg cm^{-3} (4.3x10^{-4} M) 2 g + 150 cm^3; separation method not mentioned; standard polarographic procedures
9 goethite and gibbsite	adsorption vs. pH	20-23 °C; 0.1 M NaCl; 24 h; 163 μg cm^{-3} (1.7 μmol cm^{-3}) for gibbsite and 192 μg cm^{-3} (2.0 μmol cm^{-3}) for goethite; 0.1 g + 25 cm^3; separation method not mentioned; analytical method not mentioned
149 oxides of Mn, Fe, Al, Sn and Ti	adsorption by goethite vs. concentration at pH 1.9, 3.0, 3.5, 4.1, 5.1, 5.3, and 6.2; adsorption vs. pH	?; 0.1 M KNO_3; 24 h; 1-40 μg cm^{-3}; 0.1 g + 20 cm^3; centrifuging; AAS or a colorimetric method
150 kaolinite	adsorption vs. concentration at pH 4.6; adsorption vs. pH	25±0.5 °C; 0.01 M NaCl; 24 h; 0.5-90 μg cm^{-3}; 1.00 g + 100 cm^3; filtering; flameless AAS
151 oxides of Al, Ti, and Si	adsorption vs. concentration at adsorbent's natural pH	?; H_2O; 1-14 d (occasional shaking); 10 μg cm^{-3}-211 mg cm^{-3} (≤2.2 mol dm^{-3}); 2 g + 100 cm^3; separation method not mentioned; AAS, X-ray fluorescence
152 activated carbon	adsorption vs. concentration in the pH range 1.0-6.5 adsorption vs. pH	25±1 °C; 1 M NaCl; 7-8 d; 48.7-1933 μg cm^{-3} (0.5075-20.15 mmol dm^{-3}); 0.25 g +50 cm^3; separation method not mentioned; a colorimetric method

TABLE 7 (Pages 46-49). Studies on retention of Mo(VI) by soils. (*) See caption of Table 5.

Reference; Origin of Soils	Aim of the Study	Procedure (*)
11 Australia	comparison of the ability of three soils to remove molybdate from solutions at different pH values	?; H_2O; 1+14+1 h (1+1 h shaking); 1.00 μg cm^{-3} or 10.00 μg cm^{-3}; 5 g + 50 cm^3 and 20 g + 200 cm^3; centrifuging; the dithiol method
12 Sweden	comparison of the ability of the soil to remove molybdate from a solution with that of the reference material	20 °C 0 001 M $CaCl_2$ 16 h; 0.1 μg cm^{-3} (0.001 mmol dm^{-3}); 100g + 1000cm^3; filtering; the thiocyanate method
148 California, USA	adsorption of molybdate by soils and soil-forming materials	?; 4 mM ammonium acetate; 3 d; 0.1 μg cm^{-3}; 2 g + 32 cm^3; centrifuging; the thiocyanate method
153 India	effect of complexants on retention and release of Mo applied to soils under waterlogged condition	?; 0.01-0.05 % ammonium oxalate, aluminon, KSCN, Na salicylate, 8-hydroxyquinoline and EDTA; 45 d (shaking at the beginning) an amount to make 10 ppm Mo in soil; 2 g + 20 cm^3; filtering; colorimetrically
16 Poland	effect of phosphate on the sorption and desorption of molybdate in the soil	?; 0.1 M KCl; 1+24+1 h (1+1 h shaking); 10 μg cm^{-3}; 10 g + 100 cm^3; filtering; the thiocyanate method
17 Australia	comparison of adsorption of molybdate, sulfate and phosphate by soils	25 °C; 0.01 M $CaCl_2$; 24 h; 0.1-0.4 μg cm^{-3}; 20 g + 100 cm^3; separation method not mentioned; the dithiol method

18 New Zealand	adsorption of molybdate at different pH values; effect of concentration	22 ± 2 °C; 0.2 M NaCl; 18 h; 0-7 $\mu g\ cm^{-3}$; 100 mg + 40 cm^3; centrifuging; the thiocyanate method
15 Finland	adsorption of molybdate at soil's natural pH using untreated soils and soils after different pretreatments	?; H_2O; 16 h; 0.1 mg dm^{-3} and 1.0 mg dm^{-3}; 20 g + 200 cm^3; filtering; the thiocyanate method + extraction with organic solvent
19 Australia	influence of solution concentration of Ca on the adsorption of phosphate, sulfate and molybdate	25 °C; 0-0.02 M $CaCl_2$; 24 h; 0.01-0.7 $\mu g\ cm^{-3}$; adsorbent:solution 1:5; centrifuging + filtering; the dithiol method
154 India	retention and release of applied Mo to soils under permanent water-logged condition	?; addition of glucose, Na_2CO_3, $CaCO_3$, $CaHPO_4$ or Cu, Zn, Fe and Mn as their sulphates; 45 d; Mo equivalent to 10 ppm in soil; 2 g + 20 cm^3; filtration; the thiocyanate method
155 India	retention of Mo by soils in the presence of EDTA	30 °C; H_2O; 2 h (shaking only at the beginning); 50 $\mu g\ cm^{-3}$, 500 $\mu g\ cm^{-3}$ (0.0005, 0.005 mol dm^{-3}); 2.5 g + 100 cm^3; centrifuging; colorimetrically
156 India	retention of Mo by soils and their derivatives in the presence of krillium (a soil conditioner)	30 °C; H_2O, 0.01-0.05 % krillium; 2 h; 50-500 $\mu g\ cm^{-3}$ (0.0005, 0.005 mol dm^{-3}); 2.5 g + 100 cm^3; centrifuging; colorimetrically
20 Chile	effect of pH of suspension on molybdate adsorption in different horizons of soils; adsorption isotherms for molybdate; time of equilibration	?; H_2O; 96-959 $\mu g\ cm^{-3}$ (1-10 mmol dm^{-3}); 6 h; 2.5 g + 25 cm^3; centrifuging; AAS

157 India	retention of molybdate after saturation of soils with some cations	?; H_2O; 10-80 μg cm^{-3}; 16 h; 5 or 10 g + 50 cm^3; filtering; the thiocyanate method
158 Rhodesia	relation of sorption of molybdate (and phosphate) to soil pH and other chemical factors	20 °C; 0.01 M $CaCl_2$; 0.01-0.6 μg cm-^{3}; 16 h; 10 g + 50 cm^3; centrifuging + filtering; the thiocyanate method
159 Western Oregon, USA	Mo adsorption isotherms; relation of Mo adsorption to the $(NH_4)_2C_2C_4$-extractable Fe in the soil	25 °C; 0.01 M $CaCl_2$; 0-20 μg cm^{-3}; 18 h; 2 g + 20 cm^3; centrifuging; flameless AAS
21 USA	Mo adsorption isotherms; adsorption of Mo in relation to some chemical properties of soils	23 °C; H_2O; 6 h; 9.6-96 μg cm^{-3} (0.1-1.0 mmol dm^{-3}); 1 g + 10 cm^3; centrifuging + filtering; the thiocyanate method
160 New Zealand	effect of lime and phosphate applications on the adsorption of phosphate, sulfate and molybdate by a spodosol; adsorption isotherms	25 °C; H_2O; 6 d (shaking for 1 h twice daily); 0-5 μg cm^{-3}; 3 g + 30 cm^3; centrifuging; the thiocyanate method
161 Australia	retention of Mo	25 °C; 0.01 M $CaCl_2$; 24 h; 0.1 μg cm^{-3}; 1:10; centrifuging + filtering; the dithiol method
143 South Carolina, USA	competitive interactions of phosphate and molybdate on arsenate adsorption; adsorption isotherms	25±0.5 °C; H_2O; 48 h; ~5-240 μg cm^{-3} (50-2400 μmol dm^{-3}); 500 mg + 25 cm^3; centrifuging; ICP-AES

144,162 South Carolina, USA	determination of the competitive coefficients for the adsorption of arsenate, molybdate and phosphate mixtures by soils (pH 4.5-6.9)	25 ± 0.5 °C, 15°C, 35 °C; H_2O; 48 h; 0-190 μg cm^{-3} (0-2000 μmol dm^{-3}); 1:50 or 1:2.5; centrifuging; ICP-AES
163 West Bengal	adsorption and desorption of molybdate; the role of organic matter and free Fe and Al	20°C, 40 °C; 0.01 M $CaCl_2$; 6 h (shaking) +40 h (incubating); 0.1-1.0 μg cm^{-3}; 2 g + 50 cm^3; centrifuging + filtering; the dithiol method

4.5 Displacement of native or adsorbed molybdenum

In determinations of total Mo in soils, samples are usually melted with Na_2CO_3.[15,164] However, partial extraction is often more informative, because selective extraction of soil Mo may give both a quantitative measure of the probable Mo content of plants grown on a given soil and yield information on the possible chemical forms in which the extractable Mo occurs. Reagents which can be used for extraction include the following: hot or cold water; 0.1-0.5 M KH_2PO_4 (pH 7.2); acid ammonium oxalate-oxalic acid solution AO-OA (pH 3.3); 0.01 and 0.05 M Ca lactate with and without acetate buffer; 0.3 M Na citrate + 6.9 % $NaHCO_3$ + $Na_2S_2O_4$; 15 % H_2O_2 + 0.1 M NaOH; 30 % H_2O_2 + AO-OA; 1 M ammonium acetate; 0.05 M Na_2H_2EDTA; 1.75 M NH_4OH; 0.001 M NaOH, 0.1 M NaOH; 0.275 M $NAHC_2O_4$ (pH 3.3); sat. $NaHCO_3$.[12,15,21,61,153,154,164-169] In desorption measurements, the amount of sample shaken with extractant ranges from 1.5-2 g[61,153,168] up to 50-100 g.[12,18,164] Extraction times from 1-2 h[12,163] to 48 h[167] have been used. Desorption immediately after adsorption has been carried out with a KH_2PO_4 solution[16] or $CaCl_2$.[163] Theng[18] removed a measured portion of the equilibrium solution and replaced it with an equal volume of acetate buffer solution (pH 4). Karimian and Cox[21] used an anion exchange resin. In a study using activated carbon, samples loaded with various amounts of Mo were equilibrated with solutions containing no molybdate but different amounts of clean activated carbon had been added to them.[152]

Water soluble Mo in soil includes readily soluble molybdates and water-soluble organic complexes. Usually less than 1 per cent of the total soil Mo is extracted with H_2O. Readily exchangeable Mo can be extracted by ammonium acetate. Mo loosely bound in organic complexes and associated with organic compounds is soluble in EDTA. Mo in these three categories should be available to plants, though the extent of the availability of any one form will vary with other soil characteristics. According to Williams and Thornton,[165] soil Mo not extracted by 0.1 M NaOH or 1.75 M NH_4OH is defined as non-extractable. Soils with the lowest organic carbon contents have the most non-extractable Mo. Both NaOH and NH_4OH extract appreciably more from organic than inorganic soils. It is possible that at high pH some organic compounds will be hydrolysed and some of the Mo associated with organic matter will pass into solution.

Mo will not be removed from iron compounds by H_2O or NH_4OH.[165] When Mo is extracted from mineral soils, the amount of Fe and Al oxides and sometimes Mn oxides also needs to be examined. Tamm's acid oxalate reagent (AO-OA, pH 3.3) has been widely used to extract amorphous iron and aluminium compounds from soils.[168,170] The reaction with iron is largely a photochemical reaction that requires UV light but Al ions are brought into solution as oxalate complexes. Exchangeable aluminium, $Al{\bullet}OH_2^+$ ions, and Al at edge sites are probably dissolved in addition to amorphous aluminium hydroxides and amorphous aluminosilicates.[43]

Buffered dithionite solutions have been used to reduce free iron oxides, which can then be extracted in citrate or acid solutions. These reagents will dissolve crystalline iron oxides in addition to the amorphous material. Unfortunately, dithionite extracts give no indication of the surface Fe•OH, since the iron oxides are completely dissolved. In addition, dithionite is not completely specific for extraction of iron from soil, since aluminium and silicon are also brought into solution.[170-172] It has been suggested that free iron can be removed from soils by extraction at 50 °C with sodium hydrogen sulphite in a citrate buffer at pH 4.75.[173]

5. EXPERIMENTAL

5.1. Material and methods

5.1.1 Potentiometric titrations

In determining the protonation constants of molybdate, analytical grade reagents were used, and solutions were prepared with deionised distilled water. Na_2MoO_4 powder and KCl were dried for 2 h at 105 °C. From dried KCl, a stock solution of 1 mol dm^{-3} was prepared. The 0.10 M Na_2MoO_4 stock solution was stored in a polyethene bottle, and its accurate concentration was determined gravimetrically by precipitation of molybdate as $PbMoO_4$ and as $MoO_2(C_9H_6ON)_2$.[147,174] HCl was standardized using dried TRIZMA.[175]

Protonation experiments were carried out as titrations at 25.0±0.1°C in a waterbath starting with 50.0 cm^3 of Na_2MoO_4 solution and adding standardized HCl from an autoburette. KCl (0.02 M) was used as ionic medium. Purified and medium-conditioned nitrogen was bubbled through the solution throughout the experiment. Na_2MoO_4 solutions with concentrations of 10^{-2}-10^{-5} M were titrated with 10^{-1}-10^{4} M HCl in 0.02 M KCl, respectively. Two replicate titrations were performed at all concentrations.

The free hydrogen ion concentration, **h**, was determined by measuring the potential with an Orion 920 pH meter equipped with a standard combination electrode. The relationship between the measured potential **E** (in mV) and the hydrogen ion concentration at 25 °C is given by the equation

$$\mathbf{E} = E^{\circ} + 59.16\ pH_c, \qquad (6)$$

where $pH_c = -\log\mathbf{h}$. A value for E° was determined before and after each titration of molybdate solution with acid. The procedure for titrations has been described in detail by Cruywagen[108] and Cruywagen and Heyns[23]. A MINIQUAD computer program[176] was used to calculate equilibrium data.

EMF titrations of 10^{-2} M vanadate and tungstate solutions with HCl were tried also. The equilibria were obtained so slowly that it was discouraging to carry on with titrations to obtain protonation constants.

5.1.2 Characteristics of the adsorbents

Kaolin $H_2Al_2Si_2O_8 \cdot H_2O$ (Kaolin. pond. Ph. Eur. III 180 μm) was provided by the Helsinki University Pharmacy. The X-ray diffraction pattern of the kaolin powder is given in Fig. 10. Peaks at 8.87, 17.78 and 26.76 indicate the presence of traces of muscovite. The Fe and Al contents of kaolin were determined by acid ammonium oxalate extraction in the same way as from the test soils (Paper 2). The kaolin powder contained 454±3 mg dm^{-3} AO-OA extractable Al and 116±4 mg dm^{-3} Fe, respectively. Cation exchange capacity as well as $pH(H_2O)$ and $pH(CaCl_2)$ are given in Paper 1.

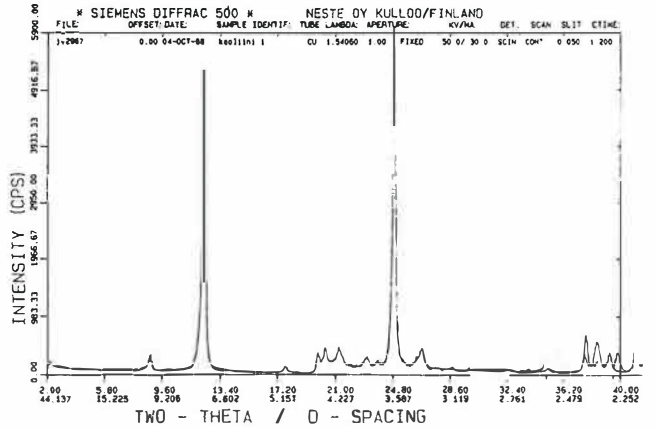


Figure 10. Powder X-ray diffraction pattern of kaolin.

The soils used in the experiments were a clay (soil 1), and two finesand samples (soils 2 and 3). They were provided by the Agricultural Research Centre of Finland. Selected characteristics of the soils, as well as a description of the soil analysis methods, are given in Paper **2**. The ammonium oxalate-oxalic acid (AO-OA) soluble amounts of Mo and W were presented in Papers **2** and **3**, respectively. The HNO_3+$HClO_4$-soluble concentrations of V (measured at 311.838 nm) were given in Paper **4**.

5.1.3 Adsorption and desorption experiments

Adsorption experiments were carried out using 1.00-g samples, 100.0 cm^3 of solution, and an equilibration time of 72 h. In desorption measurements, 0.80-g samples were shaken for 17 h with 50.0 cm^3 of 0.02 M KCl. The detailed procedures are given in Papers **1-4**. To control the ionic strength, in all adsorption experiments, V, Mo and W solutions contained 0.02 mol dm^{-3} of KCl. The concentration of KCl was selected using the following criteria: it must be high enough to keep the ionic strength constant and low enough not to damage the ICP torch system.[77] In retention experiments, a wide pH range was selected, because we wanted to study retention when different ionic species are present in solution, not only adsorption in conditions normally occurring in agricultural soils. Blank samples were prepared in the same way as samples but with no added Mo, V or W. The experiments were carried out at room temperature.

5.1.4. Elemental analyses

The HNO_3+$HClO_4$-leachable amounts of Al, Fe, Ca, Mg, Mn and P (Table 8) that can be used to approximate the total amounts of these elements in test soils, were determined as follows. In a Teflon autoclave, 0.450 g of soil was boiled with 10 cm^3 of a nitric acid-perchloric acid mixture (3:1) for 4 h, and after cooling, diluted to 50 cm^3. The insoluble residues of silicates were filtered away, and the concentrations of the elements were determined by ICP-AES. Duplicate analyses were performed. In ICP measurements with a Perkin-Elmer 2000 spectrometer, the analytical wavelengths for Al, Fe, Ca, Mg, Mn and P were 396.152, 259.940, 317.933, 279,079, 257.610, and 213.618 nm, respectively. The analyses were performed using the default values (RF power, measuring height and nebulizing rate) of the instrument for each element.

In adsorption experiments, the V, Mo and W measurements were performed using Perkin-Elmer ICP 5000 equipment at 309.11, 202.03, and 207.91 nm, respectively. Optimum conditions were calibrated manually. In desorption measurements, the ICP-AES 2000 spectrometer was used, and the parameters were optimized using a solution containing 1.00 mg dm^{-3} of V, Mo or W in 0.02 M KCl. The plasma power, measuring height and pump rate settings for V, Mo and W were (1040W, 10 mm, 1.11 cm^3 min^{-1}), (1180 W, 11 mm, 1.08 cm^3 min^{-1}), and (1240 W, 10 mm, 1.07 cm^3 min^{-1}), respectively.

The original aim was to measure adsorption and desorption using both 10^{-4} and 10^{-5} M solutions for Mo, V, and W. In the case of W, however, the ICP measurements with the Perkin-Elmer 5000 proved to be impossible from 10^{-5} M solutions with $pH < 7$ and from 10^{-4} M solutions with $pH < 2.8$. The reason was probably adsorption of tungstate by the spray chamber during nebulization.[178] During the course of the experiments, it was recognized that no corresponding difficulties occurred when 10^{-5} M W standard solutions with pH 2-7 were nebulized into the ICP 2000 spectrometer. The spray chamber of the latter is made of Ryton and seems not to adsorb tungstate.

In measuring the pH-dependence of the adsorption of V(V), Mo(VI) and W(VI) by soils, the amounts of P, Ca, Mg, and Mn present in the aqueous phase at the end of the 72-h equilibration period were measured also. To see if their release is affected by the artificial addition of rather high amounts of anions, the amounts released during adsorption were compared with those of the blank samples, which were prepared in the same way as the samples but with no added V, Mo, or W. Al and Fe concentrations of some blank samples (about 10 samples from each soil, covering pH range 2.3-7.5) were also measured. These determinations were performed with Perkin-Elmer 5000

ICP equipment.

When time-dependence of adsorption of V(V), Mo(VI) and W(VI) species at the natural pH of each soil was measured, the process was followed for 70 h. After an appropriate equilibration time, amounts of V, Mo, W and P in the filtrates were determined. When following adsorption of Mo(VI) species from acidic solutions (initial pH 2.0 and 3.0), release of Ca, Mg, Mn, P, Al, and Fe was measured also. The concentrations of the analytes were determined from the filtrates by the Perkin-Elmer 2000 spectrophotometer.

In the ICP measurements, from all matrices, at all V/Mo/W concentrations used, and from the blank samples, the standard addition method was used to control the accuracy of the elemental analyses. After adsorption and desorption experiments, standard additions were made into arbitrarily selected filtrates representing the whole pH range 2.3-7.5. In addition, standard solutions with concentrations and pH values corresponding to those of samples were equilibrated for 72 h, filtered through Whatman 40 filter paper and run as samples when the instrument was calibrated with freshly prepared standards. The latter procedure was used to insure that analytes were not adsorbed by the sample vessels or the filter papers.

5.1.5 NMR experiments

^{17}O and ^{51}V NMR spectra were measured with a JEOL GSX 270 FT NM spectrometer at 36.6 and 70.9 MHz, respectively, with number of data points 8 K, spectral width 36 kHz (^{17}O) and 50 kHz (^{51}V). Flip angle was 90°, pulse delay 0.1 s and measuring temperature 30 °C. The number of scans strongly depended on the sample, the range being ca. 1000-500000. The ^{51}V NMR chemical shifts were quoted for the signal of neat $VOCl_3$ ($\delta=0$) in a 1-mm diameter capillary tube inserted coaxially inside the 10-mm diameter NMR tube and the ^{17}O NMR shifts relative to the signal of solvent water ($\delta=0$).

5.2 Results and discussion

5.2.1 Protonation constants of the molybdate ion

The computer calculations of the titration data showed that in the 10^{-2} and 10^{-3} M molybdate solutions, polyions were present in addition to monomeric species, but these were not identified. On the other hand, MINIQUAD showed that polymeric molybdate species could be ignored in the 10^{-4} M solution, and the solution could be assumed to contain only monomeric molybdic acid and its anions:

$$\mathbf{MoO_4^{2-} + H^+ \overset{K_1}{\rightleftharpoons} HMoO_4^-} \tag{7}$$

$$\mathbf{HMoO_4^- + H^+ + 2\,H_2O \overset{K_2}{\rightleftharpoons} Mo(OH)_6} \tag{8}$$

The experimental values obtained for the protonation constants of MoO_4^{2-} were $\log K_1 = 3.98 \pm 0.06$ and $\log K_2 = 3.65 \pm 0.06$, respectively. The error limits are estimated to be 3σ. The log K values obtained in the present investigation are in good agreement with the values presented by Cruywagen and Rohwer[104] and Cruywagen and Heyns[31]: $\log K_1 = 3.74 \pm 0.07$, $\log K_2 = 3.77 \pm 0.07$ and $\log K_1 = 3.66 \pm 0.03$, $\log K_2 = 3.89 \pm 0.02$, computed from UV adsorption values at 25 °C and in 0.1 M NaCl.
The anomalous small difference in the log K values for the protonation of molybdate has been explained by an increase in the coordination number of molybdenum during the second protonation step.[31]

The distribution diagram in Fig. 11 has been calculated using the obtained log K values. It can be assumed that all Mo(VI) solutions with Mo concentration $\leq 10^{-4}$ mol dm^{-3} contain only monomeric species at the rather low ionic strength of this study, so that the distribution diagram is valid for the 10^{-5} M molybdate solution, too.

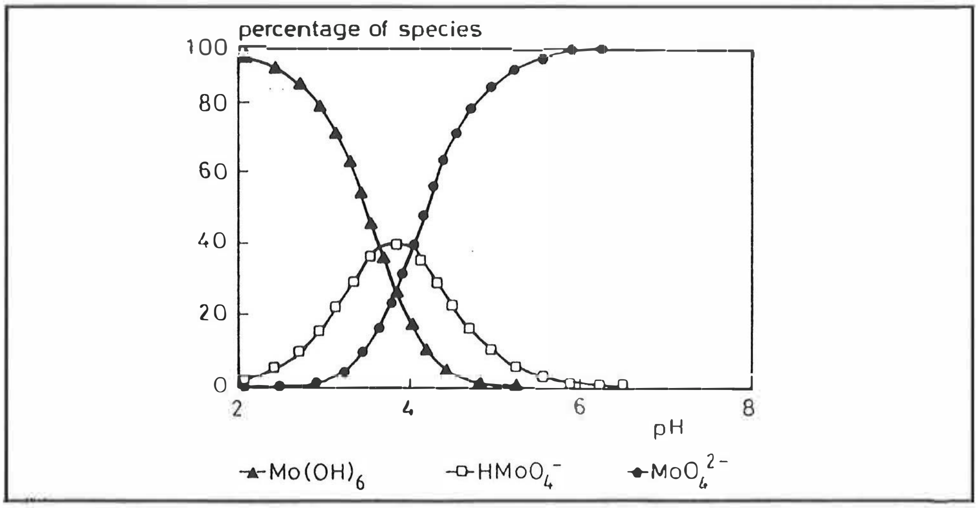


FIGURE 11. Distribution of species in $\leq 10^{-4}$ M Na_2MoO_4 solution (0.02 M KCl, 25±0.5 °C).

5.2.2 Acid-soluble Al, Fe, Ca, Mg, Mn, and P of the test soils

Soil 1 is much richer in Fe, Al, Mg, Ca, and P than the other soils (Table 8). Mn content of soil 3 is rather low. Soil 1 had been used for growing sugar beets, whereas soils 2 and 3 were for production of cereals.

TABLE 8. Acid-soluble amounts of some elements in the test soils.

Element	soil 1	soil 2	soil 3
Fe mg g^{-1}	60±3	22±2	16±2
Al mg g^{-1}	49±5	18±2	17±2
Mg mg g^{-1}	13.7±0.5	4.4±0.3	3.3±0.3
Ca mg g^{-1}	14.7±0.5	3.0±0.2	3.1±0.2
P μg g^{-1}	380±10	210±10	270±10
Mn μg g^{-1}	470±10	420±10	146±10

5.2.3 Time-dependence of adsorption of V(V), Mo(VI), and W(VI) and release of Ca, Mg, Mn, P, Al, and Fe during adsorption

The time-dependence of the adsorption of V, Mo and W at soil pH is presented in Paper **5**. The adsorption of Mo almost reaches its final level within the first few hours, whereas the adsorption of vanadium and tungsten is a slower process.

It can be surmised that nutrients as well as soil constituents begin to dissolve under acidic conditions. That is why the time-dependence of the adsorption of Mo from a 10^{-4} M solution with initial pH values of 2.0 and 3.0, and the release of Ca, Mg, Mn, and P into the aqueous phase were studied also (Fig. 12). The analyses were performed in duplicate. The release of Fe and Al under these acidic conditions was given in Paper **2**.

From acidic solutions also, adsorption of Mo occurs mainly within 3 hours after the contact between soil and liquid has been established (Fig. 12e).

Figure 12d shows that the part of the phosphorus desorbed first may later be either adsorbed or precipitated during the 72-h period (cf. soil 1, curve with initial pH 2.0). It is possible that in the most acidic suspensions phosphorus bound to oxide surfaces or present in the apatitic form or in the organic matter also begins to dissolve and becomes adsorbed on appropriate surfaces during equilibration.

Release of Ca and Mg (Fig. 12a,b), which are basic cations, reaches the final plateaux within the first three hours, whereas the release of Mn (Fig. 12c), Al and Fe (Paper **2**) is more time-dependent. Weathering of basic cations in mineral soils is the process that generates the neutralizing capacity. Soil acidification proceeds when the rate of acid input exceeds the weathering rate. Buffering characteristics can be divided into "buffer capacity", the total reservoir of buffering compounds in soil, and "buffer rate", the maximum potential rate of the reaction between buffering compounds and acid load. In some cases where the buffer capacity is high, a low buffer rate may nevertheless limit the ability of soil to buffer the acid load. Both characteristics reflect intrinsic properties of soils, such as lime content, silicate weathering rate, cation exchange capacity, and base saturation. [179,180] Cations principally involved in soil processes are H^+, Na^+, K^+,

NH_4^+, Mg^{2+}, Ca^{2+}, and Al^{3+}.[7] Of these, Ca^{2+}, Mg^{2+}, Na^+ and K^+ are basic cations.

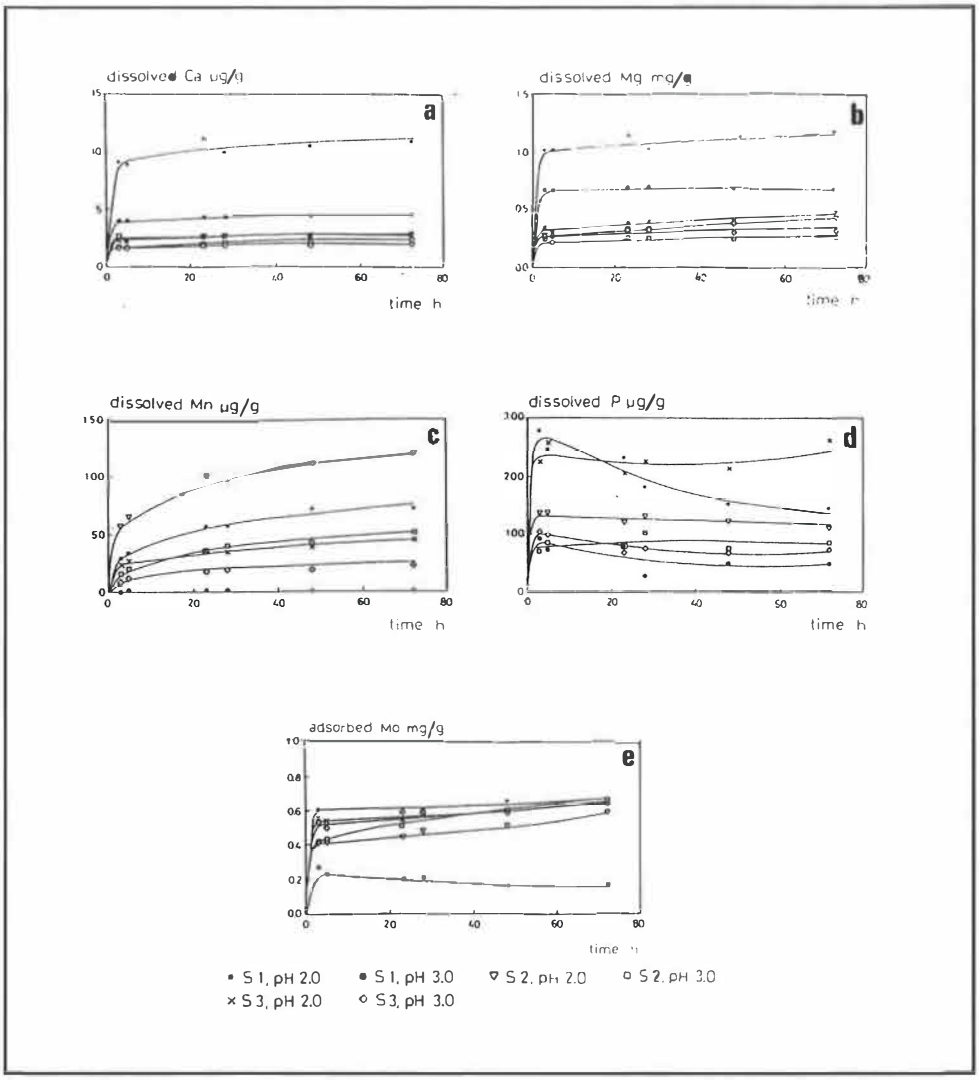


FIGURE 12. Time-dependence of the release of Ca, Mg, Mn, and P from soil samples during adsorption of Mo from 10^{-4} M Na_2MoO_4 solutions with initial pH values 2.0 or 3.0 (soil:solution 1:100 w:v). a) Ca; b) Mg; c) Mn; d) P. e) Time-dependence of adsorption of Mo.
S1 = soil 1; S2 = soil 2; S3 = soil 3.

5.2.4 Adsorption and desorption envelopes

The adsorption and desorption envelopes are the most important part of this work. To make it easier to draw conclusions, adsorption of Mo, V or W from 10^{-4} M solutions, and the corresponding desorption envelopes are presented in Fig. 13.

Adsorption of Mo from 10^{-4} M solution gives envelopes that slightly differ from those obtained using a 10^{-5} M solution (Paper 2). At pH 2.3-7.5, Mo(VI) can be retained both as $Mo(OH)_6$, $HMoO_4^-$ and MoO_4^{2-}. Soil 1 is able to adsorb Mo at higher pH values than the other soils, because no addition of OH^- ions, which can displace molybdate ions, was necessary to obtain the final desired pH values. However, when the pH becomes high enough, adsorption of molybdate ceases, and molybdate thus becomes plant-available or leachable. Desorption envelopes of all soils reach almost the same $\mu g\ g^{-1}$ plateaux, but the maximum occurs at a higher pH value in the case of soil 1. Adsorption and desorption envelopes of soils 2 and 3 are somewhat identical.

For all soils, adsorption of vanadium(V) from a 10^{-5} M solution (Paper 4) gives almost identical envelopes compared with those obtained from a 10^{-4} M solution (Fig.13c). Only small differences occur at $pH < 3$ and $pH > 5$. Soils 2 and 3 have a rather similar ability to adsorb vanadate. Soil 1 behaves independently and retains the highest amounts in pH conditions that frequently occur in agricultural soils also. As in the case of Mo, the desorption envelope of V for soil 1 differs from those obtained for the other two soils. Readsorption might have occurred. Vanadate adsorbed from the 10^{-5} M solution seems to be relatively more tightly bound than that adsorbed from a more concentrated solution.

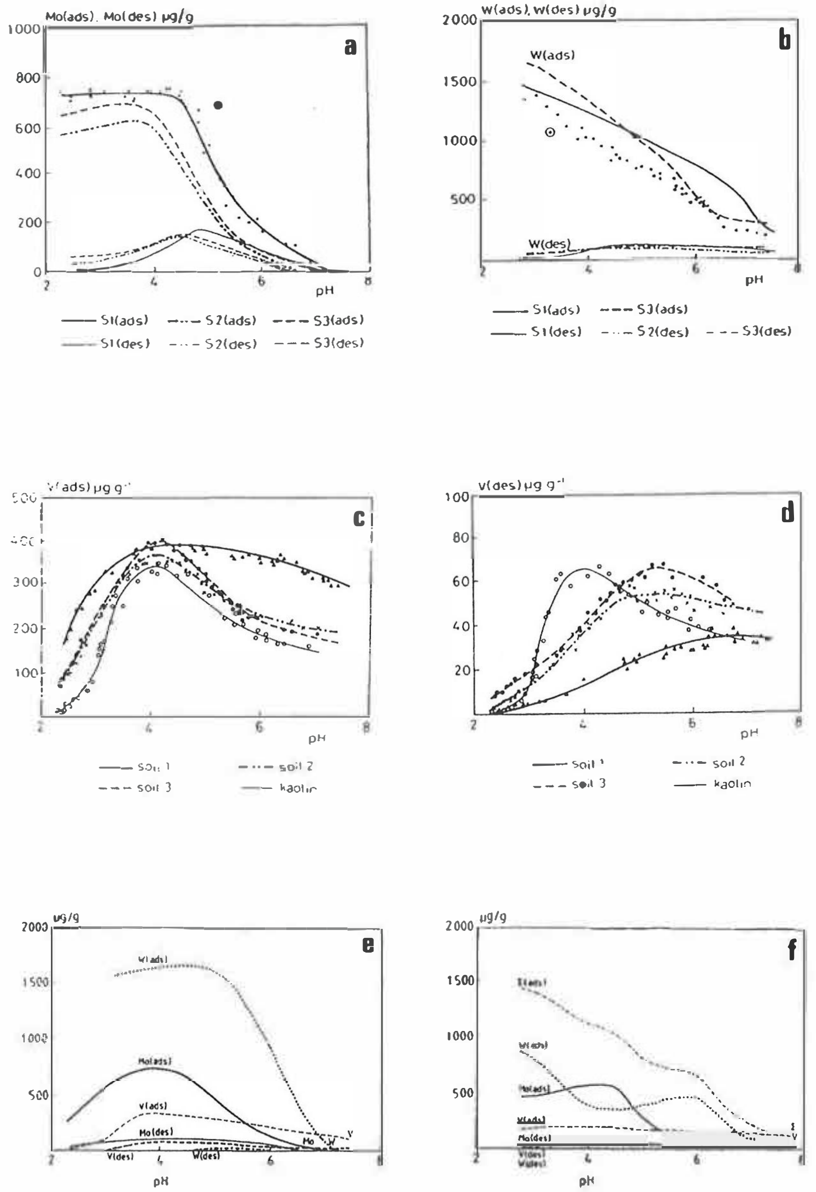


FIGURE 13. Adsorption and desorption envelopes. 10^{-4} M solutions. Adsorption and desorption of a) Mo, b) W. c) Adsorption of V, d) desorption of V. e) Adsorption and desorption of singly added Mo, V and W using kaolin as adsorbent. f) Kaolin as adsorbent; adsorption and desorption of simultaneously added Mo, V and W.

Tungsten(VI) species are strongly retained by soils in acidic conditions (Fig. 13b). As neutral pH values in soil suspensions are reached, adsorption of W by soil 1 still is rather strong. From this it can be concluded that added OH^- ions have perhaps partly prevented adsorption of tungstate ions by other two soils. The role of phosphate ions in the adsorption of tungstate species still needs further elucidation. Retained W is leached with 0.02 M KCl rather poorly. Readsorption during desorption is not excluded.

The results from adsorption studies using kaolin (Fig. 13e) explain the adsorption of Mo and V by soils 2 and 3 at pH>4 rather well, when the solution contained vanadate, molybdate or tungstate alone. However, adsorption by soil 1 and adsorption by all soils at pH<4 differ from kaolin. On the acidic side, adsorption by organic material and/or hydrous oxides of Al and Fe present in soils might explain the more pronounced adsorption. It is known[181], for example, that various organic materials (cow manure, compost, and sphagnum peat) have influence on the recovery of molybdenum added to a sandy clay loam soil.

At pH>4, molybdate and vanadate are adsorbed by kaolin to a lesser extent than by soils. It is possible that the OH^- ions which had to be added into the suspensions to obtain the final desired pH values have prevented adsorption of molybdate and vanadate. Kaolin with pH 4.7 in suspension was the most acidic of these four adsorbents. The V desorption envelope of kaolin has a maximum value at a more acidic pH value than the other adsorbents. Adsorbed molybdate seems to be most tightly bound by kaolin, probably because conditions have been suitable for readsorption during desorption.

The W adsorption envelope of kaolin clearly differs from those obtained for soils, so one cannot really use kaolin in estimating the amounts of W adsorbed by soils. Adsorbed W either is very tightly bound by kaolin or the desorbed W(VI) species were readsorbed during the 17-h shaking period.

When adsorption experiments using kaolin as adsorbent were carried out from a

V+Mo+W mixture, the results clearly differed from those presented in Fig. 13e. It is possible that all three adsorbates were adsorbed at the same adsorption sites concurrently. Mo is more strongly retained than W at pH~4, and adsorption of W predominates at pH~6. Adsorption of vanadate remains rather constant and is only slightly affected by the other adsorbates at pH 3-6. It is possible that heteropolyions (Cf. Table 4) were formed in the aqueous phase, and adsorption occurred in heteropolyanionic forms also.

The amounts of Mo, V and W adsorbed by soils can be compared with reported values of adsorbed phosphate. Schwertmann[182] reported that, at pH 5-7, about 3-4 μmol (90-120 μg) P was retained by one gram of a test soil with natural pH 5.2. According to Edzwald et al.,[183] 0.091, 0.746 and 2.51 mg P were retained at pH 7-8 by one gram of kaolinite, montmorillonite and illite, respectively. In the case of kaolinite and illite, maximum phosphate adsorption occurred at pH 4-5 with decreasing amounts of adsorption at lower and higher pHs. Phosphate adsorption by montmorillonite increased with increasing pH. The maximum amount of Mo that can be adsorbed by kaolinite[150] at pH~4 is 1.63 mg g^{-1}. Preliminary tests in the present study, using a 10^{-3} M molybdate solution and 1.00-g samples of kaolin, confirmed this observation. Jones[11] reported that 74 mg of molybdenum was retained by 1 g of ferric oxide and 42 mg of Mo by 1 g of boehmite at pH 4.35. The corresponding value for metahalloysite (a clay mineral standard) was 7.6 mg of Mo per one gram of adsorbent. Kyriacou[14] measured adsorption by Fe_2O_3 from $4.3 \cdot 10^{-4}$ M vanadate and molybdate solutions and from a $8.6 \cdot 10^{-4}$ M tungstate solution using a weight:volume ratio of 2.0 g:150 cm^3. Maximum adsorption of Mo (3.0 mg g^{-1}) occurred at pH~4, of V (1.64 mg g^{-1}) at pH 4-6 and of W (11.8 mg g^{-1}) at pH~4. Using activated carbon as adsorbent, Cruywagen and Pienaar[184] found that, at pH 2.5 and initial concentration of 20.0 mM, for instance, the amount of tungsten adsorbed was 2.85 mmol g^{-1} (524 mg g^{-1}) compared with 3.00 mmol g^{-1} (288 mg g^{-1}) in the case of molybdenum.

This comparison shows that oxides of Fe and Al as well as activated carbon retain Mo, V and W more effectively than kaolin or the soils in the present study.

5.2.5 Release of P, Ca, Mg, and Mn during adsorption of V(V), Mo(VI), and W(VI)

Release of P during the 72-h equilibration as well as the time-dependence of desorption at the natural pH of each soil is discussed in Paper **5**.

Fig. 14 gives curves at pH 2.3-7.5 for the amounts of Ca, Mg, and Mn released from the blank samples, which contained no added V, Mo, or W. Each curve consists of about 40 test points. The test points for leachable Ca and Mg from soil 1 are also given.

Fig. 15 shows the solubility of Al and Fe from the blank samples. The shapes of these curves are similar to those reported by Karlsson,[12] obtained using a soil-solution ratio of 1:10 (w:v), and show when the aluminium and iron buffer systems are reached. Silicate and cation exchange buffer systems predominate at the pH range of 4.2-6.0. Below pH 4.2, aluminium and iron buffer systems predominate. When AlOOH and $Fe(OH)_3$ react with protons, Al^{3+} and Fe^{3+} ions are liberated.[180,185,186]

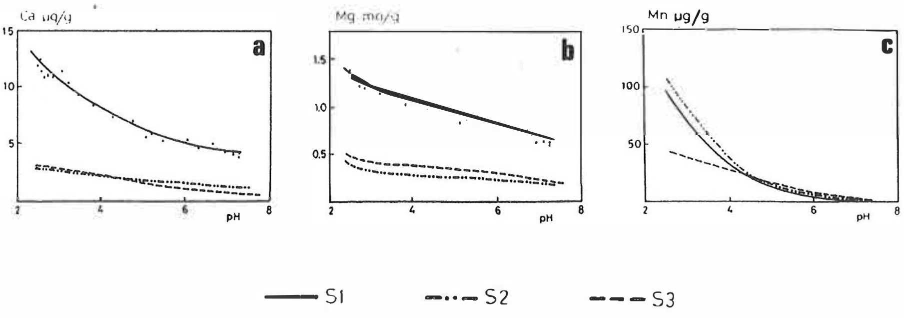


FIGURE 14. Release of a) Ca, b) Mg and c) Mn vs. pH from soils in 0.02 M KCl. pH denotes that at the end of the 72-h equilibration period.
S1 = soil 1, S2 = soil 2, S3 = soil 3.

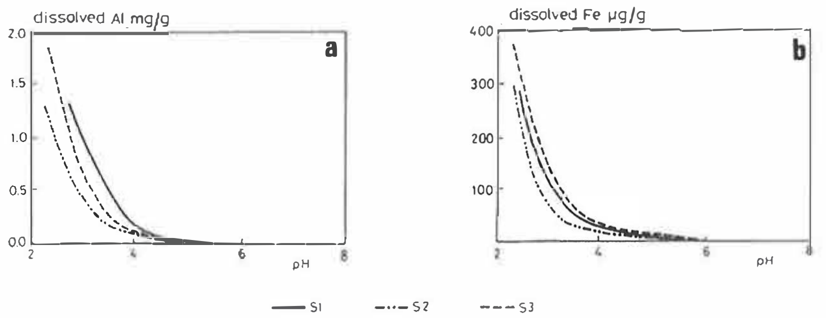


FIGURE 15. Release of a) Al and b) Fe from soils in 0.02 M KCl. pH denotes that at the end of the 72-h equilibration period. S1 = soil 1, S2 = soil 2, S3 = soil 3.

In the statistical analysis, one group of test points used were those at pH 2.3-7.5 either in the blank samples or after each V/Mo/W application. ANOVA[187] was used for statistically testing the effect of adding V or Mo at the 10^{-4} M or 10^{-5} M level or W at the 10^{-4} M level on the release of Ca, Mg, and Mn (Table 9). Because statistically significant changes in the mean values of released Ca, Mg and Mn were detected only in single cases, they are rather difficult to explain. If the release of Ca or Mg had decreased in the presence of V/Mo/W, there would have been reason to suspect that insoluble precipitates (Ca or Mg molybdates, tungstates or vanadates) had been formed. Another explanation could be that specific adsorption would have increased the cation exchange capacity of soil samples, thus making Ca and Mg less soluble.

TABLE 9. Ca, Mg and Mn release from untreated soils and differences in means of released Ca, Mg, and Mn from soil samples with a Mo, V, or W application compared with means of amounts released from blank samples. > and < denote greater and smaller means after application compared with blanks, respectively. *= P(<0.05), **=P(>0.01), ***=P(<0.001). NS= not significant.

Set of Samples		Statistical Significance of the Differences		
		soil 1	soil 2	soil 3
Ca	blank (mg g^{-1})	7.21	2.08	1.99
	10^{-4} M Mo	NS	NS	$<^{*}$
	10^{-5} M Mo	NS	NS	$<^{***}$
	10^{-4} M W	NS	NS	NS
	10^{-4} M V	$>^{**}$	NS	NS
	10^{-5} M V	NS	NS	NS
Mg	blank ($\mu g\ g^{-1}$)	923	277	355
	10^{-4} M Mo	NS	NS	NS
	10^{5} M Mo	NS	$<^{*}$	$<^{*}$
	10^{-4} M W	NS	NS	NS
	10^{-4} M V	$>^{*}$	NS	NS
	10^{-5} M V	$>^{*}$	NS	NS
Mn	blank ($\mu g\ g^{-1}$)	28.8	34.0	20.5
	10^{-4} M Mo	NS	NS	NS
	10^{-5} M Mo	NS	$>^{**}$	$<^{*}$
	10^{-4} M W	NS	$>^{***}$	NS
	10^{-4} M V	$>^{*}$	$>^{***}$	NS
	10^{-5} M V	NS	$>^{***}$	NS

5.2.6 Adsorption and desorption of different Mo(VI) and V(V) ionic species

Before considering adsorption of different ionic species, one must ensure that the ionic strength of the solution remains rather constant during equilibration. Initially the adsorbate solutions contained 0.02 mol dm^{-3} of Cl^{-}. An addition of 1.0 cm^3 of 1 M HCl into 100 cm^3 of solution results in an increase of 0.01 mol dm^{-3} of chloride ion concentration.

Fe and Al released from either mineral coatings or crystalline soil constituents were measured. According to Lindsay,[40] the solubility of silica minerals in terms of H_4SiO_4 is expected to range from $10^{-2.74}$ M (amorphous silica) to 10^{-4} M (quartz). The other Si minerals have intermediate solubilities. Thus Si needs not to be taken into account when considering increase in ionic strength. Finnish reference values[45] indicate that in arable soils the highest nutrient concentrations are those of Ca, Mg, and K. Concentrations of released potassium were not measured, because the solutions contained KCl as an inert salt. Release of Mn was measured. Release of nitrate was estimated to be low. According to Barber,[37] agricultural soils contain about 50-150 mg dm^{-3} of nitrate-nitrogen (Cf. 20-3000 mg kg^{-1} of total Mn).

In Table 10, the release of Ca and Mg from soil 1 at pH 2.3 has been used to estimate maximum Ca and Mg concentration in the aqueous phase. There was less Ca and Mg released from the other two soils. The release of Ca, Mg, Mn, P, Al or Fe has not strongly increased the ionic strength in solutions in soil suspensions. It is of course possible that a slight release of organic constituents has also occurred. It can, however, be assumed that no polymerization of the anionic species of Mo, V, or W due to strongly increased ionic strength needs to be taken into account. Higher amounts of the elements could be released if the contact between soil and a very acidic solution and soil is much longer than 72 h.

Table 10. Maximum release of Ca, Mg, Mn, P, Al and Fe from soil 1 during the 72-h equilibration period. Σ(Ca,Mg,Mn,P,Al,Fe) = $4.54 \bullet 10^{-3}$ mol dm^{-3}.

Element	Release mg g^{-1}	Molar concentration in the aqueous phase
Ca	13	$3.2 \bullet 10^{-3}$
Mg	1.3	$5.3 \bullet 10^{-4}$
Mn	0.12	$2.1 \bullet 10^{-5}$
P	0.20	$6.1 \bullet 10^{-5}$
Al	1.8	$6.7 \bullet 10^{-4}$
Fe	0.35	$6.3 \bullet 10^{-5}$

After this consideration, the log K values and the distribution diagram (Fig. 11) can now be used in approximating retention of Mo(VI) by different adsorbents from dilute sodium molybdate solutions. Generally, if it is assumed that Mo(VI) is not reduced to lower oxidation states and no pH change of several pH units occurs in the suspension during the adsorption step, then adsorption of molybdenum as different molybdate species can be calculated using the distribution curve (Fig. 11) and the equation

$$\mathbf{A} \quad = \mathbf{A}[\mathrm{Mo(OH)_6} + \mathbf{A}[\mathrm{HMoO_4^-}] + \mathbf{A}[\mathrm{MoO_4^{2-}}] \qquad (9)$$

where **A** is adsorbed Mo (μg g^{-1}), and the terms in the sum denote adsorption of the fractions, present in the solution as $Mo(OH)_6$, $HMoO_4^-$, and MoO_4^{2-}, respectively.

This approach is used in representing adsorption and desorption measurements (See Figures 16a-d). This presentation could also be used as an approximation for adsorption of molybdate and its protonated forms at soil's natural pH.

Equilibria involving MoO_4^{2-} and polymolybdates in aqueous solutions are established rapidly.[25] Adsorption of molybdate has also been reported to begin quickly after the contact between the liquid phase and solid has been established.[14,150,152] This means that the pH at the beginning of liquid-solid interaction is of great importance. It is possible that, when an acidic solution is added to soil, the pH of the suspension at first is low but then rises during the adsorption process. In the present study, the pH in some suspensions of soil 1 rose from pH 3 to 7 during adsorption (Papers **2-4**), and the fraction presented here as adsorption of MoO_4^{2-}, might contain traces of adsorbed Mo initially present as $Mo(OH)_6$ and $HMoO_4^-$, too.

The results obtained using kaolin as a reference material give reason to assume that the clay fractions of soil retain added molybdate rather effectively in conditions that normally occur in agricultural use, if the soil is not properly limed.

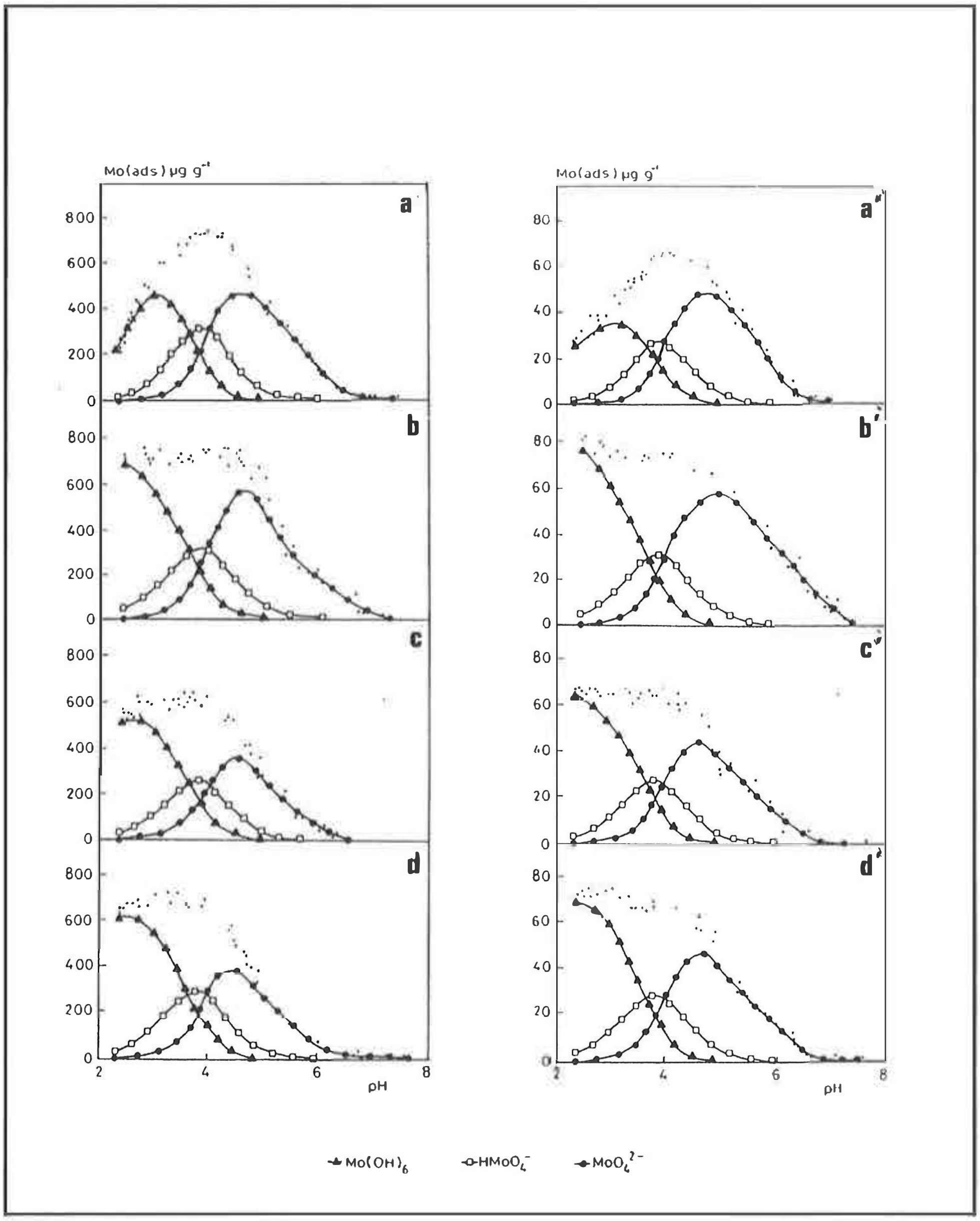


FIGURE 16. Test points for adsorption of Mo(VI) from 10^{-4} and 10^{-5} M Na_2MoO_4 solutions (959.4 or 95.94 μg Mo(VI) in 100 cm^3) and calculated curves (for clarity, single points not shown) for adsorption of $Mo(OH)_6$, $HMoO_4^-$, and MoO_4^{2-}, respectively. 10^{-4} M: a) kaolin, b) soil 1, c) soil 2, d) soil 3. 10^{-5} M: a') kaolin, b') soil 1, c') soil 2, d') soil 3. pH denotes the acidity of suspensions at the end of the 72-h adsorption period.

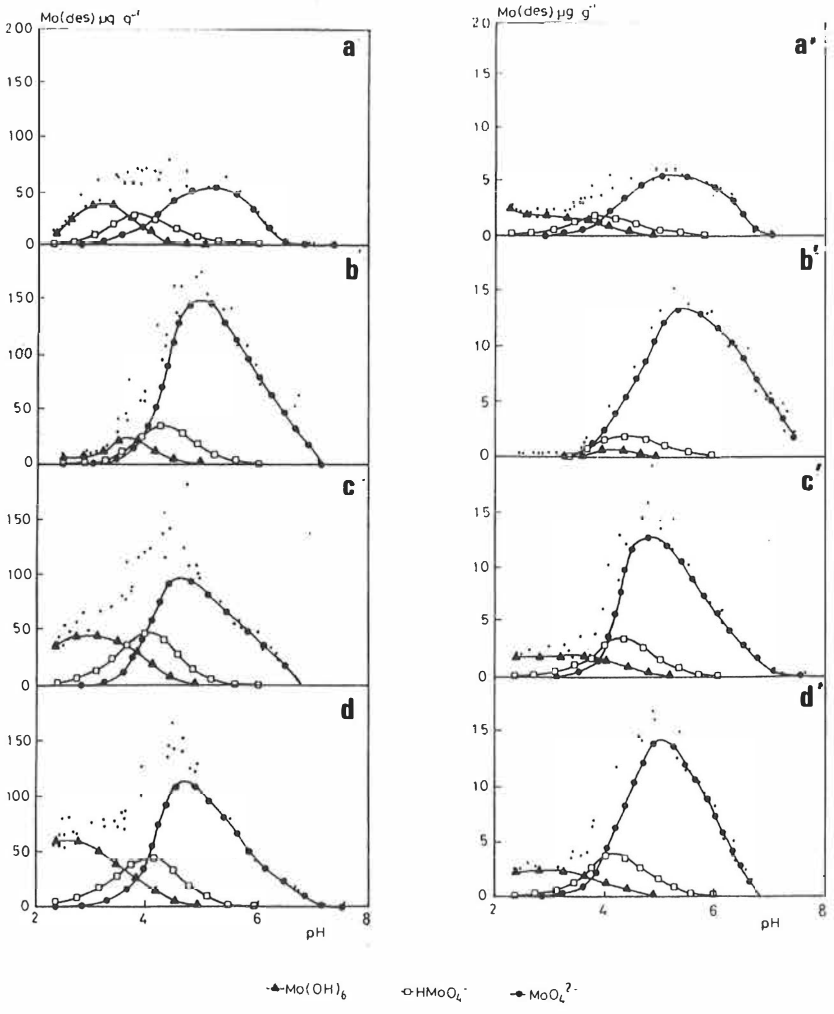


FIGURE 17. Test points for desorption of Mo(VI) adsorbed from 10^{-4} and 10^{-5} M Na_2MoO_4 solutions and calculated curves (for clarity, single points not shown) for leaching of adsorbed $Mo(OH)_6$, $HMoO_4^-$, and MoO_4^{2-}, respectively.10^{-4}M: a) kaolin, b) soil 1, c) soil 2, d) soil 3. 10^{-5} M: a') kaolin, b') soil 1, c') soil 2, d') soil 3. pH denotes the acidity of suspensions at the end of the 72-h adsorption period.

According to Jones,[11] ferric oxide should retain Mo strongly even at pH 2. The small amounts of extractable Fe and Al oxides present in kaolin (about one tenth of the amount present in the test soils) did not play an important role in retention of Mo, because the adsorption envelope had no broadening on the acidic side.

One might also suspect that in the most acidic conditions of soils during adsorption, added Mo may have formed poorly soluble compounds with dissolved soil constituents, especially because all three soils are rich in Fe and Al. Follett and Barber[64] have, however, reported that calcium molybdate and ferrous molybdate are too soluble for their solid phases to exist in soil. Cruywagen and De Wet[152] propose that the strong adsorption of Mo(VI) by activated carbon in acidic conditions can be ascribed to chemical bonding with basic oxygen atoms available at the surface of the adsorbent. $Mo(OH)_6$ might have been retained by the oxygen-containing groups in the organic matter of soils, and this could give, in addition to possible readsorption during the desorption step, one more explanation for the rather poor leachability of Mo adsorbed as $Mo(OH)_6$ (See Fig. 17).

When retention of different vanadate species is discussed (see Paper **4**), the conclusions are based on the distribution diagram in Paper **4**. It has been obtained using log K values from refs. 25, 30 and 188. Pettersson et al.[120,121] did not detect the presence of H_3VO_4 in a 0.3 mM V(V) solution. Their opinion was, however, that H_3VO_4 possibly occurs in more dilute solutions.

The adsorption envelope of V(V) (Fig. 13 c) serves as a good example of adsorption when two anionic species $H_2VO_4^-$ and HVO_4^{2-} are simultaneously present in solution. This feature makes adsorption of vanadate at neutral or nearly neutral conditions different from that of molybdate, as adsorption is strong at neutral conditions also.

5.2.7 Comparison of three extractants in Al, Fe, Ca, Mg, Mn, and P analyses

It is generally estimated that the acidic ammonium acetate (pH 4.65) extraction, or HAAc+EDTA extraction, gives the amounts of nutrients that are plant-available in soils.[45] These amounts were measured from the test soils at the Agricultural Research Centre, Jokioinen. They are presented in Fig. 18 compared with the acid-leachable amounts from Table 8. In addition, the acid ammonium oxalate (AO-OA) extractable amounts of Al and Fe from Paper **2**, which give estimates of hydrated Fe and Al oxides, are presented. The bulk density of each soil (Paper **2**, Table 1) has been used in transforming concentrations expressed in μg g^{-} to mg l^{-1}. Fig. 18 clearly shows how important the choice of the extractant is.

5.2.8 NMR experiments

Results of preliminary ^{17}O NMR measurements[189] during the present study revealed that the only ionic species detected from 1 M molybdate solution was MoO_4^{2-} at pH > 6. In the case of 0.05 M sodium tungstate solution, more than 500000 scans were accumulated. From an 0.8 M vanadate solution, a signal was obtained only at pH > 12. Heteropolyionic species were formed in solutions containing both V and W (pH 9.01), and the signal of W almost disappeared in the presence of V. Unfortunately, at the natural abundance of ^{17}O, this method could not be utilized in measurements from the dilute solutions that were used in the adsorption experiments.

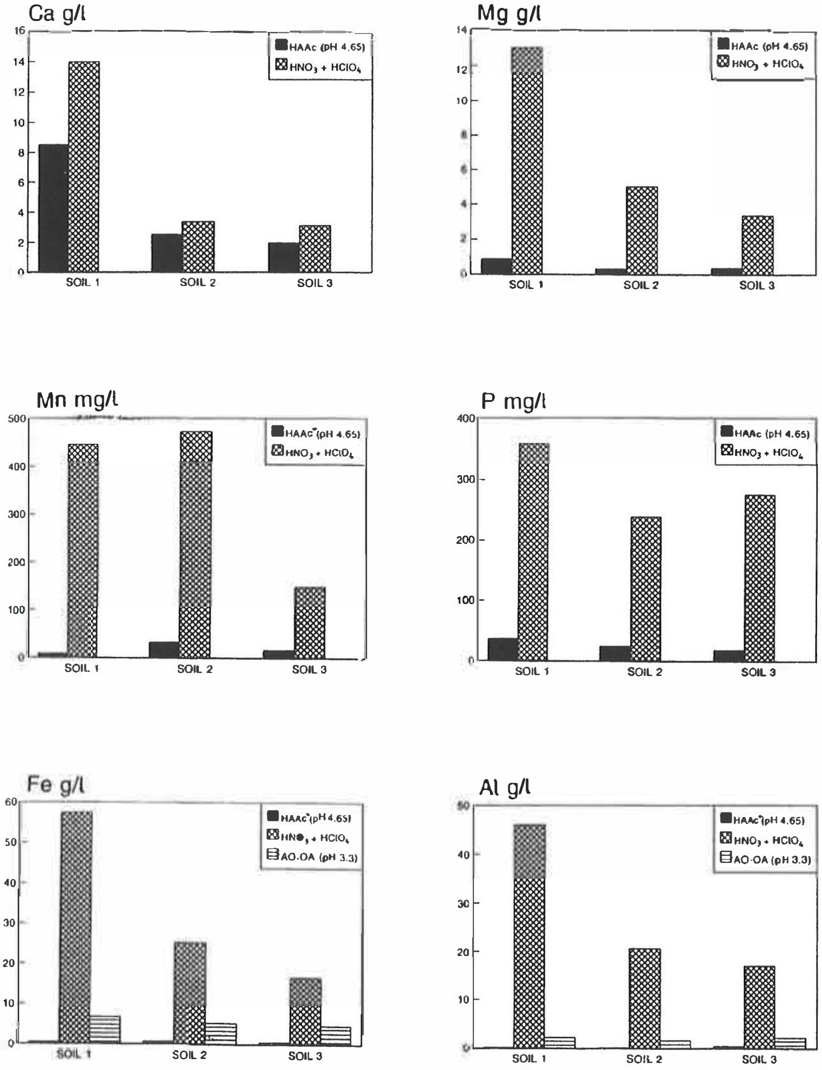


FIGURE 18. HNO_3+HClO_4-soluble amounts of Ca, Mg, Mn, P, Fe and Al compared with those extracted with acidic ammonium acetate HAAc (Ca, Mg, P) or with HAAc+EDTA (Mn, Fe, Al). For brevity, HAAc* denotes HAAc+EDTA. For Al and Fe, the oxalate extractable amounts are also given.

On the other hand, ^{51}V NMR proved to be a versatile method in elucidating species in aqueous solutions. Experiments were carried out at pH 3-12, and a wide concentration range ($3.7 \bullet 10^{-6}$-$1.9 \bullet 10^{-2}$ mol dm^{-3}) was utilized. Fig. 19 shows the concentration-dependence, and Fig. 20 the pH-dependence observed.

Because there were references[190,191] which argued that V(V) could be reduced by the organic matter of soil, it was necessary to try to estimate possible reduction. A ^{51}V NMR spectrum was recorded from a filtrate of a suspension in which 1.00 g of soil 2 was equilibrated for 72 h with 100.0 cm^3 of 10^{-4} M V(V) solution (in 0.02 M KCl) at soil's natural pH (Fig. 21a). The reference spectrum was obtained using a freshly prepared solution with corresponding pH, V(V) concentration, and number of scans. Because the spectra are identical and as V(IV) is NMR silent,[120] it can be concluded that reduction during adsorption needs not to be taken into account. Corresponding spectra were obtained for the other test soils, also.

Additional preliminary tests aimed at elucidating the possibility of the reduction of V(V) to V(IV) are discussed in Paper **4**. Using concentrated (0.1 M) and very acidic solutions ($\mathrm{pH} < 1$), reduction was detected when the solutions were also in contact with the test soils, but this occurred slowly (not within one week). The conclusion is that in conditions prevailing in mineral soils naturally, vanadate species have enough time to be adsorbed before reduction needs to be taken into account. For comparison, when chromium(VI), for example, is in contact with adsorbents containing organic matter, reduction plays an important role.[192,193] In the absence of reducing material, chromate is strongly retained by kaolinite.[194]

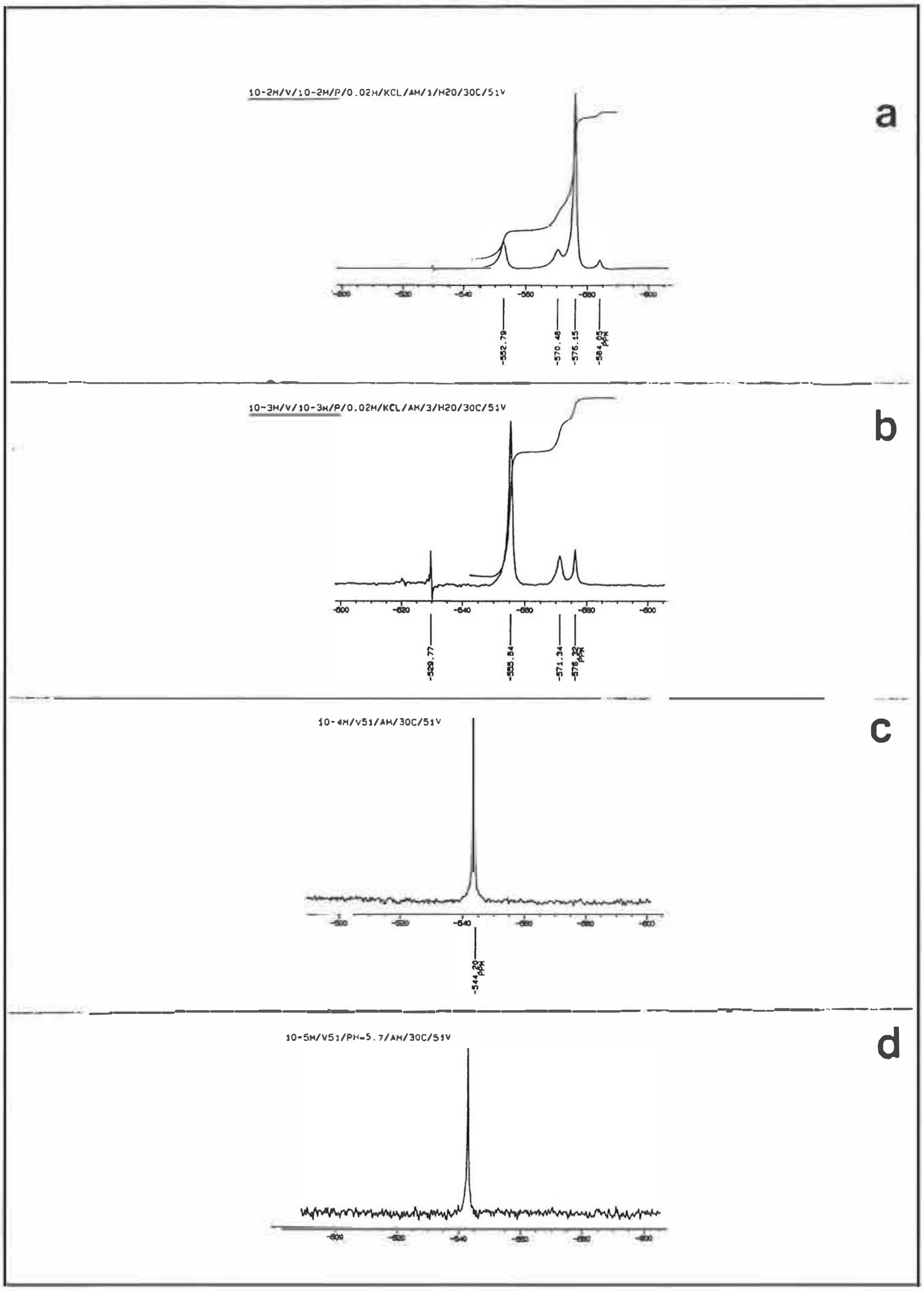


FIGURE 19. ^{51}V NMR spectra from dilute V(V) solutions. a) 10^{-2}, b) 10^{-3}, c) 10^{-4}, d) 10^{-5} M.

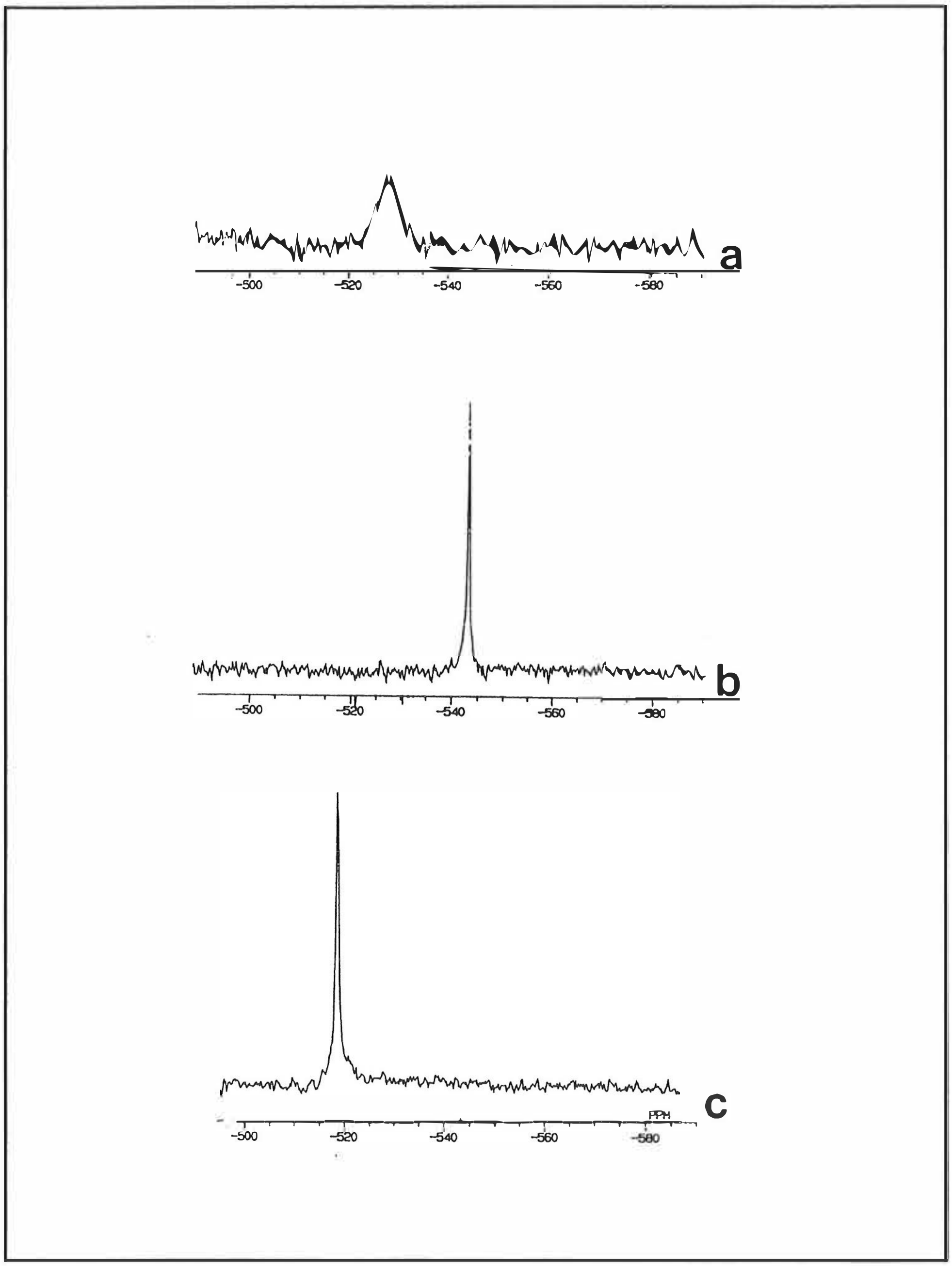


FIGURE 20. ^{51}V NMR spectra of a 10^{-5} M V(V) solution. a) pH 3, 274556 scans, b) pH 5.7, 84737 scans, c) pH 12, 317310 scans.

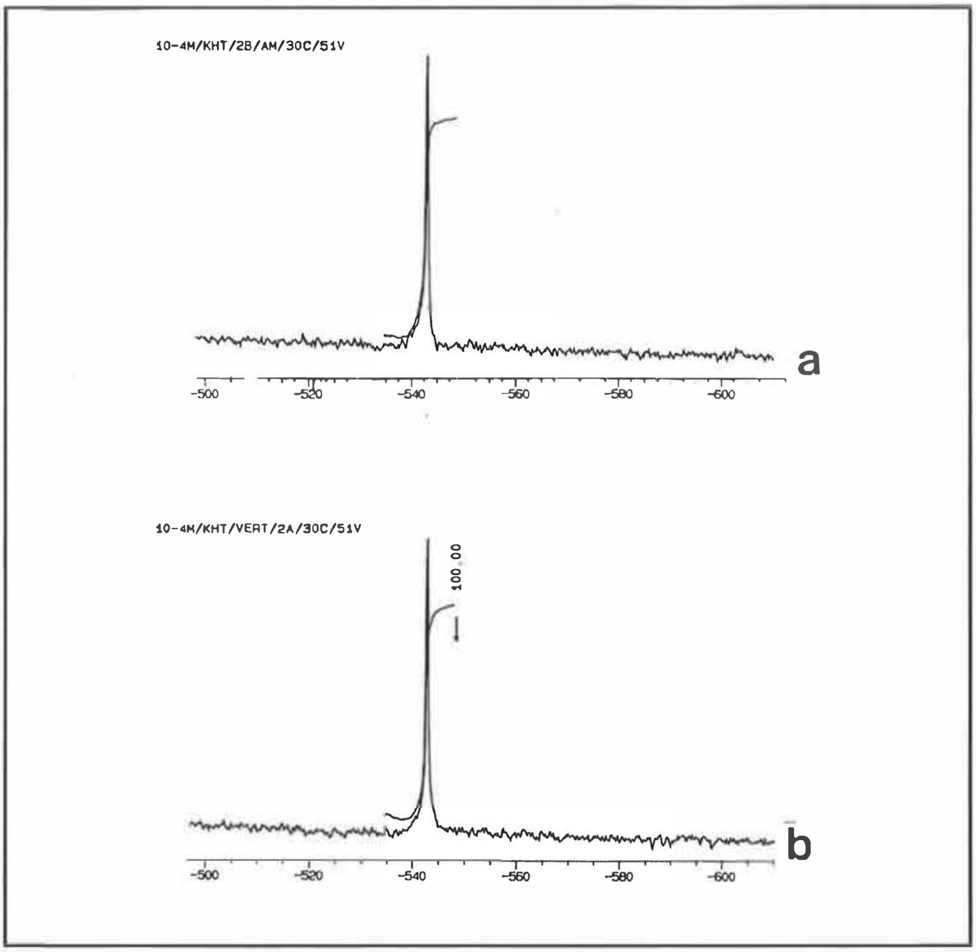


FIGURE 21. ^{51}V NMR spectra of V(V) solutions, concentration 3.35 μg cm^{-3}, pH = 5.99. a) a solution of initial C = 5.09 μg cm^{-3} which has been equilibrated with soil 2 for 72 h and then filtered (final concentration of V given above); b) a reference solution. 10000 scans.

6. CONCLUDING REMARKS

At the beginning of this study, we thought the lack of comprehensive knowledge about the soil chemistry and aqueous chemistry of Mo, V and W would not hinder our ease in performing adsorption and desorption experiments. Encountering some difficulties during the analytical work, we realized this study was quite a challenge. Soils seem to be unique materials, and Mo, V and W behave independently in aqueous solutions.

V(V), Mo(VI), and W(VI) were retained by kaolin and all test soils under appropriate conditions. At soils' natural pH, 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.

Although this study concentrates mainly on arable soils, it is hoped that it could be of use in predicting the behaviour of molybdenum, vanadium and tungsten in other environmental areas. Strictly speaking, the obtained results on adsorption are totally relevant only under the conditions used. First of all, this study explains adsorption of molybdate, vanadate or tungstate by mineral soils, not by soils high in organic matter. Second, in the adsorption procedure, critical factors were the equilibration time, concentration of V, Mo or W in the solution, mixing, temperature, concentration of the added inert salt and its cation, as well as the amounts of released cations and anions present in soil suspensions. When these results are used to predict the behaviour of these adsorbates by other soils, the characteristics of soils under consideration need to be known. One should always bear in mind the role of ionic strength also.

If adsorption occurs from a mixture containing several species capable of being adsorbed, their molar ratio can be of great importance. In the case where V, Mo or W are present simultaneously, one should not forget the possibility that heteropolyanions can be formed. In soils there may be competing species, like phosphate and sulphate present also, and these may make the aqueous chemistry of Mo, V, and W still more complicated.

Plasma emission spectrometry proved to be an excellent method for determination of the analytes in this work. Dilutions were necessary only in determining the acid-soluble amounts of Al, Fe, and some of the analyte nutrients. In adsorption and desorption experiments, all analyses could be carried out from the filtrates directly. No spiking of samples with known additions, or dilution was needed in routine runs. This made the measurements rather easy to perform. However, it became clear that if one wanted accurate analytical work, the minimum size of the soil samples had to be one gram. If the determinations are performed with Perkin-Elmer 2000 ICP Spectrophotometer, the concentrations of analytes at the beginning of the adsorption experiments cannot be less than 10^{-5} M.

At this stage one could say that the problems encountered in the determination of W from acidic samples proved fortunate as they prevented our carrying out fruitless analytical work. It is perhaps best to wait for exact information from scientists in solution chemistry before carrying out questionable experiments, in which extremely low concentrations of W are used.

It is not possible to explain retention of Mo, V or W thoroughly before the equilibria in aqueous solutions with different ionic strengths are known. Much research is therefore still needed, and the well-regarded, older methods, potentiometry and spectrophotometry, need to be used in conjunction with current methods, for example, NMR methods. Today, ^{51}V NMR seems to be very promising. It became obvious in this work also that Baes and Mesmer's[195] book, frequently used as a reference by soil scientists, is now outdated and should be replaced by more current material. Finally, it would be good to remember what Pope[25] wrote in the preface of his book:

"The field of polyoxometalates deserves wider attention, for example, from organic chemists, especially those concerned with homogenous and heterogenous catalysis, and from biochemists, solid state- and materials scientists."

REFERENCES

1. Mikkonen, A. and Tummavuori, J. *Acta Agric. Scand. Sect. B. Soil and Plant Sci. 43* (1993) 11.

2. Mikkonen, A. and Tummavuori, J. *Acta Agric. Scand. Sect. B. Soil and Plant Sci. 43* (1993) 206.

3. Mikkonen, A. and Tummavuori, J. *Acta Agric. Scand. Sect. B. Soil and Plant Sci. 43* (1993) 213.

4. Mikkonen, A. and Tummavuori, J. *Eur. J. Soil Sci.* 1994. In press.

5. Mikkonen, A. and Tummavuori, J. *Agric. Sci. Finl.* 1994. In press.

6. Travis, C.C. and Etnier, E.L. *J. Environ. Qual. 10* (1981) 8.

7. Bohn, H.L., McNeal, B.L. and O'Connor, G.A. *Soil Chemistry.* Wiley-Interscience, New York 1979. pp. 69-101, 171-192, 272-293.

8. Muljadi, D., Posner, A.M. and Quirk, J.P. *J. Soil Sci. 17* (1966) 213,230,238.

9. Hingston, F.J., Posner, A.M. and Quirk, J.P. *J.Soil Sci. 23* (1972) 177.

10. Barrow, N.J. *J. Soil Sci. 34* (1983) 751.

11. Jones, L.H.P. *J. Soil Sci. 8* (1957) 313.

12. Karlsson. N. *On Molybdenum in Swedish Soil and Vegetation and some related Questions.* Statens lantbrukskem. Kontrollanst. Medd. 23, 1961. pp. 13-23, 50-53, 61-106, 210-223.

13. Reyes, E.D. and Jurinak, J.J. *Soil Sci. Soc. Amer. Proc. 31* (1967) 637.

14. Kyriacou, D. *Surf. Sci. 8* (1967) 370.

15. Jaakkola, A. *Availability to Plants of Molybdenum in Finnish Mineral Soils.* Acta Agralia Fennica 126 (1972). The Scientific Agricultural Society of Finland. pp. 14, 22-41, 61-63, 85-86.

16. Gorlach, E., Gorlach, K. and Compała, A. *Agrochimica 6* (1969) 506.

17. Barrow, N.J. *Soil Sci. 109* (1970) 282.

18. Theng, B.K.G. *N.Z. J. Sci. 14* (1971) 1040.

19. Barrow, N.J. *Soil Sci. 113* (1972) 175.

20. Gonzalez B.R., Appelt, H., Schalscha, E.B. and Bingham, F.T. *Soil Sci. Soc. Amer. Proc. 18* (1974) 903.

21. Karimian, N. and Cox, F.R. *Soil Sci. Soc. Am. J. 42* (1978) 757.

22. Tytko, K.H., Baethe, G. and Cruywagen, J.J. *Inorg. Chem. 24* (1985) 3132.

23. Cruywagen, J.J. and Heyns, J.B.B. *Inorg.Chem. 26* (1987) 2569.

24. Cruywagen, J.J. and Heyns, J.B.B. *Polyhedron 10* (1991) 249.

25. Pope, M.T., *Heteropoly and Isopoly Oxometalates.* Springer-Verlag, Berlin Heidelberg New York Tokyo 1983. pp. 1-14, 33-57, 128-132, 136-141.

26. Kabata-Pendias, A. and Pendias, H. *Trace Elements in Soils and Plants.* CRC Press, Boca Raton, Fl. 1985. pp. 34-36, 64, 172, 178-182, 186, 199-208.

27. Quin, B.F. In: Aggett, J., Kjellström, T. and Crowe, D. (Eds.) *Proceedings of the Second New Zealand Seminar on Trace Elements and Health.* The New Zealand Trace Element Group 1979. pp.71-79.

28. Wiklander, L. *Grundförbättring 27* (1975/76) 125.

29. Barrow, N.J. *J. Soil Sci. 37* (1986) 267.

30. Ryden, J.C. and Syers, J.K. *J. Soil Sci. 26* (1975) 395.

31. Cruywagen, J.J. and Heyns, J.B.B. *J. Chem. Ed. 66* (1989) 861.

32. Cruywagen, J.J. and Heyns, J.B.B. *Talanta 37* (1990) 741.

33. Cruywagen, J.J. and van der Merwe, I.F.J. *J. Chem. Soc. Dalton Trans.* (1987) 1701.

34. Maksimovskaya, R.I. and Burtseva, K.G. *Polyhedron 4* (1985) 1559.

35. Hastings, J.J. and Howarth, O.W., *J. Chem. Soc. Dalton Trans.* 1992, 209.

36. Brady, N.C. *The Nature and Properties of Soils.* 9th ed. McMillan, New York 1984. pp. 381, 406-413.

37. Barber, S.A. *Soil Nutrient Bioavailability. 1. A Mechanistic Approach.* Wiley-Interscience. New York 1984. pp. 1-54, 331, 306-311, 338-345.

38. Brown, G., Newman, A.C.D., Rayner, J.H. and Weir, A.H., In: Greenland, D.J. and Hayes, M.H.B.(Eds.) *The Chemistry of Soil Constituents.* Wiley-Interscience, New York 1978. pp. 29-177.

39. Greenwood, N.N. and Earnshaw, A. *Chemistry of the Elements.* Pergamon Press, Oxford 1984. pp. 406-413, 1138-1186.

40. Lindsay, W.L. *Chemical Equilibria in Soils.* Wiley-Interscience. New York 1979. pp. 2-9, 51-55, 365-372, 389-390.

41. Bohn, H.L., McNeal, B.L. and O'Connor, G.A. *Soil Chemistry* 2nd ed. Wiley-Interscience, New York 1985. p. 129.

42. Bolt, G.H. and Bruggenwert, M.G.M. *Soil Chemistry. A. Basic Elements.* 2nd revised ed. Elsevier Scientific Publishing Company, Amsterdam Oxford New York 1978. p. 148.

43. Parfitt, R.L. *Adv. Agron. 30* (1978) 1.

44. Allen, B.L. and Hajek, B.F. In Dixon, J.B. and Weed, S.B. (Eds.) *Minerals in Soil Environments.* 2nd Ed. Soil Science Society of America, Madison, Wis. 1989. pp. 199-263.

45. *Viljavuustutkimuksen tulkinta peltoviljelyssä.* Viljavuuspalvelu Ltd. 1991.

46. Wild, A. In: Greenland, D.J. and Hayes, M.H.B. (Eds.) *The Chemistry of Soil Processes.* Wiley-Interscience, New York 1981.pp. 37-80.

47. Parks, G.A. *Adv. Chem. 67* (1967) 121.

48. Greenland, D.J. and Hayes, M.H.B. In: Greenland, D.J. and Hayes, M.H.B. (Eds.) *The Chemistry of Soil Processes.* Wiley-Interscience, New York 1981. pp. 1-35.

49. Wiklander, L. *NATO Conference Series 4* (1980) 239.

50. Bergeaux, P.J. *Bull. No 784.* Univ. Georgia, Coll. Agric. Coop. Ext. Service 1976, 1-18.

51. Gupta, U.C. and Lipsett, J. *Adv. Agron. 34* (1981) 73.

52. Vlek, P.L.G. and Lindsay, W.L. *Soil. Sci. Soc. Am. J. 41* (1977) 42.

53. Kelley. B.C. *Polyhedron 5* (1986) 597.

54. Koljonen, T. (Ed.) *Geochemical Atlas of Finland. Part 2. Till.* Geological Survey of Finland, Espoo 1992.

55. *Lannoitteiden ominaisuudet ja käyttö.* Kemira Ltd. 1988/13.

56. Bortels, H. *Arch. Mikrobiol. 1* (1930) 333.

57. Arnon, D.I. and Stout, P.R. *Plant Physiol. 14* (1939) 599.

58. Nicholas, D.J.D. In: Nicholas, D.J.D. and Egan, A.R. (Eds.) *Trace Elements in Soil-Plant-Animal Systems.* Academic Press, New York 1975, 181-198.

59. Schrauzer, G.N. In: Chappell, W.R. and Petersen K.K. (Eds.) *Molybdenum in the Environment.* Vol. I Dekker, New York 1976. pp. 243-265.

60. Hewitt, E.J. and Jones, E.W. *Annu. Rep. Long Ashton, Bristol Res. Sta.* 1948. pp. 81-90.

61. Petterson, N.K. and Purvis, E.R. *Soil Sci. Soc. Proc.* 1961, 111.

62. Smith, B.H. and Leeper, G.W. *J. Soil Sci. 20* (1969) 246.

63. Lavy, T.L. and Barber, S.A. *Soil Sci. Soc. Amer. Proc. 28* (1964) 93.

64. Follett, R.F. and Barber. S.A. *Soil Sci. Soc. Amer. Proc. 31* (1967) 26.

65. Follett, R.F. and Barber, S.A. *Soil Sci. Soc. Amer. Proc. 31* (1967) 191.

66. Stout, P.R., Meagher, W.R., Pearson, G.A. and Johnson, C.M. *Plant Soil 3* (1951) 51.

67. Barshad, I. *Soil Sci. 71* (1951) 387.

68. Kubota, J., Lazar, V.A., Langan, L.N. and Beeson, K.C. *Soil Sci. Soc. Amer. Proc. 25* (1961) 227.

69. Hornick, S.B., Baker, D.E. and Guss, S.B. *Crop production and animal health problems associated with high molybdenum soils.* Symposium on molybdenum in the environment. Denver, June 1975, p. 665.

70. Parker, R.D.R., Sharma, R.P. and Miller, G.W. In. Hemphill, D.D. (Ed.) *Trace Subst. Environ. Health.* Vol 12. University of Missouri 1978. pp. 340-350.

71. Cotton, F.A. and Wilkinson, G. *Advanced Inorganic Chemistry. A Comprehensive Text.* 4th ed. Wiley-Interscience, New York 1980. pp. 708-714, 844-861.

72. Faulkner Hudson, T.G. *Vanadium, Toxicology and Biological Significance.* Elsevier Publishing Co., Amsterdam 1964.

73. Andrews, M.J., Ball, T.K., Fuge, R., Nicholson, R.A. and Peachey, D. *Proc. Ussher Soc. 6* (1987) 536.

74. Hudson, M. *Chem. Brit.* 1982, 438.

75. Gough, L.P., Shacklette, H.T. and Case, A.A. *U.S. Geol. Surv. Bull. 1466* (1979) 55.

76. Tyler, G. *J. Environ. Qual. 5* (1976) 216.

77. Jacks, G. *Environ. Pollut. 11* (1976) 289.

78. Fu, M.H. and Tabatabai, M.A. *J. Environ. Qual. 17* (1988) 146.

79. Lahann, R.W. *Water Air Soil Poll. 6* (1976) 3.

80. Furr, A.K., Parkinson, T.F., Bache, C.A., Gutenmann, W.H., Pakkala, I.S. and Lisk, D.J. *J. Agric. Food Chem. 28* (1980) 660.

81. Levinen, R. *Kem.-Kemi 18* (1991) 116.

82. Pope, M.T. and Dale, B.W. *Q. Revs. 22* (1968) 527.

83. Shannon, R.D. *Acta Cryst. A 32* (1976) 751.

84. Baker, L.C.W., Lebioda, L., Grochowski, J., Mukherjee, H.G. *J. Am. Chem. Soc. 102* (1980) 3274.

85. Lebioda L., Giechanowicz-Rutkowska, M., Baker, L.C.W., Grochowski, J. *Acta Cryst. B36* (1980) 2530.

86. Souchay, P., Boyer, M. and Chauveau, F. *Kgl. Tek. Högsk. Handl.* No 259, 1972, pp. 159-172.

87. Lindqvist, I. *Acta Chem. Scand. 5* (1951) 568.

88. Schwarzenbach, G. and Meier, J. *J. Inorg. Nucl. Chem. 8* (1958) 302.

89. Sasaki, Y. and Sillén, L.G. *Ark. Kem. 29* (1967) 253.

90. Saxena, R.S. and Saxena, G.P. *Z. Phys. Chem. (N.F.) 29* (1961) 181.

91. Sasaki. Y., Lindqvist, I. and Sillén, L.G. *J. Inorg. Nucl. Chem. 9* (1959) 93.

92. Rohwer, E.F.C.H. and Cruywagen, J.J. *J. Suid-Afrikaanse Chem. Inst. 16* (1963) 26.

93. Sasaki, Y. and Sillén, L.G. *Acta Chem. Scand. 18* (1964) 1014.

94. Aveston, J., Anacker, E.W. and Johnson, J.S. *Inorg. Chem. 3* (1964) 735.

95. Glemser, O. and Höltje, W. *Angew. Chem. 78* (1966) 756.

96. Baldwin, W.G. and Wiese, G. *Ark. Kemi 31* (1968) 419.

97. Pungor, E. and Halasz, A. *J. Inorg. Nucl. Chem. 32* (1970) 1187.

98. Honig, D.S. and Kustin, K. *J. Phys. Chem. 76* (1972) 1575.

99. Wiese, G. and Böse, D. *Z. Naturforsch. 27B* (1972) 897.

100. Honig, D.S. and Kustin, K. *J. Inorg. Chem. 11* (1972) 65.

101. Jespersen, N.D. *J. Inorg. Nucl. Chem. 35* (1973) 3873.

102. Wiese, G. and Böse, D. *Z. Naturforsch. 29B* (1974) 630.

103. Tytko, K.H. and Schönfeld, B. *Z. Naturforsch. 30B* (1975) 471.

104. Cruywagen, J.J. and Rohwer, E.F.C.H. *Inorg. Chem. 14* (1975) 3136.

105. Cruywagen, J.J., Heyns, J.B.B. and Rohwer, E.F.C.H. *J. Inorg. Nucl. Chem. 38* (1976) 2033.

106. Cruywagen, J.J., Heyns, J.B.B. and Rohwer, E.F.C.H. *J. Inorg. Nucl. Chem. 40* (1978) 53.

107. Johansson, G., Pettersson, L. and Ingri, N. *Acta Chem. Scand. A33* (1979) 305.

108. Cruywagen, J.J. *Inorg. Chem. 19* (1980) 552.

109. Tytko, K.H. *Polyhedron 5* (1986) 497.

110. Baethe, G., *Untersuchungen am System* H^+/MoO_4^{2-} *in wässrigen Medien.* Ph. D. Thesis, Göttingen 1985.

111. Folorunso Ojo, J.F., Taylor, R.S. and Sykes, A.G. *J.C.S., Dalton Trans.* 1975, 500.

112. Brown, P.L., Shying, M.E. and Sylva, R.N. *J. Chem. Soc., Dalton Trans.* 1987, 2149.

113. Mellström, R. and Ingri, N. *Acta Chem. Scand. A 28* (1974) 703.

114. Tytko, K.H. and Trobisch, U. Mo. Oxide hydrates. Molybdate ions. In Katscher, H. and Schröder. F. (Eds.) *Gmelin Handbook of Inorganic Chemistry.* Supplement vol. B 3a. 8th ed. Springer-Verlag, Berlin 1987.

115. Ingri, N. and Brito, F. *Acta Chem. Scand. 13* (1959) 1971.

116. Brito, F. *Acta Chem. Scand. 21* (1967) 1968.

117. Habayeb, M.A. and Hileman, Jr. O.E. *Can. J. Chem. 58* (1980) 2255.

118. Heath, E. and Howarth, O.W. *J.C.S. Dalton Trans.* 1981, 1105.

119. Pettersson, L., Andersson, I. and Howarth, O.W. *Inorg. Chem. 31* (1992) 4032.

120. Pettersson, L., Hedman, B., Nenner, A.-M. and Andersson, I. *Acta Chem. Scand. A 39* (1985) 499.

121. Pettersson, L., Andersson, I. and Hedman, B. *Chem. Scripta 25* (1985) 309.

122. Harnung, S.E., Larsen, E. and Pedersen, E.J. *Acta Chem. Scand. 47* (1993) 674.

123. Pettersson, L., Andersson, I. and Öhman, L.O. *Acta Chem. Scand. A 39* (1985) 53.

124. Courtin, P., *Bull. Soc. Chim. France* 1974, 2747, 2751.

125. Maksimovskaya, R.I. and Chumanenko, N.N. *Polyhedron 6* (1987) 1813.

126. Howarth, O.W., Pettersson, L. and Andersson, I., *J. Chem. Soc. Dalton Trans.* 1989, 1915.

127. Howarth, O.W., Petterson, L. and Andersson, I. *J. Chem. Soc. Dalton Trans.* 1991, 1799.

128. Harrison, A.T. and Howarth, O.W. *J. Chem. Soc. Dalton Trans.* 1985, 1953.

129. Leparulo-Loftus, M.A. and Pope, M.T. *Inorg. Chem. 26* (1987) 2112.

130. Howarth, O.W. and Hastings, J.J. *Polyhedron 9* (1990) 143.

131. Mott, C.J.B. In: Greenland, D.J. and Hayes, M.H.B. (Eds.) *The Chemistry of Soil Processes*. Wiley-Interscience, New York 1981.pp. 179-219.

132. Stumm, W., Kummert, R. and Sigg, L., *Croat. Chem. Acta 53* (1980) 291.

133. Cradwick, P.D.G., Farmer, V.C., Russell, J.D., Masson, C.R., Wada, K. and Yoshinaga, N. *Nature(London), Phys. Sci. 240* (1972) 187.

134. Parfitt, R.L., Thomas, A.D., Atkinson, R.J. and Smart, R.St.C. *Clays Clay Miner. 22* (1974) 455.

135. Bowden, J.W., Bolland, M.D.A., Posner, A.M. and Quirk, J.P. *Nature(London) Phys. Sci. 245* (1973) 81.

136. Bowden, J.W., Posner, A.M. and Quirk,J.P. *Aust. J. Soil Res. 15* (1977) 121.

137. Davis, J.A. and Leckie, J.O. *ACS Symposium Series 93* (1979) 299.

138. Goldberg, S. and Traina, S.J. *Soil Sci. Soc. Am. J. 51* (1987) 929.

139. Langmuir, I. *J. Amer. Chem. Soc. 40* (1918) 1361.

140. Freundlich, H. *Colloid and Capillary Chemistry*. (English transl.) Methuen and Co. Ltd, London 1918.

141. Barrow, N.J. *J. Soil Sci. 40* (1989) 415.

142. Murali, V. and Aylmore, L.A.G. *Soil Sci. 136* (1983) 279.

143. Roy, W.R., Hassett, J.J. and Griffin, R.A. *Soil Sci. 142* (1986) 203.

144. Roy, W.R., Hassett, J.J. and Griffin, R.A. *Soil Sci. Soc. Am. J. 50* (1986) 1176.

145. Johnson, C.M. and Arkley, T.H. *Anal. Chem. 26* (1954) 572.

146. Bermejo-Barrera, P., Vazquez-Gonzalez, J.F. and Bermejo-Martinez, F. *Analyst 112* (1987) 473.

147. Williams, W.J. *Handbook of Anion Determination.* Butterworths, London 1979. pp. 103-119.

148. Reisenauer, H.M., Tabikh, A.A. and Stout, P.R. *Soil Sci. Soc. Amer. Proc. 26* (1962) 23.

149. McKenzie, R.M. *Austr. J. Soil Res. 21* (1983) 505.

150. Motta, M.M.G. and Ferreira de Miranda, C. *Rev. Port. Quim. 27* (1985) 505.

151. Van Veen, J.A.R. and Hendriks, P.A.J.M. *Polyhedron 5* (1986) 75.

152. Cruywagen, J.J. and De Wet, H.F. *Polyhedron 7* (1988) 547.

153. Misra, s.G. and Mishra, K.C. *Technology 6* (1969) 140.

154. Mishra, K.C. and Misra, S.G. *J. Indian Soc. Soil Sci. 20* (1972) 259.

155. Lal, S., De, S.K. and Srivastava, S.K. *An. Edafol. Agrobiol. 32* (1973) 283.

156. Lal, S., De, S.K. and Tripathi, C.M. *J. Indian Chem. Soc. 50* (1973) 535.

157. Pasricha, N.S. and Randhawa, N.S. *Agrochimica 21* (1977) 105.

158. Tanner, P.D. *Rhod. J. Agric. Res. 16* (1978) 31.

159. Jarrell, W.M. and Dawson, M.D. *J. Soil Sci. Soc. Am. 42* (1978) 412.

160. Haynes, R.J. *Soil Sci. 135* (1983) 221.

161. Barrow, N.J., Leahy, P.J., Southey, I.N. and Purser, D.B. *Austr. J. Agric. Res. 36* (1985) 579.

162. Roy, W.R., Hassett, J.J. and Griffin, R.A. *J. Soil Sci. 40* (1989) 9.

163. Thakur, D.N. and Das, B. *J. Indian Soc. Soil Sci. 35* (1987) 647.

164. Ferreira de Miranda, C., Manuela Mota Batista, M. and De Lourdes Pimenta da Silva, M. *Rev. Port. Quim. 25* (1983) 45.

165. Williams, C. and Thornton, I. *Plant Soil 39* (1973) 149.

166. Lowe, R.H. and Massey, H.F. *Soil Sci. 100* (1965) 238.

167. Barrow, N.J. *Soil Sci. 116* (1974) 423.

168. Tamm, O. *Medd. Statens Skogsförsöksanstalt 19* (1922) 387.

169. Grigg, J.L. *N.Z.J. Sci. Technol. 34* (1953) 405.

170. McKeague, J.A. and Day, J.H. *Can. J. Soil Sci. 46* (1966) 13.

171. Deshpande, T.L., Greenland, D.J. and Quirk, J.P. *J. Soil Sci. 19* (1968) 108.

172. Roth, C.B., Jackson, M.L. and Syers, J.K. *Clays Clay Miner. 17* (1969) 253.

173. Coffin, D.E. *Can J. Soil Sci. 43* (1963) 7.

174. Bassett, J., Denney, R.C., Jeffrey, G.H. and Mendham, J. (Eds.) *Vogel's Textbook of Quantitative Inorganic Analysis.* 4th Ed. Longman Group Ltd., London 1975. pp.471-472.

175. Fossum, J.H., Markunas, P.C. and Riddick, J.A. *Anal. Chem. 23* (1951) 491.

176. Sabatini, A., Vacca, A. and Gans, P. *Talanta 21* (1974) 53.

177. Mikkonen, A. and Tummavuori, J. *Determination of Molybdenum, Tungsten and Vanadium by ICP-AES from Potassium Chloride Solutions.* Abstracts, 12th NASTEC, Stenungsbaden, Sweden 1989.

178. Mikkonen, A. and Tummavuori, J. *Determination of Tungsten by ICP-AES from Acidic samples.* University of Oulu, Report Series in Chemistry, Special report 29, 1990, p. 50-51.

179. Alcamo, J., Amann, M., Hettelingh, J.P., Holmberg, M., Hordijk, L., Kämäri, J., Kauppi, L., Kauppi, P., Kornai, G. and Mäkelä, A. *Ambio 16* (1987) 232.

180. Kauppi, P., Kämäri, J., Posch, M., Kauppi, L. and Matzner, E. *Ecol. Modell. 33* (1986) 231.

181. Gupta, U.C. *Plant Soil 34* (1971) 249.

182. Schwertmann, U. In: Schachtschabel, P., Blume, H.-P., Brümmer,G., Hartge, K.-H. and Schwertmann, U.(Eds) *Lehrbuch der Bodenkunde.* 12th edition. Ferdinand Enke Verlag, Stuttgart 1989.

183. Edzwald, J.K., Toensing, D.C. and Chi-Yew Leung, M. *Environ. Sci. Technol. 10* (1976) 485.

184. Cruywagen, J.J. and Pienaar, A.T. *Polyhedron 8* (1989) 71.

185. Ulrich, B. Z. *Pflanzenehrnähr. Bodenkd. 144* (1981) 647.

186. Ulrich, B. In: Ulrich, B. and Pankrath, J. (Eds.) *Effects of Accumulation of Air Pollutants in Forest Ecosystems.* Reidel Dordrecht, The Netherlands 1983. pp. 127-146.

187. Miller, J.C. and Miller, J.N. *Statistics for Analytical Chemistry*. Ellis Horwood Ltd., England 1984.

188. Cruywagen, J.J., Heyns, J.B.B. and Visagie, J.L. *Polyhedron 8* (1989) 1800.

189. Mikkonen, A. and Kolehmainen, E. *^{17}O NMR Study of Vanadate, Molybdate and Tungstate Equilibria in Aqueous Solutions*. Department of Chemistry, University of Jyväskylä, Research Report N:o 40. Jyväskylä 1992. pp.78-79.

190. Szalay, A. and Szilágyi, M. *Geochim. Cosmochim. Acta 31* (1967) 1.

191. Goodman, B.A. and Cheshire, M.V. *Geochim. Cosmochim. Acta 39* (1975) 1711.

192. Bartlett, R.J. and Kimble, J.M. *J. Environ. Qual. 5* (1976) 379, 383.

193. Cary, E.E., Allaway, W.H. and Olson, O.E. *J. Agric. Food Chem. 25* (1977) 305.

194. Griffin, R.A., Au, A.K. and Frost, R.R. *J. Environ. Sci. Health A12* (1977) 431.

195. Baes, C.F. and Mesmer, R.E. *The Hydrolysis of Cations*. Wiley-Interscience, New York 1976.

PAPER 1

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Retention of Vanadium(V), Molybdenum(VI) and Tungsten(VI) by Kaolin

Mikkonen, A. and Tummavuori, J. (University of Jyväskylä, Department of Chemistry, PO Box 35, SF-40351 Jyväskylä, Finland). Retention of vanadium(V), molybdenum(VI) and tungsten(VI) by kaolin. Accepted September 9, 1992. Acta Agric. Scand., Sect. B, Soil and Plant Sci. 43: 11–15, 1993. © Acta Agric. Scand. 1993.

The ability of kaolin (approximately $H_2Al_2Si_2O_8 \cdot H_2O$), a well known clay mineral constituent, to retain V(V) andMo(VI) species from 10^{-5} and 10^{-4} M solutions, and W(VI) species from 10^{-4} M solutions was investigated in the pH range 2–7.5 using a solid/liquid ratio 1:100 (w:v). The equilibration time in the adsorption studies was 72 h, and the shaking time in the desorption studies was 17 h. 0.02 M KCl was used as ionic medium and desorbing liquid. V(V), Mo(VI) and W(VI) were all retained by kaolin to some extent, and the amounts of the elements which could be washed away from kaolin with 0.02 M KCl were very small. The pH dependence of the adsorption was considerable: when added alone, all three elements were adsorbed strongly at about pH 4, but above pH 6.5 only V was retained in noticeable amounts. When V, Mo and W were added simultaneously, the adsorption curves showed that adsorption of Mo(VI) predominates at pH 4, whereas W(VI) and V(V) predominate at pH 5–6 and pH > 6.5, respectively.

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Key words: clay, adsorption, desorption.

Introduction

Molybdenum is an essential element for plants because it is needed in nitrogen fixation and nitrate reduction. It is added to soils as fertilizer, because the plant-available concentrations occurring naturally in many soils are too low (Kabata-Pendias & Pendias, 1985). In order to explain the behaviour of molybdenum in soils, many adsorption studies have been conducted using both different soils and various ‘reference materials’, of which clays, Al and Fe oxides, and activated carbon are the most important.

The geochemical behaviour of W resembles that of Mo. The soil phosphatase activity is known to be influenced by V (Tyler, 1976). The concentrations of W and V in some areas may be quite high, due to ore mining, sewage sludge application or fuel oil combustion (Fu & Tabatabai, 1988; Jacks, 1976). Because it is assumed that V and W could substitute for molybdenum in the nitrate reductase enzyme (Heimer et al., 1969; McKenna et al., 1970; Burns et al., 1971; Benemann et al., 1972) it is important to know how these elements are retained by various adsorbing materials.

Retention of Mo(VI) by different adsorbing reference materials has been studied by Jones (1957), Karlsson (1961), Kyriacou (1967), Theng (1971), Hingston et al. (1972), McKenzie (1983), Motta & Ferreira de Miranda (1985) and Cruywagen & de Wet (1988). Adsorption of W(VI) has been investigated by Kyriacou (1967) and Cruywagen & Pienaar (1989). Kyriacou (1967) has also measured retention of V(V) by α-hematite.

The aim of the present research was to study systematically adsorption of V(V), Mo(VI) and W(VI) by kaolin under similar conditions, so that the results obtained for adsorption of single elements could be directly compared. The concentrations used here were the lowest that could be accurately measured with our ICP equipment. In 10^{-5} and 10^{-4} M solutions the monoionic species predominate, but in 10^{-4} M V(V) and W(VI) solutions, in particular, polyanions also exist. Desorption of V(V), Mo(VI) and W(VI) was also studied systematically. Investigations are scarce on desorption for Mo and unavailable for the other two elements.

Material and methods

Adsorption

Kaolin, approximately $H_2Al_2Si_2O_8 \cdot H_2O$ (Kaolin.-pond.Ph.Eur.III 180 µm) was provided by the Helsinki University Pharmacy. X-Ray diffraction analysis showed that it contained kaolinite and traces of muscovite. The powder used was for medicinal use, and the amounts of Mo, V and W and other heavy metals in kaolin were neglible. The following characteristics were also measured: pH(H_2O) 4.5, pH($CaCl_2$) 3.9, and CEC(KCl) 3.1 mequiv./100 g.

Vanadium, Mo and W stock solutions (0.100 M) were prepared by dissolving 0.100 mol of each sodium salt in water (V salt in hot water) and diluting with water to the final volume of 1000 ml. After the accurate concentrations had been checked against commercial 1000 mg l^{-1} stock solutions, these solutions were stored in polyethylene bottles. The stock solutions were diluted to 10^{-3} and 10^{-4} M solutions and made 0.2 M with respect to KCl. The mixture of Mo, V and W was prepared by putting 10.0 ml from each 0.100 M stock solution into a 1 l bottle, and after adding 0.2 mol of KCl, diluting the mixture to 1000 ml with distilled water.

1.000 g portions of kaolin were placed in 250 ml beakers. 90.0 ml of deionized water and 10 ml aliquots of 10^{-3} M Na_2MoO_4, Na_2WO_4 or $NaVO_3$ or their mixture in 0.2 M KCl were added. For Mo and V, another series of experiments were conducted by adding 10^{-4} M solutions instead of 10^{-3} M solutions. Dilute HCl or NaOH was added to the suspensions in order to approximate the pH sought. The sample beakers were covered with Parafilm and then shaken manually for 2–3 min. A period of 72 h at room temperature was allowed for acid–base equilibration. The final pH values in the suspensions were recorded prior to filtration using an Orion EA 920 pH meter and a combination electrode. The reliability of the pH measurements was checked after every tenth sample using pH 7.00 or 4.01 buffer solutions. The samples were filtered through Whatman 40 filter paper. About 40 samples were needed to produce each adsorption curve.

Desorption

The kaolin samples from the first filtration were air-dried at room temperature, and after storage for 3–4 months (for technical reasons), weighed and placed in 100 ml polyethylene bottles. Aliquots of 50 ml of 0.02 M KCl (initial pH 5.2) were added to the samples. The bottles were shaken for 17 h in a mechanical stirrer. After shaking, the samples were filtered through Whatman 40 filter paper.

Determination of Mo, V and W in the adsorption filtrates was made by a Perkin-Elmer ICP 5000 plasma emission spectrometer, and in the desorption filtrates by a Perkin-Elmer 2000 ICP-AES spectrometer. 1000 mg l^{-1} commercial stock solutions were used for preparation of the working standards, which were 0.02 M with respect to KCl. The measuring wavelengths were 309.31(1), 202.03(0) and 207.91(1) nm for V, Mo and W, respectively. The standard addition method was used as a control. The amounts of adsorbed Mo, V and W were calculated as the difference of the initial concentration of the added salt solution and the amount left in the solution after equilibration. Desorption was calculated by measuring the concentrations of Mo, V and W in the filtrates after a 17 h shaking period and expressing the desorbed amount per gram of dry kaolin.

To check that no significant loss of molybdenum, tungsten or vanadium occurred during the filtration steps or ICP measurements, standard solutions with pH values and concentrations corresponding to the samples were filtered as samples through the Whatman 40 filter paper. This step revealed that adsorption experiments of tungsten could not be carried out using an initial concentration of 10^{-5} mol l^{-1}. In the most acidic samples, tungsten was retained by the nebulizer-torch system of the ICP, so that serious memory effects occurred. This phenomenon was also noticed when measuring the most acidic samples (pH < 2.8) of 10^{-4} M solutions, so that adsorption and desorption at this concentration were finally measured

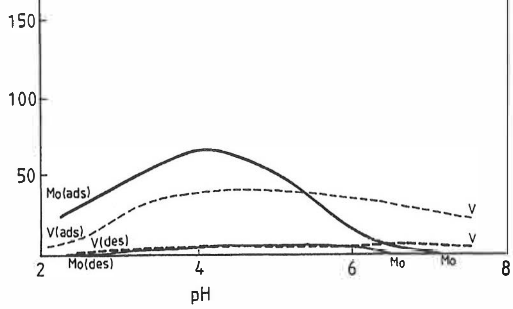

Fig. 1. Adsorption of V(V) and Mo(VI) from 10^{-5} M solutions. The solutions initially contained 50.94 µg of V and 95.94 µg of Mo in 0.02 M KCl.

only at pH 2.8–7.5, where ICP determinations were reliable.

Results and discussion

Adsorption of vanadium(V) and molybdenum(VI) versus pH from 10^{-5} M solutions containing entirely V(V) or Mo(VI) in 0.02 M KCl was measured (Fig. 1). Adsorption of V(V), Mo(VI) and W(VI) from 10^{-4} M solutions of these elements (in 0.02 M KCl) was also measured (Fig. 2). Adsorption when all three elements were added simultaneously is presented in Fig. 3. Each curve has been fitted using about 40 analytical test points. No replicate analyses were conducted. The pH interval between the test points was 0.1–0.2 pH units, and as adsorption was plotted versus pH in the suspension, the shape of each curve could immediately be seen.

The various chemical forms of Mo(VI) and V(V), and the pH intervals where they occur, have been reviewed by Pope (1983). W(VI) equilibria in 10^{-4} or 10^{-5} M solutions are not known, but equilibria in more concentrated solutions have been investigated by Cruywagen & van der Merwe (1987).

10^{-5} M solutions of V(V) and Mo(VI) contain only monomeric species (Pope & Dale, 1968; Cruywagen & Heyns, 1989). Below pH 3 vanadium was very poorly adsorbed (Fig. 1). This means that adsorption of VO_2^+ was neglible. At pH 3–8, where H_3VO_4 and $H_2VO_4^-$ predominate, significant adsorption occurred. The pK_a values of these two forms are 3.8 and 7.8 (Pope, 1983), respectively, and it is probable that both forms were adsorbed. The pK_a value of the HVO_4^{2-} ion in dilute alkaline salt solution is about 13.2 (Cruywagen & Heyns, 1990), so this ion did not occur at the pH range of this study. The adsorption curve of V(V) had no sharp maximum value. The adsorption of Mo(VI) reached its maximum at pH 4. The pK_a values of molybdic acid are 3.66 and 3.81 (Cruywagen & Heyns, 1989). At about pH 4 all three forms of molybdic acid, $Mo(OH)_6$, $HMoO_4^-$ and MoO_4^{2-} were adsorbed. As the pH decreased, adsorption of $Mo(OH)_6$ also decreased. At pH > 5, where the MoO_4^{2-} ion is the predominating ionic form, adsorption also started to decrease. At pH > 7 molybdenum was not retained by kaolin. Both vanadium and molybdenum were strongly held, and only a small amount of adsorbed elements could be washed away with 0.02 M potassium chloride. This extractant was selected because it was also present during the adsorption step. A period of 17 h was selected for shaking, because it is technically more suitable than the 16 h which has frequently been used in desorption of phosphate (e.g. Bayomi & Rehan, 1984). It may be that readsorption of the leached elements occurred during shaking, because the pH in the solutions after shaking was about 4. The pH in the second suspension rose to about 6 only during shaking of the most basic samples with initial pH > 6.

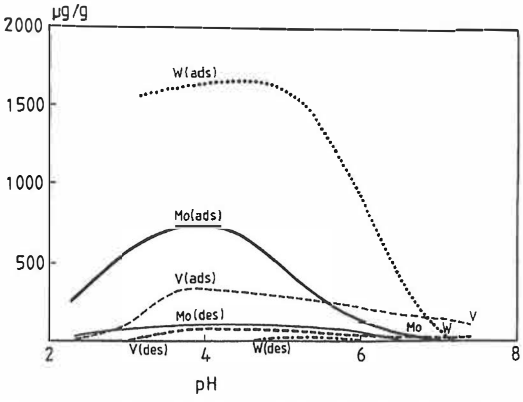

Fig. 2. Adsorption of V(V), Mo(VI) and W(VI) from 10^{-4} M solutions. The solutions initially contained 509.4 µg of V, 959.4 µg of Mo and 1838.5 µg of W in 0.02 M KCl.

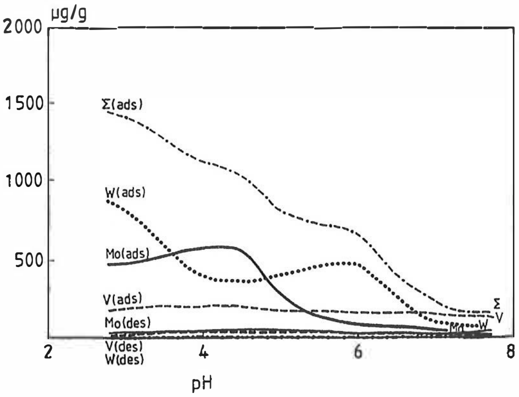

Fig. 3. Adsorption of vanadium, molybdenum and tungsten from a 10^{-4} M V+Mo+W solution, which initially contained 509.4 µg of V, 959.4 µg of Mo and 1838.5 µg of W.

At below pH 3, and especially above 5, vanadium was adsorbed relatively more from 10^{-5} M than from 10^{-4} M solution (Fig. 2). At pH 2 to about 4.5, 10^{-4} M vanadium solutions contain vanadyl cations, VO_2^+, and polyanions $H_2V_{10}O_{28}^{4-}$ and $HVO_{10}O_{28}^{5-}$ (Pope & Dale, 1968). The $H_2VO_4^-$ ion is the predominating species at pH 4.5–8. The presence of polyions in 10^{-4} M solution did not change the shape of the adsorption curve dramatically in comparison with the curve presented in Fig. 1, so that adsorption of these species was not very marked. The maximum amount of vanadium that could be adsorbed from 10^{-5} M solution was 75–80%, which makes about 40.8 µg of V(V). From 10^{-4} M solution only about 65% (331µg) was adsorbed, but it can be seen that kaolin has a capacity to retain far more vanadium than had been adsorbed from 10^{-5} M solution.

Molybdenum was adsorbed relatively more at pH < 4 and relatively less at pH 5–6 from 10^{-4} M solution than from 10^{-5} M solution. It can be assumed that in 0.02 M KCl 10^{-4} M Mo(VI) solutions contain only the same monomeric species which are present in 10^{-5} M solutions. Part of the Mo which was adsorbed from 10^{-4} M solution was not very tightly held by kaolin and could be washed away by shaking with 0.02 M KCl. About 70% of Mo present in 100 ml of 10^{-4} M Na_2MoO_4 solution (959.4 µg) was adsorbed at pH 4. This means that a loading of 671 µg of Mo per gram of kaolin has been obtained. When adsorption took place from 10^{-5} M solution, all adsorption sites were not occupied, perhaps because during the equilibration period not all the molybdate ions reached the surface of the adsorbent. Shaking the suspensions would perhaps have increased the adsorption of ions from the more dilute solutions.

Tungsten (Fig. 2) was effectively adsorbed by kaolin from acidic solutions, and even at pH 5.5 about 90% of W(VI) present in 10^{-4} M (1838 µg) was retained. This means that a loading of about 1650 µg of W per gram kaolin could be obtained. Kaolin holds W very tightly, and practically nothing could be leached away by shaking with 0.02 M KCl.

The adsorption curves of Fig. 3 differ clearly from those of Fig. 2. At pH < 3, adsorption of W(VI) is most significant. It may be that a small part of V formed some kind of a new polyion with tungsten, and was adsorbed simultaneously with W. A preliminary study showed that a 0.001 M V(V) + W(VI) solution is light yellow in colour. Combination of 10^{-3} M sodium metavanadate and sodium molybdate solutions produced a colourless solution. In the kaolin salt solution suspensions the light yellow colour was also observed. Our ^{17}O NMR studies showed that the signal of the WO_4^{2-} ion disappeared in the presence of vanadate salt. One explanation might also be that a redox reaction occurred in the solution which contained all three metals.

It is possible that the adsorbed species were not exactly the same as in the situation where the metals were added separately. Condensation to polyions may have occurred, because the ionic strength in the V + Mo + W solution was slightly higher than in solutions containing V, Mo or W alone in 0.02 M KCl. From the mixture, adsorption of Mo reached its maximum at pH 4, and simultaneously adsorption of W had a local minimum. These two elements seem to have been adsorbed onto the same adsorption sites, and Mo is more strongly adsorbed than W. When adsorption of Mo decreased, W again started to be adsorbed (at pH 6). At pH > 7, adsorption of V became predominant. The sum of adsorbed metals has two maxima (Fig. 3), one at pH 4 due to maximum adsorption of Mo and the other at pH 6, which shows the strong adsorption of W. 100 ml of 10^{-4} M V + Mo + W solution contained 509.4 µg of V(V), 959.4 µg of Mo(VI) and 1838.5 µg of W(VI), 3307.8 µg in total. At about pH 3, where maximum adsorption took place, only about 1500 µg was adsorbed. This means that only about 45% of the total amount of metals was retained by kaolin. The adsorbed species of V, Mo and W were strongly held by kaolin, and only a very small amount of Mo could be leached with 0.02 M KCl (Fig. 3). During the long storage time, 3–4 months after the adsorption step, transformation of the adsorbed species to less soluble or penetrated forms may have taken place.

The results obtained here for adsorption of molybdate are principally the same as those obtained by Jones (1957), Theng (1971) and Motta & Ferreira de Miranda (1985). Molybdenum is retained from dilute solutions mainly at pH 4, the $HMoO_4^-$ ion being the most strongly adsorbed species. An ionic medium, shaking of the samples and equilibration time seem to be less important factors than expected. In more concentrated solutions of Mo they would probably be more dominant, and adsorption of polyionic species could also occur. According to Kyriacou (1967) and Cruywagen & De Wet (1988), α-hematite and activated carbon might be more efficient adsorbents of Mo than clay minerals, with respect either to the velocity of the adsorption reaction or to the amount that can be adsorbed.

The results obtained for adsorption of V and W can also be compared with the results of Kyriacou (1967) and Cruywagen & De Wet (1988), who used α-hematite and activated carbon as adsorbents, respectively. It is logical to assume that activated carbon is more effective as an adsorbent than kaolin, because its surface area is very great, 300–2000 m^2/g (Greenwood & Earnshaw, 1984). The adsorption curves of V and W obtained in the present study were slightly different from those of Kyriacou, who found that at pH 8 about 60% of W and about 80% of V from the initial 8.6×10^{-4} M and 4.3×10^{-4} M solutions were still adsorbed. Kyriacou used a solid to liquid ratio of 2 g per 150 ml, an equilibration period of 10 min and 0.1 M NaCl as ionic medium, and these factors may explain the differences between the adsorption curves.

Because clays are an essential component of cultivated soils, the results obtained in this paper might perhaps be utilized in predicting the behaviour of V, Mo and W in soils. It is possible, however, that when these metals are adsorbed by soils, some other soil constituents, for instance organic material or amorphous oxides of Fe of Al, are more efficient adsorbents than clay minerals. Adsorption from a mixture revealed that the results which are obtained for adsorption of a single element cannot be generalized to mixtures of elements. It is probable that in soils which contain moderate amounts of P, the shapes of the adsorption curves could be different, because the phosphate ion is known to be more strongly adsorbed than molybdate (Barrow, 1970). If adsorption by soils would be similar to that of kaolin, then at pH 5–7, which is common in cultivated soils, Mo would be readily available for plants, and V and W would be partly adsorbed.

Kaolin might be used to collect anions from waste waters which would otherwise constitute environmental risks. By regulating pH, V, Mo and W could be collected sequentially from a dilute solution of their mixture. In this study the mixture solution is 10^{-4} M with respect to V, Mo and W. If there had been great differences in the relative concentrations of these elements, the adsorption curves might have been different.

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References

Barrow, N. J. 1970. Comparison of the adsorption of molybdate, sulfate and phosphate by soils. Soil Sci. 109, 282–288.

Bayomi, N. A. & Rehan, M. R. 1984. Phosphate adsorption and desorption as affected by soil properties. Egypt. J. Soil Sci. 24, 53–66.

Benemann, J. R., McKenna, C. E., Lie, R. F., Taylor, T. G. & Kamen, M. D. 1972. Vanadium effect in nitrogen fixation by Azotobacter. Biochem. Biophys. Acta 264, 25–38.

Burns, R. C., Fuchsman, W. H. & Hardy, R. W. F. 1971. Nitrogenase from vanadium-grown Azotobacter: isolation, characteristics and mechanistic implications. Biochem. Biophys. Res. Commun. 42, 353–358.

Cruywagen, J. J. & van der Merwe, I. F. J. 1987. Tungsten(VI) equilibria: A potentiometric and calorimetric investigation, J. Chem. Soc., Dalton Trans. 1701–1705.

Cruywagen, J. J. & De Wet, H. F. 1988. Equilibrium study of the adsorption of molybdenum(VI) on activated carbon. Polyhedron 7, 547–556.

Cruywagen, J. J. & Heyns, J. B. B. 1989. Spectrophotometric determination of the thermodynamic parameters for the first two protonation reactions of molybdate. J. Chem. Ed. 66, 861–863.

Cruywagen, J. J. & Pienaar, A. T. 1989. The adsorption of tungsten on activated carbon from 1.0 M Na(H)Cl solution. Polyhedron 8, 71–76.

Cruywagen, J. J. & Heyns, J. B. B. 1990. Spectrophotometric determination of the first protonation constant of orthovanadate. Talanta 37, 741–744.

Fu, M. H. & Tabatabai, M. A. 1988. Tungsten content of soils, plants, and sewage sludges in Iowa. J. Environ. Qual. 17, 146–148.

Greenwood, N. N. & Earnshaw, A. 1984. Chemistry of the Elements. Pergamon Press, Oxford. 1542 pp.

Heimer, Y. M., Wray, J. L. & Filner, P. 1969. The effect of tungstate on nitrate assimilation in higher plant tissues. Plant Physiol. 44, 1197–1199.

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.

Jacks, G. 1976. Vanadium in area just outside Stockholm. Environ. Pollut. 11, 289–295.

Jones, L. H. P. 1957. The solubility of molybdenum in simplified systems and aqueous soil suspensions. J. Soil Sci. 8, 313–327.

Kabata-Pendias, A. & Pendias, H. 1985. Trace Elements in Soils and Plants, CRC Press, Boca Raton, Fl. 301 pp.

Karlsson, N. 1961. Om molybden i svensk vegetation och mark samt några därmed sammanhängande frågor. Ph.D. Thesis. Statens lantbrukskemiska kontrollanstalt, meddelande 23. 241 pp. (English summary).

Kyriacou, D. 1967. The pH-dependence of adsorption of metallic oxyanions by ferric oxide powder. Surf. Sci. 8, 370–372.

McKenna, C. E., Benemann, J. R. & Taylor, T. G. 1970. Vanadium-containing nitrogenase preparation: implications for the role of molybdenum in nitrogen fixation. Biochem. Biophys. Res. Commun. 41, 1501–1508.

McKenzie, R. M. 1983. The adsorption of molybdenum on oxide surfaces. Aust. J. Soil Res. 21, 505–513.

Motta, M. M. G. & Ferreira de Miranda, C. 1985. Adsorption of molybdate by clay minerals: 1. Kaolinite. Rev. Port. Quim. 27, 505–510.

Pope, M. T. 1983. Heteropoly and Isopoly Oxometalates. Springer-Verlag, Berlin. 175 pp.

Pope, M. T. & Dale, B. W. 1968. Isopoly-vanadates, -niobates, and -tantalates. Q. Rev. Chem. Soc. 22, 527–548.

Theng, B. K. G. 1971. Adsorption of molybdate by some crystalline and amorphous soil clays, N. Z. J. Sci. 14, 1040–1056.

Tyler, G. 1976. Influence of vanadium on soil phosphatase activity. J. Environ. Qual. 5, 216–217.

PAPER 2

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Retention of Molybdenum(VI) by Three Finnish Mineral Soils

Mikkonen, A. and Tummavuori, J. (Department of Chemistry, University of Jyväskylä, PO Box 35, SF–40351 Jyväskylä, Finland). Retention of molybdenum(VI) by three Finnish mineral soils. Accepted April 19, 1993. Acta Agric. Scand., Sect. B, Soil and Plant Sci. 43: 206–212, 1993.
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Retention of molybdate by three Finnish mineral soils from 10^{-4} and 10^{-5} M sodium molybdate solutions at room temperature was investigated at pH 2.3–7.5. In the adsorption experiments 0.02 M KCl was used as ionic medium, and the samples were left to equilibrate for 72 h. The solid:solution ratio was 1:100 (w:v). Maximum adsorption occurred below pH 4.5, where about 60–80 % of added molybdenum was retained. Desorption of the adsorbed molybdenum was measured by adding 50 ml of 0.02 M KCl into weighed soil samples and shaking for 17 h in an apparatus with a mechanical stirrer. In each soil an appreciable amount of Mo was so tightly bound that it could not be removed by KCl treatment.

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Key words: adsorption, desorption, clay, fine sand.

Introduction

Molybdenum is known to be essential for the growth of plants. Its principal functions in plants are implicated in the electron-transfer system; for instance, nitrate reductase and nitrogenase require Mo in the reduction of NO_3^- and in the fixation of N_2, respectively. The basic enzymatic role of Mo is related to its function as a redox carrier and is apparently reflected in the valency change from Mo^{6+} to Mo^{5+} (Nicholas, 1975). Plant-available Mo content has not been found to be closely related to the total Mo content of soils (e.g. Barrow & Shaw, 1975; Barrow et al., 1985). Total soil Mo can be subdivided into mineral, organic, adsorbed or labile, and solution forms (Lindsay, 1979; Gupta & Lippsett, 1981; Barber, 1984; Kelley, 1986). In acidic soils, adsorption of molybdate ion, like phosphate and sulfate, is of great importance.

There are a number of published reports on retention of Mo(VI) by soils (Jones, 1957; Karlsson, 1961; Reisenauer et al., 1962; Barrow, 1970; 1972; Jaakkola, 1972; Mishra & Misra, 1972; Lal et al., 1973a,b; Gonzalez et al., 1974; Karimian & Cox, 1978; Tanner, 1978; Haynes, 1983; Roy et al., 1986a; 1986b). Retention of molybdate by adsorbents other than soil has been reviewed in our recent paper (Mikkonen & Tummavuori, 1993). In describing the adsorption of molybdate, investigators have often presented either adsorption curves (amount adsorbed vs. Mo concentration at constant pH) or adsorption envelopes (amount adsorbed vs. pH at constant Mo concentration). In some papers, adsorption at the soil's natural pH, replacement of adsorbed Mo, or the changes in adsorption caused by added components, e.g. another nutrient, have been discussed (e.g. Gorlach et al., 1969; Roy et al., 1986a; 1986b). Retention of molybdate has also been calculated using different mathematical models (Barrow, 1986; 1989; Roy et al., 1989).

It is difficult to compare results of various investigations, because adsorption studies have been carried out using different procedures. Variables in the procedures are, for instance, the adsorbent/solution ratio, temperature, equilibrating time, shaking, the amount of adsorbate, the concentration of inert salt, pH adjustments, and separation of supernatant from the solid phase.

In earlier studies on adsorption of molybdate, some authors used high concentrations of Mo but were not aware of the presence of polyionic forms, and did not discuss the role of various protolysation products in detail.

Desorption of molybdenum from soils and other adsorbents is not so widely studied as adsorption.

However, some investigators (Gorlach et al., 1969; Theng, 1971; Jaakkola, 1972; Misra & Mishra, 1969; 1972; Thakur & Das, 1987) have measured desorption of molybdate immediately after the adsorption step. In addition, there are some published investigations in which Mo retained near field conditions has been extracted (e.g. Karlsson, 1961; Smith & Leeper, 1969; Barrow, 1974). In these investigations phosphate solution, ammonium oxalate solution, dilute NaOH and water, for example, have been used as extractants.

Much new information has been obtained about the solution chemistry of Mo in the last few years. Today it is known that a p*K* value of 4.5 for molybdate anion (Hingston et al., 1972; Gonzalez et al., 1974; Barber, 1985) is erratic. The exact protonation constants of many mono- and polynuclear species were not, however, well known before the 1980s (Cruywagen & Heyns, 1987; 1989). This motivated us to explore what happens when 10^{-4} and 10^{-5} M Mo(VI) solutions are in contact with three different fertilized mineral soils. At the concentration levels selected, the presence of polyionic forms can be ignored, and at pH 2–8 different monomeric species of molybdic acid, $Mo(OH)_6$, $HMoO_4^-$, and MoO_4^{2-}, can be expected to be present. We also wanted to determine how easily adsorbed Mo can be washed away with 0.02 M KCl, which was used as an ionic strength adjustor during adsorption, and to compare the results of this study with those obtained in similar conditions for kaolin (Mikkonen & Tummavuori, 1993).

Material and methods

The plough-layer soil samples were obtained from the Agricultural Research Centre of Finland. The soil samples were initially air dried, homogenized and lightly hand-crushed to pass through a 2 mm sieve. Selected characteristics of the soils are presented in Table 1. Some analyses were performed at the Agricultural Research Centre of Finland using their routine methods. Organic carbon was determined by the dry combustion method (Sippola, 1982). Ca, Mg, P and K were extracted using a 0.5 M ammonium acetate, 0.5 M acetic acid solution (pH 4.65); the extraction ratio was 1:10 v:v (Vuorinen & Mäkitie, 1955). Mn was extracted with a 0.5 M ammonium acetate, 0.5 M acetic acetate, 0.02 M EDTA (AAAc–EDTA) solution (Lakanen & Erviö, 1971). These extractions give concentrations which usually correlate with plant-available reserves. CEC_{ef} values were determined by scientists at Soil Analysis Service Ltd. Mo, Fe and Al were extracted with an ammonium oxalate–oxalic acid solution (pH 3.3) using a soil:solution ratio 10:100 (v:v) and a shaking time of 16 h. After filtration, Al and Fe were determined by ICP-AES, and for the determination of Mo, the extracts were treated as described by Sillanpää (1982) except that Mo was determined by ICP-AES using the standard addition method. For comparison, the AO-OA extractable amounts of Fe and Al were determined after a shaking period of 2 h also. The analyses were performed in triplicate. The AO-OA extractable concentration of Mo in cultivated fields with organic carbon 15 % has been reported to be 0.12–1.94 μg g^{-1} (Jaakkola, 1972), and in fertilized soils in Southern Finland 0.086–2.071 mg l^{-1} (Sillanpää, 1982). Reference values for AO-OA extractable Fe and Al in Finnish soils have been presented by Jaakkola (1972).

Table 1. Selected characteristics of the soil samples

	Soil 1	Soil 2	Soil 3
Colour and texture	Dark grey clay	Brown coarser fine sand	Grey–brown finer fine sand
[a] 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
[a] pH ($CaCl_2$); 1:2.5	7.3	6.1	5.6
pH (KCl); 1 g/100 ml	7.1	6.1	6.0
[a] electrical conductivity, 10 mS/cm	3.52	4.10	2.39
[a] bulk density kg/l	0.95	1.14	1.02
[a] AO-OA extractable Fe, g/l;			
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
[a] AO-OA extractable Al, g/l;			
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
AO-OA extractable Mo, mg/l	1.0±0.1	0.7±0.1	1.3±0.1
[a] organic C, %	4.2	2.3	4.6
[a] extractable Ca, mg/l	8536	2543	1989
[a] extractable K, mg/l	378	224	217
[a] extractable Mg, mg/l	894	335	364
[a] extractable P mg/l	37.2	25.3	18.8
[a] extractable Mn, mg/l (pH corrected)	8.1	32.6	16.6
CEC_{ef}, mequiv./100 g (extractant: unbuffered KCl)	34.7	13.4	13.1

[a] Determination made at the Agricultural Research Centre, Jokioinen.

Adsorption

Into 250 ml beakers were placed 1.00 g subsamples of each soil. Aliquots of 100.0 ml of 10^{-4} or 10^{-5}

M Na_2MoO_4 in 0.02 M KCl were added. The pH adjustments were made by adding dilute HCl or NaOH. The sample beakers were covered with Parafilm and shaken manually for 2–3 min. The samples were then left to equilibrate at room temperature for 72 h. This period was selected because a preliminary study showed that pH values in the suspensions of soil 1 tend to rise slowly (Fig. 1). The final pH values of suspensions were recorded prior to the filtration using a standard combination electrode. The accuracy of the pH measurements was checked after every tenth soil sample using pH 7.00 or 4.01 buffer solution, which were used in calibrating the pH meter. The samples were filtered through Whatman 40 filter paper, and the Mo concentrations in the filtrates were measured by Perkin-Elmer ICP 5000 equipment. The analytical wavelength was 202.03 nm. Working standards, which were 0.02 M with respect to KCl, were prepared with a 1000 mg l^{-1} commercial stock solution. Some samples were also analyzed using the standard addition method. The amount of adsorbed Mo was calculated as the difference of the initial Mo concentration of Na_2MoO_4 solution and the amount left after filtration. At both Mo concentrations, about 40 samples were prepared from each soil to produce an adsorption envelope.

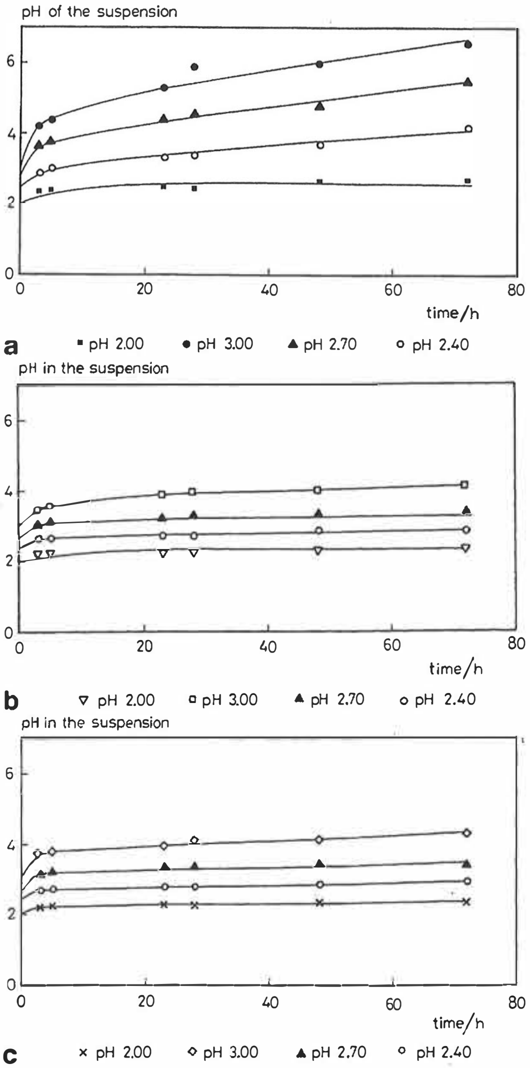

Fig. 1. pH of the soil suspensions during the equilibration period of 72 h. The H^+ additions at the beginning of equilibration were 0.1 mequiv. (which gives pH 3.0), 0.2 (pH 2.7), 0.4 (pH 2.4) and 1.0 mequiv. (pH 2.0), respectively. (a) Soil 1; (b) Soil 2; (c) Soil 3.

Desorption

The procedure for the present desorption studies was adapted from reports on adsorption and desorption of inorganic phosphate by different soils (Ryden & Syers, 1975; Bayomi & Rehan, 1984) except that, for convenience, the shaking time was 17 instead of 16 h. In desorption studies 0.01 M $CaCl_2$ is frequently used as extractant, because Cl^- has no specific replacing power (Ryden & Syers, 1975). In a preliminary study we compared the ability of 0.02 M KCl and 0.01 M $CaCl_2$ to leach adsorbed molybdate. The desorption experiments were started 1 day after adsorption, because it was believed that Mo could be most easily washed away almost immediately after adsorption. For each soil, the experiments were carried out at three different pH values. Since 0.02 M KCl was more effective in leaching than 0.01 M $CaCl_2$ (Table 2), it was chosen as extractant for the desorption studies.

After filtration at the end of the 72 h adsorption step, the soil samples were air-dried at room temperature and stored for 4 months to obtain comparable results with those obtained for kaolin (Mikkonen & Tummavuori, 1993). Accurately weighed 0.80 g soil samples were placed into 100 ml polyethylene bottles. Aliquots of 50.0 ml of 0.02 M KCl were added into the samples. The bottles were shaken for 17 h in an apparatus with a mechanical stirrer. After shaking, the samples were filtered through Whatman 40 filter paper.

The pH values of some filtrates were measured in order to approximate the correlation between the pH in the initial soil suspensions and the pH in the suspensions at the end of the desorption period.

After the desorption step, Mo was determined in the filtrates by Perkin-Elmer 2000 ICP-AES. To check that no significant loss of Mo occurred during the filtration steps, standard solutions with pH values and Mo concentrations corresponding to the

Table 2. Comparison of KCl and $CaCl_2$ as extractants of adsorbed Mo

Sample[a]	pH in the KCl suspension after 72 h	Adsorption, µg/g; 0.02 M KCl	Desorption, µg/g; 0.02 M KCl	Adsorption, µg/g; 0.02 M KCl	Desorption, µg/g; 0.01 M $CaCl_2$
Soil 1; A	2.8	702	7	723	0
Soil 1; B	6.6	163	76	174	35
Soil 1; C	7.3	72	35	80	10
Soil 2; A	2.4	555	22	569	7
Soil 2; B	4.1	681	90	669	49
Soil 2; C	6.3	68	41	159	12
Soil 3; A	2.3	650	40	645	15
Soil 3; B	4.3	666	103	665	50
Soil 3; C	6.0	112	59	101	6

[a] A, B and C denote subsamples.

samples were filtered as the samples through Whatman 40 filter paper and analyzed by ICP-AES.

Results and discussion

Figures 2 and 3 give the adsorption of Mo by the soils at a pH range 2.3–7.5 from 10^{-4} and 10^{-5} M solutions, and the amounts of adsorbed Mo that could be leached with 0.02 M KCl. Each curve consists of about 40 test points. The pH interval between test points was only 0.1–0.3 pH units. As adsorbed/desorbed Mo was plotted against pH, the shape of the corresponding curve could easily be seen. Some test points had to be omitted because of deviation from the curve, probably resulting from the heterogeneity of the adsorbent, caused by small residues of straw or lime.

As an example, the test points close to the adsorption envelopes of soil 1 are given in Figs. 2 and 3. The adsorption envelopes for the two concentrations do not have identical shapes. A shift in adsorption takes place from the 10^{-5} M solution towards higher pH values, and below pH 3, the proportion of adsorbed Mo, is relatively higher from the 10^{-5} M solution.

Soil 1, a limed clay, retains Mo most effectively. Soil 2, with the coarsest texture, has the lowest ability to adsorb Mo. At pH 5–7, soil 1 seems to be able to adsorb much higher amounts of Mo than the other soils. Fig. 4, which shows the pH values of the soil suspensions measured 72 h after different acid additions, seems to explain the adsorption behaviour of various soils. To obtain desired final pH values in the suspensions, the samples in most cases

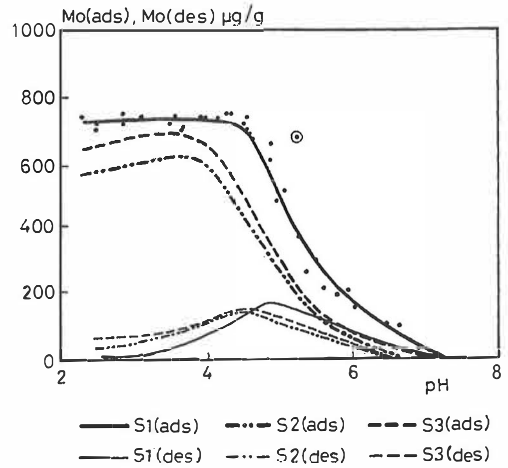

Fig. 2. Adsorption of Mo by soils from 10^{-4} M Na_2MoO_4 solution and corresponding desorption envelopes. pH in all curves denotes the acidity of suspensions at the end of the 72 h adsorption period. $Mo_{tot} = 959.4$ µg. Test points of soil 1 are given (eight points under the drawn line). The point with a circle has been omitted.

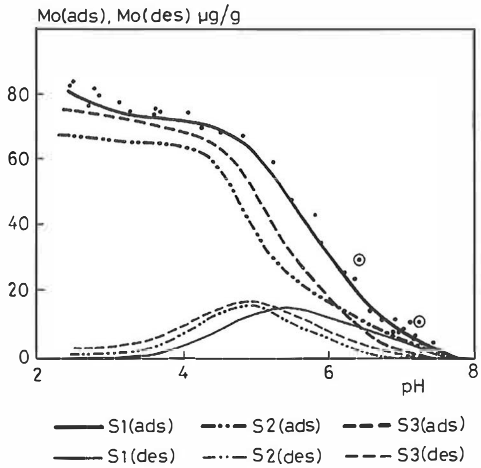

Fig. 3. Adsorption of Mo by soils from 10^{-5} M Na_2MoO_4 solution and corresponding desorption curves. pH in all curves denotes the acidity of suspensions at the end of the 72 h adsorption period. $Mo_{tot} = 95.94$ µg. Test points of soil 1 are given (nine points perfectly under the drawn line). Points with a circle have been omitted.

had to be made more acidic in the beginning. Soil 1 has a higher buffer capacity than the other soils. Immediately after an addition of, e.g. 0.1 mequiv. of H^+ into 100 ml of Na_2MoO_4 solution or into soil suspension, the pH falls to about 3, but during the equilibration period the pH of the suspension of soil 1 rises to about 6. It is possible that Mo is adsorbed strongly during the most acidic conditions, and as the pH in the suspension rises, the adsorbed Mo has not begun to dissolve. In the suspensions of soils 2 and 3, the change of pH is smaller (Fig. 4). The main reason for the pH increase in the suspensions of soil 1 is probably the dissolving of lime and not the removal of OH^- ions from the coordination shell of the adsorbent, which is assumed to happen in the ligand exchange process during adsorption (Hingston et al., 1972).

The possible effect of the adsorption of Mo on the pH of the suspensions was, however, approximated using blank samples, prepared in the same way as the soil suspensions but with no added Mo. Fig. 4 gives the pH values of blank suspensions measured 72 h after the acid additions for soil 1. It can be concluded that the pH of the suspensions of this soil remains at a slightly lower level if Mo is not present. For soils 2 and 3, no difference in pH values was observed at the Mo concentration level of 10^{-4} M. The adsorption of Mo from 10^{-5} M solution caused no measurable change in the pH values compared to the blank suspensions.

This investigation showed that Mo is strongly retained by these three mineral soils in acidic conditions, even when the suspensions are not shaken continuously during the adsorption period. These soils seem to have far more capacity to retain Mo than was expected on the basis of the study of Jaakkola (1972), who used additions of 1 and 10 $\mu g\ g^{-1}$, respectively. The adsorption envelopes of Fig. 1 and 2 can be compared with those obtained for soil clays (Theng, 1971) and kaolinite (Motta & Ferreira de Miranda, 1985; Mikkonen & Tummavuori, 1993), because in all four studies the concentration of Mo was 10^{-5}–10^{-4} M. Below pH 4 the soils used in this study seem to have a greater ability to retain Mo than the clay minerals. Here the hydrated oxides of Al and Fe, which are extracted by the 16 h AO-OA treatment (Table 1), play an important role. The leachability of Fe and Al during adsorption of Mo from 10^{-4} M solution was measured in a preliminary study, which showed that relatively high amounts of Fe and Al are dissolved during equilibration (Figs. 5 and 6). This means that new adsorption sites may become available for Mo. It has also been postulated that, at least at low pH, Mo is retained by organic matter (Jaakkola, 1972; Cruywagen & De Wet, 1988).

The desorption envelopes (Figs. 1 and 2) show that Mo, presumably adsorbed in the MoO_4^{2-} form (the predominating form above pH 4), is leached to some extent from all soils, and that the other retained forms, $HMoO_4^-$ and $Mo(OH)_6$, are very poorly leached from soil 1. In the desorption studies, the final pH in the suspensions ranged from 4 to 6 for soils 2 and 3. Soil 1 (clay) had an additional ability to raise the pH during the shaking period of 17 h. The correlation between the pH of the soil suspensions at the end of adsorption and at the end of the desorption period is shown in Figs. 7a and 7b.

The desorption results of this paper can be compared with those of Barrow (1983) for adsorption and desorption of inorganic phosphate. Barrow found that plots of concentration against phos-

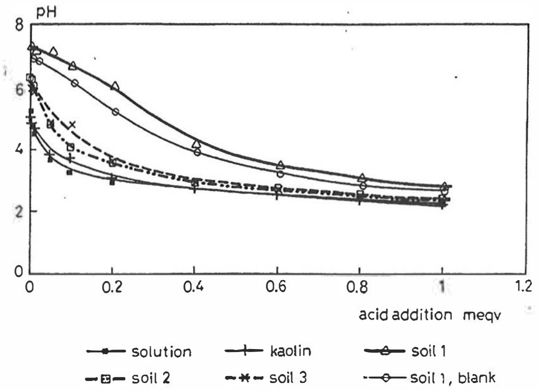

Fig. 4. pH measured 72 h after different acid additions into 10^{-4} M Na_2MoO_4 (100 ml), into kaolin–molybdate or soil–molybdate suspensions (w:v 1.00 g: 100 ml) and into a blank suspension of soil 1 (1.00 g of soil 1 + 100 ml of 0.02 M KCl). All molybdate solutions contained 0.02 mol l^{-1} of KCl.

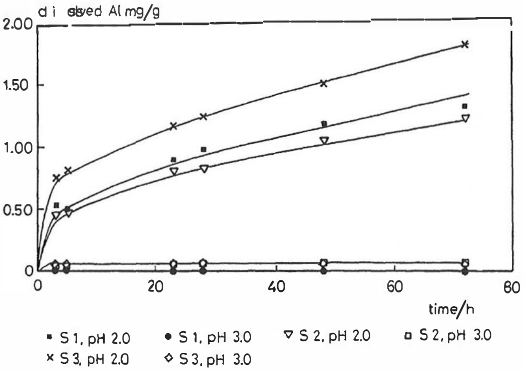

Fig. 5. Dissolving of Al during the 72 h equilibration period in the suspensions of soils and 10^{-4} M Na_2MoO_4 solution after two different acid additions at the beginning. Cf. caption of Fig. 1.

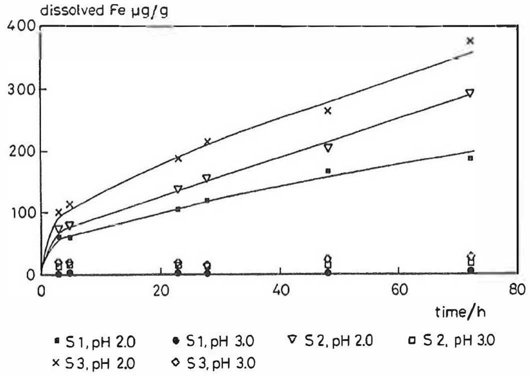

Fig. 6. Dissolving of Fe during the 72 h equilibration period in the suspensions of soils and 10^{-4} M Na_2MoO_4 solution after two different acid additions at the beginning. Cf. caption of Fig. 1.

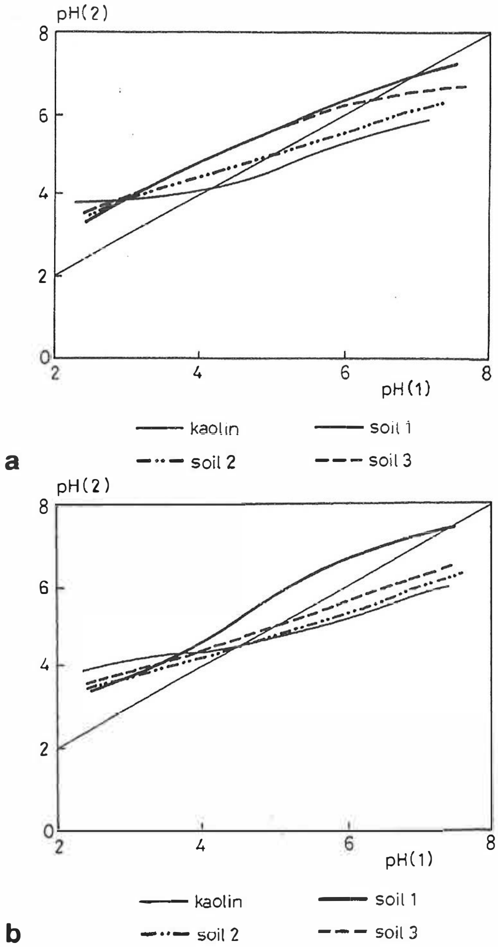

Fig. 7. pH of soil and kaolin suspensions at the end of the extraction period (17 h) vs. pH of the suspensions at the end of the adsorption period (72 h). pH(1) denotes adsorption and pH(2) desorption. (a) 10^{-4} M, (b) 10^{-5} M.

phate retained at the end of the desorption step did not correspond to plots of concentration against sorption at the end of the sorption step. Both sorption and desorption continued for long periods even though the rate of change became slow.

According to Barrow, there are three categories of phosphate: solution phosphate, adsorbed phosphate and diffused or penetrated phosphate. The amount of phosphate in the last category is strongly influenced by time. Parallel results were also obtained by Smith & Leeper (1969), who found that Mo is not leached by rain from acidic soils other than sands, but is adsorbed on sesquioxide surfaces and slowly changed into less soluble forms. On the other hand, Theng (1971), who measured desorption of freshly adsorbed molybdate by removing a known portion of the equilibrium solution and replacing it with an equal volume of buffer solution (pH 4), reported that the adsorption of molybdate could not be reversed by simply decreasing the solution concentration at constant pH and ionic strength.

On the basis of our results, it can be said that Mo(VI), adsorbed below pH 5, is leached in 0.02 KCl more easily from the coarser soils than from the clay studied, but Mo adsorbed at pH > 5 is most easily leached from clay. Kaolinite, a clay mineral, holds adsorbed Mo more tightly than any of these soils (Mikkonen & Tummavuori, 1993). The reason for the difference in the desorption curves of soil 1 and kaolin is obviously liming of soil 1. During the desorption, the pH in the suspension of soil 1 remained so high that no readsorption occurred, whereas the samples of kaolin and soils 2 and 3 were so acidic that 0.02 M KCl was not able to leach the adsorbed Mo effectively. To ensure that retained Mo is extracted from soils and other adsorbents effectively, it is important to select an extractant that allows no readsorption to occur.

Our experiences during this study showed that even if the laboratory experiments are made as simple as possible and the Mo solutions contain only monomeric ionic species, the soil–solution interaction is still rather complicated. In the case of higher Mo concentrations, which fortunately are not likely to occur in cultivated soils, retention of Mo would still be more difficult to explain.

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References

Barber, S.A. 1984. Soil Nutrient Bioavailability. John Wiley & Sons, New York, 1984, pp. 338–345.

Barrow, N.J. 1970. Comparison of the adsorption of molybdate, sulfate and phosphate by soils. Soil Sci. 109, 282–288.

Barrow, N.J. 1972. Influence of solution concentration of calcium on the adsorption of phosphate, sulfate, and molybdate by soils. Soil Sci. 113, 175–180.

Barrow, N.J. 1974. On the displacement of adsorbed anions from soil: 1. Displacement of molybdate by phosphate and by hydroxide. Soil Sci. 116, 423–431.

Barrow, N.J. 1983. On the reversibility of phosphate sorption by soils. J. Soil Sci. 34, 751–758.

Barrow, N.J. 1986. Testing a mechanistic model. I. The effects of time and temperature on the reaction of fluoride and molybdate with a soil. J. Soil Sci. 37, 267–275.

Barrow, N.J. 1989. Testing a mechanistic model. IX. Competition between anions for sorption by soil. J. Soil Sci. 40, 415–425.

Barrow, N.J. & Shaw, T.C. 1975. The slow reactions between soil and anions: 4. Effect of time and temperature of contact between soil and molybdate on the uptake of molybdenum by plants and on the molybdate concentration in the soil solution. Soil Sci. 119, 301–310.

Barrow, N.J., Leahy, P.J., Southey, I.N. & Purser, D.B. 1985. Initial and residual effectiveness of molybdate fertilizer in two areas of south western Australia. Aust. J. Agric. Res. 36, 579–587.

Bayoumi, N.A. & Rehan, M.R. 1984. Phosphate adsorption and desorption as affected by soil properties. Egypt. J. Soil Sci. 24, 53–66.

Cruywagen, J.J. & Heyns, J.B.B. 1987. Equilibria and UV spectra of mono- and polynuclear molybdenum(VI) species. Inorg. Chem. 26, 2569–2572.

Cruywagen, J.J. & De Wet, H.F. 1988. Equilibrium study of the adsorption of molybdenum(VI) on activated carbon. Polyhedron 7, 547–556.

Cruywagen, J.J. & Heyns, J.B.B. 1989. Spectrophotometric determination of the thermodynamic parameters for the first two protonation reactions of molybdate. J. Chem. Educ. 66, 861–863.

Gonzalez B.R., Appelt, H., Schalscha, E.B. & Bingham, F.T. 1974. Molybdate adsorption characteristics of volcanic-ash-derived soils in Chile. Soil Sci. Soc. Am. Proc. 38, 903–906.

Gorlach, E., Gorlach, K. & Compala, A. 1969. The effect of phosphates on the sorption and desorption of molybdates in the soil. Agrochimica 6, 506–512.

Gupta, U.C. & Lippsett, J. 1981. Molybdenum in soils, plants, and animals. Adv. Agron. 34, 73–115.

Haynes, R.J. 1983. Effect of lime and phosphate applications on the adsorption of phosphate, sulfate and molybdate by a spodosol. Soil Sci. 135, 221–227.

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.

Jaakkola, A. 1972. Availability to plants of molybdenum in Finnish mineral soils. Ph.D. Dissertation. Acta Agralia Fenn. 126, 92 pp.

Jones, L.H.P. 1957. The solubility of molybdenum in simplified systems and aqueous soil suspensions. J. Soil Sci. 8, 313–327.

Karimian, N. & Cox, F.R. 1978. Adsorption and extractability of molybdenum in relation to some chemical properties of soil. Soil Sci. Soc. Am. J. 42, 757–761.

Karlsson, N. 1961. On molybdenum in Swedish soil and vegetation and some related questions. Ph. D. Thesis. Statens lantbrukskemiska kontrollanstalt. Meddelande 23. 241 pp. (English summary).

Kelley, B.C. 1986. Biological contributions to mineral cycling in nature with reference to molybdenum. Polyhedron 5, 597–606.

Lakanen, E. & Erviö, R. 1971. A comparison of eight extractants for determination of plant available micronutrients in soils. Acta Agralia Fenn. 123, 223–232.

Lal, S., De, S.K. & Srivastava, S.K. 1973. Retention of molybdenum by soils in aqueous media in presence of EDTA. An. Edafol. Agrobiol. 32, 283–287.

Lal, S., De, S.K. & Tripathi, C.M. 1973. Retention of molybdenum by soils and their derivatives in presence of krillium. J. Ind. Chem. Soc. 50, 535–541.

Lindsay, W.L. 1979. Chemical Equilibria in Soils, J. Wiley, New York, 1979, pp.365–372.

Mikkonen, A. & Tummavuori, J. 1993. Retention of vanadium(V), molybdenum(VI) and tungsten(VI) by kaolin. Acta Agric. Scand., Sect. B 43, 11–15.

Mishra, K.C. & Misra, S.G. 1972. Retention and release of applied molybdenum to soils under permanent water-logged condition. J. Ind. Soc. Soil Sci. 20, 259–262.

Misra, S.G. & Mishra, K.C. 1969. Effect of complexants on retention and release of molybdenum applied to soils under water-logged condition. Technology 6, 140–142.

Motta M.M.C. & Ferreira de Miranda, C. 1985. Adsorption of molybdate by clay minerals: 1. Kaolinite. Rev. Port. Quim. 27, 505–510.

Nicholas, D.J.D. 1975. The functions of trace elements in plants. In Nicholas, D.J.D. & Egan, A.R. (eds.) Trace Elements in Soil–Plant–Animal systems. Academic Press, New York, pp. 181–241.

Reisenauer, H.M., Tabikh, A.A. & Stout, P.R. 1962. Molybdenum reactions with soils and the hydrous oxides of iron, aluminium and titanium. Soil Sci. Soc. Proc. 23–27.

Roy, W.R., Hassett, J.J. & Griffin, R.A. 1986. Competitive interactions of phosphate and molybdate on arsenate adsorption. Soil Sci. 142, 203–210.

Roy, W.R., Hassett J.J. & Griffin, R.A. 1986. Competitive coefficients for the adsorption of arsenate, molybdate, and phosphate mixtures by soils. Soil Sci. Soc. Am. J. 50, 1176–1182.

Roy, W.R., Hassett, J.J. & Griffin, R.A. 1989. Quasi-thermodynamic basis of competitive-adsorption coefficients for anionic mixtures in soils. J. Soil Sci. 40, 9–15.

Ryden, J.C. & Syers, J.K. 1977. Desorption and isotopic exchange relationships of phosphate sorbed by soils and hydrous ferric oxide gel. J. Soil Sci. 28, 596–609.

Sillanpää, M. (ed.) 1982. Micronutrients and the nutrient status of soils: a Global study. FAO Soils Bulletin. 444 pp.

Sippola, J. A comparison between a dry-combustion method and a rapid wet-combustion method for determining soil organic carbon. Ann. Agric. Fenn. 21, 146–148.

Smith, B.H. & Leeper, G.W. 1969. The fate of applied molybdate in acidic soils. J. Soil Sci. 20, 246–254.

Tanner, P.D. 1978. Relations of sorption of molybdate and phosphate by clays and clay loams to soil pH and other chemical factors, Rhod. J. Agric. Res. 16, 31–41.

Thakur, D.N. & Das, B. 1987. Adsorption and desorption of molybdate by some soils of West Bengal. J. Ind. Soil Sci. 35, 647–653.

Theng, B.K.G. 1971. Adsorption of molybdate by some crystalline and amorphous soil clays, N. Z. J. Sci. 14, 1040–1056.

Vuorinen, J. & Mäkitie, O. 1955. The method of soil testing in use in Finland. Agrogeological Publ. 63, 1–44.

PAPER 3

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Retention of Tungsten(VI) by Three Finnish Mineral Soils

Mikkonen, A. & Tummavuori, J. (Department of Chemistry, University of Jyväskylä, PO Box 35, SF-40351 Jyvöskylä, Finland). Retention of tungsten(VI) by three Finnish mineral soils. Accepted April 19, 1993. Acta Agric. Scand., Sect. B, Soil and Plant Sci. 43: 213–217, 1993. © Acta Agric. Scand. 1993.

Retention of W(VI) by three Finnish mineral soils from 10^{-4} M solutions for 72 h was studied at pH 2.8–7.5, using an adsorbent:solution ratio 1:100 (w:v) and 0.02 M KCl as a support medium. Retention was greatest from the most acidic samples, and at pH 3, 75–87% of the added W was retained. The W adsorption curves obtained for these mineral soils had different shapes compared with those reported for activated carbon, ferric oxide and kaolin. Retention of W by soils was strong, and only a small amount of the retained W was desorbed during a 17 h treatment with 0.02 M KCl.

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Key words: adsorption, desorption, clay, fine sand.

Introduction

Concentrations of W usually found in rocks range from 0.10 to 2 μg g^{-1}, but concentrations as high as 211–1480 μg g^{-1} around a W deposit in Britain have been reported (Kabata-Pendias & Pendias, 1985; Andrews et al., 1987). In Finnish till the W content is 0.6–2.2 μg g^{-1} (Koljonen, 1992).

The geochemical behaviour of W is believed to resemble that of Mo. Processes that run the risk of contaminating ecosystems with W are purification of ores for industrial use and application of sewage sludge on agricultural land. In sewage sludge samples from different wastewater-treatment plants in Iowa, for example, the concentrations of W varied from 0.5 to 62 mg kg^{-1} (Fu & Tabatabai, 1988). In Finland, the concentration of W in sewage sludges seems to be low, because problems with hazardous wastes have not been reported (Levinen, 1991).

Apparently, like Mo, W is readily available to plants under certain conditions, and its concentrations are likely to be elevated in plants growing on soil overlying W ore bodies. It is generally assumed that plants probably take up an anionic form, WO_4^{2-} (Wilson & Cline, 1966). Studies by Quin & Brooks (1972, 1974) and Quin et al. (1972) showed that W accumulates in the roots of some trees and that a small portion of the W taken up by those trees is translocated to the stems and leaves. Other studies by the same authors with silver beech (*Nothofagus menziesii*) showed that although W accumulation was most pronounced in the roots without ill effects, under controlled greenhouse conditions, the concentrations of W in the root, stems, and leaves were all related to levels in the soil.

The WO_4^{2-} ion seems to have a marked antagonistic effect on the metabolism of MoO_4^{2-} by *Aspergillus niger* and *Azotobacter vinelandii* (Higgins et al., 1956; Keeler & Varner, 1957) and an inhibitory effect on NO_3^- reduction and, therefore, on its assimilation by barley plants and cell cultures of tobacco (Heimer et al., 1969). The WO_4^{2-} ion also seems to be a competitive inhibitor of phosphatases and arylsylphatase in soils (Fu & Tabatabai, 1988). Quin (1979) noticed that a ryegrass/clover pasture, growing on a Mo-deficient New Zealand soil, showed significant responses to W (given as Na_2WO_4) alone and in the presence of added Na_2MoO_4. Tungstate application resulted in slightly increased concentrations of Mo in the herbage. It is assumed that at low application rates, W has a beneficial effect as it "soaks up" (Quin, 1979) non-functional binding sites otherwise occupied by Mo. This would increase the effectiveness of the Mo already in the plant, and allow more to reach the aerial parts. Heavy applications may deactivate the enzymes by blocking the entrance of Mo, thereby inhibiting nitrogen fixation and nitrate reduction. Quin (1979) suggested that a combination of W and Mo added to highly deficient soils would greatly benefit them, as a better balanced sward would result and, in animals, Cu deficiency induced by excessive amounts of Mo fertilizer would be prevented.

The solution chemistry of W is extremely complex. Aqueous solutions with W(VI) concentration less than ca. 0.1 mol l^{-1} may contain monomeric ions WO_4^{2-}, HWO_4^- and $W(OH)_6$ and four polymeric species $[W_6O_{20}(OH)_2]^{6-}$, $[W_7O_{24}]^{6-}$, $[HW_7O_{24}]^{5-}$ and $[H_2W_{12}O_{42}]^{10-}$ (Pope, 1983; Maksimovskaya & Burtseva, 1985; Cruywagen & van der Merwe, 1987). In more concentrated solutions other ionic species may also be present (MacInnis & Kim, 1979; Hudson, 1982). The formation constant of heptatungstate is much greater than that of heptamolybdate, which reflects the greater tendency towards condensation of W. The greater tendency of W(VI) than Mo(VI) to increase its coordination number with respect to oxygen implies a significantly greater protonation constant for $[HWO_4]^-$ to form $W(OH)_6$ than for $[HMoO_4]^-$ to form $Mo(OH)_6$. Values of the protonation constant for $[HWO_4]^-$ ($\log K=4.6$) and $[HMoO_4]^-$ ($\log K=3.8$) at 20°C and in 0.1 M NaCl are in agreement with such a prediction. The protonation constants of $[WO_4]^{2-}$ ($\log K=3.5$) and $[MoO_4]^{2-}$ ($\log K=3.7$) have about the same values (Cruywagen & van der Merwe, 1987).

Up until now, retention of tungstate by different adsorbents has not been widely investigated. Kyriacou (1967) has, however, used ferric oxide powder as an adsorbing material, and Cruywagen & Pienaar (1989) have studied adsorption of W onto activated carbon. Retention of W by kaolin (both adsorption and desorption) has also been measured (Mikkonen & Tummavuori, 1993a). The authors are not aware of other published desorption studies on W.

The aim of this 'purely academic' investigation was to study the ability of some Finnish mineral agricultural soils to retain W in neutral and acidic conditions from a 10^{-4} M W(VI) solution. The procedure of this research was similar to that used for the retention of Mo(VI) by these soils (Mikkonen & Tummavuori, 1993b) and kaolin, so that the results can be directly compared.

Material and methods

The soils used as adsorbents were a limed clay (soil 1; organic C 4.2%; ammonium oxalate – oxalic acid extractable Fe 6.6 g l^{-1}; AO-OA extractable Al 2.3 g l^{-1}), a coarser finesand (soil 2; organic C 2.3%; Fe 5.1 g l^{-1}; Al 1.6 g l^{-1}), and a finer finesand (soil 3; organic C 4.6%; Fe 4.6 g l^{-1}; Al 2.2 g l^{-1}). Other properties of the soils have been characterized in connection with adsorption of molybdate (Mikkonen & Tummavuori, 1993b). The AO-OA soluble concentrations of W were determined from the same extractants as Mo using the method described by Sillanpää (1982) except that W in the filtrates was determined by ICP-AES using the standard addition method. The concentrations of W for soils 1, 2 and 3 were 2.5 ± 0.2, 1.7 ± 0.2 and 2.7 ± 0.2 mg l^{-1}, respectively. The tungsten initially present in soils was not soluble in 0.02 M KCl, because no traces of W were detected in the blank samples prepared in the same way as the samples but with no added W. It should also be noted that these initial concentrations (about 2 μg g^{-1}) were negligible compared with the added amount of 1838.5 μg g^{-1}.

Adsorption

The soil samples were air-dried, homogenized and hand-crushed to pass through a 2 mm sieve. Subsamples of 1.00 g were weighed and placed into 250 ml beakers. A 100 ml solution of 10^{-4} M Na_2WO_4 in 0.02 M KCl was added into each beaker. After this, the procedure was similar to that used for adsorption of Mo. The concentration of W in the filtrates was measured by the plasma emission technique (Perkin-Elmer AAS/ICP 5000) at 207.91 nm. Standard solutions for plasma emission measurements were prepared by dilution from a 1000 mg l^{-1} commercial stock solution. Arbitrarily selected samples were also analysed by the standard addition method. The concentrations were volume-corrected because of the HCl/NaOH addition. The amount of adsorbed W was calculated as the difference of the initial W concentration of the added Na_2WO_4 solution and the amount left after equilibration. About 40 samples were prepared from each soil to produce an adsorption envelope.

To check that no significant loss of W occurred during the filtration step, standard solutions with pH values and concentrations corresponding to the samples were filtered as the samples through Whatman 40 filter paper. This test revealed that from 10^{-4} M solutions with $pH < 2.8$, W was partially adsorbed by the spray chamber of the ICP equipment. For this reason, the adsorption of W was measured only at $pH > 2.8$. Adsorption from a 10^{-5} M solution could not be investigated, because serious memory effects in the ICP determinations by Perkin-Elmer ICP 5000 prevented quantitative measurements of W.

Desorption

The extractant in the desorption measurements was 0.02 M KCl, because it proved to be more effective than 0.01 M $CaCl_2$ (Table 1). In this preliminary study, retained W was extracted 1 d after filtration at the end of the 72 h adsorption period, because it was believed that W would be more easily leachable immediately after adsorption.

The soil samples from the filtration at the end of the 72 h adsorption period were air-dried at room temperature and, to obtain comparable results with our investigations on retention of Mo and W by the soils and kaolin, stored at room temperature for ca. 4 months. Samples of 0.80 g were weighed and placed in 100 ml polyethene bottles. Aliquots of 50.0 ml of 0.02 M KCl were added to the samples. The bottles were shaken for 17 h in an apparatus with a mechanical stirrer. After shaking, the samples were filtered through Whatman 40 filter paper and the concentration of W in the filtrates was measured. These measurements were carried out using Perkin-Elmer 2000 ICP equipment with a spray chamber made of Ryton. When acidic solutions were nebulized, no memory effects, such as in the determinations with the older ICP equipment, were observed.

The pH values of some filtrates were measured in order to approximate the correlation between pH in the initial soil suspensions and the pH in the suspensions at the end of the desorption period.

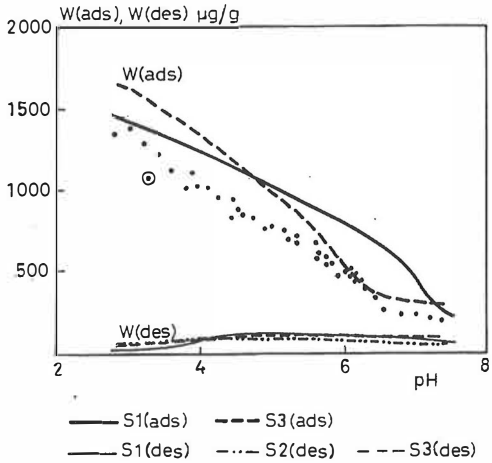

Fig. 1. Adsorption and desorption envelopes of W vs. pH in the suspension after an equilibration period of 72 h and the test points for soil 2. W(added) = 1838.5 µg g^{-1}.

Results

Fig. 1 gives the adsorption envelopes for soils 1–3, the test points for adsorption by soil 2, and the desorption envelopes for all soils. As the pH in the soil suspensions decreases, the amount of retained W increases. All three soils retain high amounts of W. The adsorption envelopes of soils 1 and 3 have two intercepts, one at ca. pH 4.7 and the other at ca. pH 7.3. It can be assumed that during equilibration, hydrous oxides of Al and Fe start to dissolve in the most acidic conditions in the same way as during retention of Mo (Mikkonen & Tummavuori, 1993b). Soluble Al and Fe do not act as sorption components. At low pH the surface charge of hydrated oxides becomes more positive, and adsorption is thus enhanced. It could also be assumed that if Al and Fe are most leachable from soil 3, then this soil provides more new adsorption sites than the other two soils. Soil 2, with the coarsest texture, has the lowest ability to retain W over the whole pH range except at pH 6, where the adsorption envelopes of soils 2 and 3 overlap.

Fig. 2 shows the pH changes of the soil suspensions which are caused by different acid additions.

Table 1. Comparison of KCl and $CaCl_2$ as extractants of adsorbed W, when 0.80 g of soil was shaken for 17 h with 50 ml of extractant. Extraction was started 1 d after the filtration at the end of the 72 h adsorption period

Sample[a]	pH in the KCl suspension after 72 h	Adsorption, µg/g 0.02 M KCl	Desorption, µg/g 0.02 M KCl	Adsorption, µg/g 0.02 M KCl	Desorption, µg/g 0.01 M $CaCl_2$
Soil 1; A	2.7	1477	4	1480	2
Soil 1; B	6.6	672	112	632	56
Soil 1; C	7.2	196	106	183	51
Soil 2; A	2.4	1226	52	1220	15
Soil 2; B	4.1	994	69	732	7
Soil 2; C	6.3	161	99	248	54
Soil 3; A	2.4	1592	29	1570	8
Soil 3; B	4.3	1188	63	1094	5
Soil 3; C	6.0	327	101	381	38

[a] A, B and C denote subsamples of each soil.

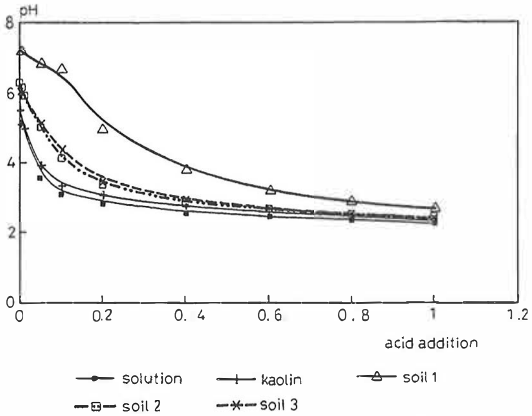

Fig. 2. pH values in the tungstate suspensions of kaolin and soils 1, 2 and 3 at the end of the 72 h equilibration period.

These pH values are measured after equilibration for 72 h. Soil 1 has a much higher buffer capacity than the other soils. After addition of, e.g., 0.10 mequiv. of H^- to soil suspension, the initial solution pH 3 rose to about 7. W was probably adsorbed in great amounts in the acidic suspension, and as the pH rose, all of the adsorbed W was not dissolved. This could explain the adsorption curve of soil 1 at pH range 5–7, where tungsten is still adsorbed in relatively high amounts as compared with the adsorption by the other soils. Similar results were also obtained in adsorption of molybdate.

Only a very small amount of the retained W is desorbed (Fig. 1). Below pH 4, W is retained most tightly by soil 1. Otherwise, there are no great differences between the desorption curves of the soils. More of the retained W can be leached from these soils than from kaolin, from which almost nothing was leachable (Mikkonen and Tummavuori, 1993a). Fig. 3 shows the correlation between pH in the soil suspension at the end of the 72 h adsorption period and pH in the suspension after shaking for 17 h in 0.02 M KCl. The pH values of the most acidic samples of soils 2 and 3 remain below pH 4 even after shaking with KCl, but for samples with initial pH 4, there is a rapid increase in pH during shaking, giving S-shaped curves. The pH of the suspensions of soil 1 is at a slightly higher level than that of the other soils. Almost all suspensions of kaolin had a final pH of 4–6 after the shaking period. During the shaking, readsorption may have occurred. It is also possible that adsorbed tungstate has been transformed to penetrated or otherwise more tightly bound, perhaps even precipitated, forms.

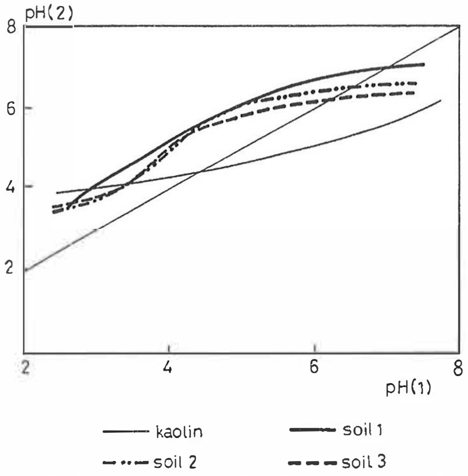

Fig. 3. pH of the suspensions of kaolin and soils after the 17 h desorption step vs. pH of the suspensions after the 72 h adsorption step.

Discussion

The length of time required to establish adsorption equilibrium and equilibrium in the time-dependent reactions occurring in dilute tungstate solutions is not known precisely. We selected 72 h, because this period was used in our other adsorption experiments (Mikkonen & Tummavuori, 1993a,b).

At the beginning of the equilibration, most of the suspensions had to be acidified to obtain an appropriate final pH. The buffer capacity of each soil is of great importance, and the pH change is difficult to predict without careful preliminary experiments.

The results of the adsorption can be compared with those of Kyriacou (1967) and Cruywagen & Pienaar (1989). Kyriacou reported that when α-hematite was the adsorbent, more than 90% of the adsorption occurred within less than 2 min. He used an equilibration period of only 10 min. According to him, both polymerization of ions and surface charge of the adsorbent are important factors for adsorption. Adsorption proceeds mainly by a process similar to that of polymerization of oxyanions: water is liberated at the surface of the site of adsorption, a proton from the adsorbent surface and an OH^- from the polymerized ion.

Cruywagen & Pienaar (1989) found that adsorption of W by activated carbon from 5×10^{-4} to 2×10^{-2} M solutions was very strong. At pH 2.3, for example, about 97% of the tungstate in the aqueous phase was adsorbed. They concluded that W is adsorbed mainly in the dimeric form. Significant adsorption of the monomeric species,

$[HWO_4]^-$ and $W(OH)_6$ occurred only at $pH > 5.5$ and $pH < 3.0$, respectively. They represented the overall adsorption equilibria by the equations

$$2\,WO_4^{2-} + 3\,H^+ + C^* \rightleftarrows HW_2O_7^-(ads)$$

$$WO_4^{2-} + H^+ + C^* \rightleftarrows HWO_4^-(ads)$$

$$WO_4^{2-} + 2H^+ + C^* \rightleftarrows W(OH)_6(ads),$$

where C^* represents the activated carbon. The chemisorption was strong at $pH < 4.5$ and was explained in terms of complexation of tungsten(VI) with basic oxygen atoms at the surface of the activated carbon.

In our previous investigation (Mikkonen & Tummavuori, 1993a), we found that about 90% of the tungstate in the aqueous phase was adsorbed by kaolin at pH 3–4 in 72 h. In equilibration studies using soil as adsorbent, it is necessary to equilibrate for several days, because the pH in the soil suspension tends to rise slowly after acid addition.

Because the equilibria occurring in dilute solutions ($\leq 10^{-4}$ M) are not exactly known, the question concerning adsorption of different anionic W(VI) species cannot be answered from this study. It can be said, however, that if tungstate at a concentration level of 10^{-4} M was in contact with cultivated soils similar to those in the present study, then at $pH > 4$, W would be partly retained by soils and partly be either available to plants or leached by rain water. The tungsten retained by soil particles would not be very easily leached with rain water other than through erosion.

If appropriate methods for investigating equilibria in dilute W(VI) solutions are developed in the near future, retention of W by soils and uptake by plants could be discussed more thoroughly. Before exact information on ionic species has been obtained, it is too early to say anything for certain about the ionic forms which are plant-available or retained by soils. At this moment, tungsten is still a rather unknown element.

References

Andrews, M. J., Ball, T. K., Fuge, R., Nicholson, R. A. & Peachey, D. 1987. Trace elements in soils around the Hemerdon tungsten deposit, Devon; implications for exploration. Proc. Ussher Soc. 6, 536–541.

Cruywagen, J. J. & van der Merwe, I. F. J. 1987. Tungsten(VI) equilibria: A potentiometric and calorimetric investigation. J. Chem. Soc., Dalton Trans. 1701–1705.

Cruywagen, J. J. & Pienaar, A. T. 1989. The adsorption of tungsten(VI) on activated carbon from 1.0 M Na(H)Cl solution. Polyhedron 8, 71–76.

Fu, M. H. & Tabatabai, M. A. 1988. Tungsten content of soils, plants, and sewage sludges in Iowa. J. Environ. Qual. 17, 146–148.

Heimer, Y. M., Wray, J. L. & Filner, P. 1969. The effect of tungstate on nitrate assimilation in higher plant tissues. Plant Physiol. 44, 1197–1199.

Higgins, E. S., Richert, D. A. & Westerfeld, W. W. 1956. Tungstate antagonism of molybdate in *Aspergillus niger.* Proc. Soc. Exp. Biol. Med. 92, 509–511.

Hudson, M. 1982. Tungsten: its sources, extraction and uses. Chem. Br. 438–442.

Kabata-Pendias, A. & Pendias, H. 1985. Trace elements in soils and plants. CRC Press, Boca Raton, 315 pp.

Keeler, R. F. & Varner, J. E. 1957. Tungstate as an antagonist of molybdate in *Azotobacter vinelandii.* Arch. Biochem. Biophys. 70, 585–590.

Koljonen, T. (Ed.) 1992. The Geochemical Atlas of Finland. Part 2. Till. Geological Survey of Finland, Espoo, 218 pp.

Kyriacou, D. 1967. The pH dependence of adsorption of metallic oxyanions by ferric oxide powder. Surf. Sci. 8, 370–372.

Levinen, R. 1991. New Finnish guidelines for the use of sewage sludge. Kem.-Kemi 18, 116–119 (English summary).

MacInnis, M. B. & Kim, T. K. 1979. The impact of solvent extraction and ion exchange on the hydrometallurgy of tungsten and molybdenum. J. Chem. Tech. Biotechnol. 29, 225–231.

Maksimovskaya, R. I. & Burtseva, K. G. 1985. ^{17}O and ^{183}W NMR studies of the paratungstate anions in aqueous solutions. Polyhedron 4, 1559–1562.

Mikkonen, A. & Tummavuori, J. 1993a. Retention of vanadium(V), molybdenum(VI) and tungsten(VI) by kaolin. Acta Agric. Scand. Sect. B 43, 11–15.

Mikkonen, A. & Tummavuori, J. 1993b. Retention of molybdenum(VI) by three Finnish mineral soils. Acta Agric. Scand., Sect. B 43, 206–212.

Pope, M. T. 1983. Heteropoly and isopoly oxometalates. Springer-Verlag, Berlin, 175 pp.

Quin, B. F. 1979. A pasture response to tungsten on a molybdenum deficient soil – facts and theories. In: Aggelt, J., Kjellström, T. & Crowe, D. (eds.) Proc. 2nd New Zealand Seminar on Trace Elements and Health, University of Auckland, pp. 71–79.

Quin, B. F. & Brooks, R. R. 1972. The tungsten content of some plants from a mineralized area in New Zealand. N.Z. J. Sci. 15, 308–312.

Quin, B. F. & Brooks, R. R. 1974. Tungsten concentrations in plants and soils as a means of detecting scheelite-bearing orebodies in New Zealand. Plant Soil 41, 177–188.

Quin, B. F., Brooks, R. R. & Reay, P. F. 1972. The accumulation of tungsten by *Nothofagus menziesii.* Plant Soil 36, 699–703.

Sillanpää, M. (ed.) 1982. Micronutrients and the Nutrient Status of Soil: a Global Study. FAO Soils Bulletin. 444 pp.

Wilson, D. O. and Cline, J. F. 1966. Removal of plutonium-239, tungsten-185, and lead-210 from soils. Nature (London) 209, 941–942.

PAPER 4

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Retention of vanadium (V) by three Finnish mineral soils

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Summary

Retention of V(V) by three Finnish mineral soils from 10^{-4} M and 10^{-5} M sodium vanadate solutions was investigated at room temperature in the pH range 2.3–7.5. In adsorption experiments, 0.02 M KCl was used as ionic medium, and the samples were left to equilibrate for 72 h. The solid : solution ration was 1 : 100 (m : v). Maximum adsorption occurred at pH ~4, where 70–80% of the added V (350–400 μg g^{-1} from 10^{-4} M solution and 35–40 μg g^{-1} from 10^{-5} M solution) was retained by each soil. Retention was significant even at pH 6, where adsorption of a similar anion, molybdate, is negligible. Desorption of the retained V was measured by adding 50.0 cm^3 of 0.02 M KCl into weighed soil samples and shaking for 17 h in a mechanical stirrer. Only a minor part of retained V could be removed from each soil by the KCl treatment.

Retention of different ionic species of V from 10^{-5} M solution is approximated using values of log K obtained from the literature. In these calculations, kaolin is used as a reference material.

Introduction

The average vanadium content of soils worldwide is 90 μg g^{-1}. Fine soil fractions may contain large amounts of V which exceed that of the parent material (Kabata-Pendias & Pendias, 1985). In Finnish till, the HNO_3-soluble V concentration ranges between 15 and 70 μg g^{-1} (Koljonen, 1992).

The geochemical characteristics of V strongly depend on its oxidation state (+2 to +5) and on the acidity of the media. The presence of V(III) indicates that an extremely powerful reducing environment exists, whereas V(IV) and V(V) predominate in systems of intermediate and high oxidation potential, respectively (Wanty & Goldhaber, 1985). It is postulated that V migrates in soils both as vanadyl cation (Szalay & Szilagyi, 1967; Taylor & Giles, 1970; Goodman & Cheshire, 1975) and as an anionic V(IV) complex (Bloomfield & Kelso, 1973). Vanadium is readily associated with soil organic matter, and humic substances are able to reduce V(V) to V(IV) (Szalay & Szilagyi, 1967; Goodman & Cheshire, 1975; Jacks, 1976; Tyler, 1978). In addition, V can be retained either by the clay fraction (Butler, 1953; Berrow *et al*., 1978) or secondary iron oxides (Le Riche & Weir, 1963; Taylor & Giles, 1970).

It has been proposed that V can substitute for Mo in the fixation of N_2 by *Azotobacter* species (Bortels, 1933), and that V is essential for the growth of the alga *Scenedesmus obliquus* (Arnon & Wessel, 1953). By contrast, Allen (1956) and Holm-Hansen (1968) were unable to establish a V requirement for nitrogen fixation in blue-green algae. V can replace Mo in the nitrogenase enzyme, but under these conditions the fixation of N_2 is only about 10% of that by the Mo-containing enzyme (McKenna *et al*., 1970; Burns *et al*., 1971; Benemann *et al*., 1972). V has also been found to inhibit the fixation of N_2 by the blue-green alga *Anabaena cylindrica*, and the presence of V in Mo-deficient cultures increased Mo deficiency (Fay & de Vasconcelos, 1974; Nicholas, 1975).

Some plant species accumulate vanadium (Cannon, 1963; Wallace *et al*., 1977; Parker *et al*., 1978). Generally, seeds accumulate a relatively low concentration of V, even when grown in V-supplemented solutions (Welch & Cary, 1975). It has been reported by Welch (1973) that cationic V species occurring under acid conditions probably are more rapidly adsorbed by roots than the anionic species that predominate in neutral and alkaline solutions. One should, however, remember that the solution chemistry of V was still rather poorly understood in 1973.

Industrial processing of certain mineral ores (ore smelters, cement, and phosphate-rock plants) may increase the deposition of V residues in soils. Combustion of fossil fuels is an especially serious source of contamination of soils with V (Jacks, 1976; Tyler, 1976). It is not probable that V would be toxic under field conditions. Under man-induced conditions, V concentrations as high as 0.5 μg cm^{-3} in the nutrient solution (Pratt, 1966), and 140 μg cm^{-3} in the soil solution (Cannon, 1963), have been measured. Phytotoxicity of V, resulting in chlorosis and dwarfing, may appear at about 2 μg V g^{-1} dry mass in some plants (Davis *et al*., 1978; Gough *et al*., 1979). Vanadium reduces acid phosphatase activity in soil, which alters the rate of mineralization of organic matter and may reduce the productivity (Tyler, 1976).

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Up until now, interaction of V with nutrients in soils and adsorption of V by soils and other adsorbents have not been systematically investigated. A report by Wells (1956) postulates that retention of molybdate may be substantially decreased by adding vanadate, phosphate or hydroxyl ions to the system. In addition, Kyriacou (1967) studied adsorption of oxyanions of V, Cr, Mo and W by ferric oxide powder, but he was not able to explain the mechanism of V retention in detail.

Since the ionic equilibria at various concentrations *versus* pH are now well established (Pope, 1983), adsorption processes can be reconsidered. According to Pope (1983), in the pH range 2–10, a 10^{-4} M solution contains monomeric ionic species VO_2^+, H_3VO_4, $H_2VO_4^-$, HVO_4^{2-} and, among others, polymeric decavanadate ions $HV_{10}O_{28}^{5-}$ and $H_2V_{10}O_{28}^{4-}$. Cyclic polymeric $[V_6O_{18}]^{6-}$ ions may also be present as possible precursors to the decavanadate structure (Heath & Howarth, 1981). More concentrated solutions may contain other additional species, whereas $\leqslant 10^{-5}$ M V(V) solutions contain only monomeric species.

The aim of the present study was to measure the ability of three Finish mineral soils to retain V(V) from 10^{-4} and 10^{-5} M vanadate solutions. At these concentrations, in nutrient solution in laboratory experiments, vanadium has been reported to be harmful to some plant species (Wallace *et al.*, 1977; Davis *et al.*, 1978). The procedure selected for the adsorption and desorption experiments was similar to the method used for measuring retention of Mo and W by these same soils and retention of V, Mo and W by kaolin (Mikkonen & Tummavuori 1993*a*, *b*, *c*), so that the results obtained by V, Mo and W could be readily compared. The possibility of reduction of V(V) to lower oxidation states under the experiments is also briefly discussed.

Table 1. Selected characteristics of the soil samples

	Soil 1	Soil 2	Soil 3
Colour and texture	Dark grey clay	Brown coarser fine sand	Grey-brown finer fine sand
[a]Particle-size fraction / g kg^{-1} particle diameter			
<0.002 mm	770	282	277
0.002–0.02 mm	100	167	177
0.02–0.06 mm	51	88	268
0.06–0.2 mm	27	245	241
0.2–2 mm	52	218	37
>2 mm	0	0	0
[a]pH ($CaCl_2$); 1 : 2.5	7.3	6.1	5.6
pH (KCl); 1g : 100 cm^3	7.1	6.1	6.0
[a]Electrical conductivity / dS m^{-1}	0.35	0.41	0.24
[a]Bulk density kg dm^{-3}	0.95	1.14	1.02
[a]AO-OA extractable Fe / g dm^{-3};			
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
[a]AO-OA extractable Al / g dm^{-3};			
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
[a]Organic C / g kg^{-1}	42	23	46
[a]Extractable Ca / mg dm^{-3}	8540	2540	1990
[a]Extractable K / mg dm^{-3}	378	224	217
[a]Extractable Mg / mg dm^{-3}	894	335	364
[a]Extractable P / mg dm^{-3}	37.2	25.3	18.8
[a]Extractable Mn / mg dm^{-3} (pH corrected)	8.1	32.6	16.6
CEC$_{ef}$ (extractant: unbuffered KCl) / mmol$_c$ kg^{-1}	347	134	131

[a]A determination made at the Agricultural Research Centre, Jokioinen.
AO-OA = Ammonium oxalate–oxalic acid

Materials and methods

Selected characteristics of the soils are presented in Table 1. The analytical methods used in soil analyses are discussed in detail elsewhere (Mikkonen & Tummavuori, 1993*b*). The soil samples were air dried, homogenized and hand crushed to pass through a 2-mm mesh. For determination of the initial V concentrations of the soils, subsamples of 0.50 g were boiled with 10 cm^3 of a 1 + 3 mixture of concentrated $HClO_4$ and HNO_3 for 4 h at 120°C in steel autoclaves with teflon lining, diluted to 25 cm^3 and filtered through Whatman 40 filter paper. V determinations were performed using a Perkin–Elmer ICP 2000 spectrophotometer at 311.838 nm. The total concentrations obtained using two replicates for each soil were 73 ± 5 µg g^{-1} (soil 1), 44 ± 5 µg g^{-1} (soil 2) and 27 ± 5 µg g^{-1} (soil 3), respectively.

Adsorption

Subsamples of 1.00 g were weighed and placed into 250-cm^3 beakers. Aliquots of 100.0 cm^3 of 10^{-4} M or 10^{-5} M V(V) solution in 0.02 M KCl were added to each beaker. These solutions were prepared by diluting from a 0.100 M stock solution, containing 12.121 g dm^{-3} of $NaVO_3$. Solutions of 0.02 M KCl were used throughout in our adsorption experiments to adjust the ionic strength. The pH adjustments were made by adding dilute HCl or NaOH (e.g. 1 cm^3 of 1 M HCl to obtain a final pH of *c.* 2.5 and 0.4 cm^3 of 0.1 M NaOH to obtain a final pH of *c.* 7.5, respectively). The sample beakers were tightly covered with Parafilm and shaken manually for 2–3 min. After this, the samples were left to equilibrate for 72 h at room temperature. At both V concentrations, about 40 samples were prepared from each soil. A calibrated combination electrode was used for the pH measurements, and the suspensions were stirred with a magnetic rod during the pH measurements. Buffer solutions (pH 7.00 and 4.01) were used as test solutions after every tenth sample to check that the colloidal particles of the suspensions had not caused deviation from the correct pH values. The samples were then filtered through Whatman 40 filter paper. The concentration of V in the filtrates was measured by a

Table 2. Comparison of KCl and $CaCl_2$ as extractants of adsorbed V, when 0.80 g of soil was shaken for 17 h with 50 cm^3 of extractant. Extracting began 1 d after filtration at the end of the 72-h adsorption period. V added = 509.4 $\mu g\ g^{-1}$.

Sample	pH in the KCl suspension after 72 h	Adsorption 0.02 M KCl / $\mu g\ g^{-1}$	Desorption 0.02 M KCl / $\mu g\ g^{-1}$	Adsorption 0.02 M KCl / $\mu g\ g^{-1}$	Desorption 0.01 M $CaCl_2$ / $\mu g\ g^{-1}$
Soil 1	2.7	204	8	200	8
Soil 1	6.4	297	33	287	19
Soil 1	7.1	239	30	242	20
Soil 2	2.3	55	4	65	3
Soil 2	4.1	309	28	307	25
Soil 2	6.3	127	44	116	22
Soil 3	2.4	47	7	63	7
Soil 3	4.2	360	30	360	28
Soil 3	5.9	138	42	180	37

Perkin–Elmer ICP 5000 spectrophotometer at 309.31 nm. Standard solutions were prepared by dilution from a 1000 mg dm^{-3} commercial stock solution and contained 0.02 mol dm^{-3} of KCl. Recovery of V was routinely checked by spiking various samples with known amounts of the standard, and the concentrations were volume-corrected because of the addition of HCl/NaOH. The amount of adsorbed V was calculated by subtracting the amount left after equilibration from the initial V concentration of the added solution. Vanadium initially present in the soils was not soluble in the KCl suspensions even in the most acidic conditions, because no traces of V were detected in the blank samples (pH 2.3–7.5), prepared in the same way as the samples but with no added V. The detection limit in the measurements was 0.010 mg dm^{-3}.

Desorption

The soil samples from the filtration at the end of the 72-h adsorption period were air dried at room temperature and stored for 4 months to get comparable results with our other investigations. Accurately weighted 0.80-g subsamples were placed into 100-cm^3 polyethene bottles. Aliquots of 50.0 cm^3 of 0.02 M KCl were added to the samples. The bottles were shaken for 17 h in a mechanical stirrer at room temperature. The pH values of some filtrates were measured in order to calculate the correlation between the pH in the initial soil suspensions and the pH in the suspensions at the end of the desorption period. After pH measurements, the samples were filtered through Whatman 40 filter paper, and the concentration of V in the filtrates was measured by a Perkin–Elmer ICP 2000 spectrophotometer at 309.311 nm.

In a preliminary test we measured the ability of 0.01 M $CaCl_2$ and 0.02 M KCl to extract retained V from freshly prepared samples. In this test, desorption was carried out 1 d after the first filtration, because the same procedure was used in the preliminary extractions of Mo and W. Table 2 shows that 0.01 M $CaCl_2$ and 0.02 M KCl are almost equal extractants. The latter was selected because it was also used as extractant in our earlier investigations (Mikkonen & Tummavuori, 1993*a*, *b*, *c*).

To check that no significant loss of V occurred during the filtration steps, standard solutions with pH values and concentrations corresponding to the samples were filtered in the same way as the samples through Whatman 40 filter paper. No vanadium was lost during the filtration or during the aspiration of samples to the plasma torch.

Results and discussion

The expressions 'adsorption envelope' and 'desorption envelope' are used here to denote adsorption and desorption *versus* pH (Hingston *et al*., 1972). 'Adsorption curve' usually gives adsorption *versus* concentration of the analyte in solution. Figure 1a shows retention (absorption envelopes fitted to the groups of test points) from the 10^{-4} M solution, and Fig. 1b gives the corresponding desorbed amounts. For making comparisons with kaolin easier, the adsorption and desorption envelopes of kaolin published earlier (Mikkonen & Tummavuori, 1993*a*) are presented here; the same scale is used for kaolin and the soils. Figure 2 gives the ability of the soils and kaolin to change the pH of the suspension in 72 h after different acid additions, when the 1.00-g samples were mixed with 100 cm^3 of the 10^{-4} M V(V) solution.

Because soil organic matter has an ability to reduce V(V) to V(IV), it was necessary to check if the test soils could cause reduction. Because reduction of V(V) is likely to happen only in acidic samples (Dean, 1985), 30-cm^3 aliquots of 1000 mg dm^{-3} V(V) solutions were made acidic ($pH < 1$) by adding 4 M HCl. Into these yellow solutions, 2-g samples of each test soil were added. No colour change from yellow to blue, characteristic of V(IV), could be detected during a 3-d equilibration period. For comparison, this test was performed also using Fe, Al and Zn powder (which are strong reductants), dried peat and a soil sample rich in decomposing plant material. In all these cases the colour of vanadate solution changed from yellow to greenish blue or blue within some hours. So it could be concluded that reduction of V(V) to lower oxidation states was negligible in the presence of our test soils. Neither did kaolin show any signs of reducing V(V).

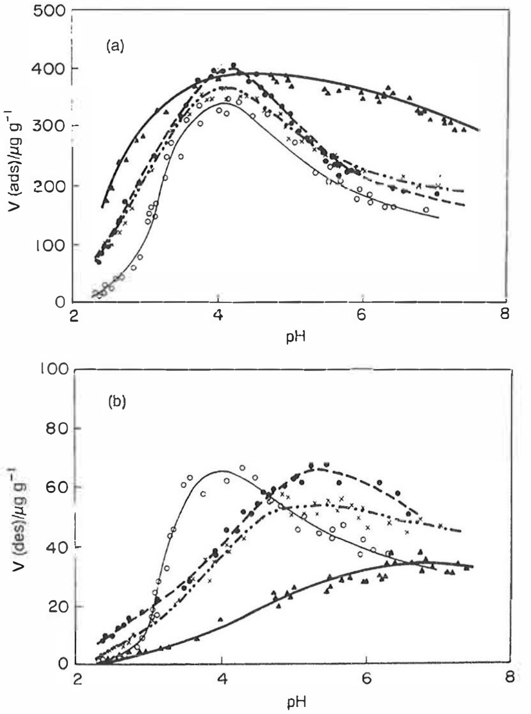

Fig. 1. (a) Retention of vanadium from 10^{-4} M solution. pH denotes pH at the end of the 72-h equilibration period. (b) Desorption of adsorbed vanadium after adsorption from 10^{-4} M solution. pH denotes the acidity at the end of the 72-h adsorption process. ▲, soil 1; ×, soil 2; ●, soil 3; ○, kaolin.

Figure 3 gives the distribution of V(V) ionic species, present in the 10^{-5} M aqueous solution over a pH range of 2–8. In calculating this distribution diagram, only monomeric ionic species are assumed to be present (Pope, 1983), and log *K* values of 3.2, 3.8, 7.8 and 13.2 are used for the protonation of H_3VO_4, $H_2VO_4^-$, HVO_4^{2-} and VO_4^{3-}, respectively (Pope, 1983; Cruywagen *et al.*, 1989).

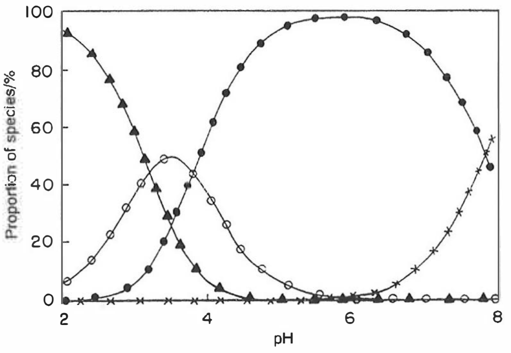

Fig. 3. Distribution of different V(V) species in 10^{-5} M solution. ▲, VO_2^+; ○, H_3VO_4; ●, $H_2VO_4^-$; ×, HVO_4^{2-}.

Our ^{51}V NMR studies have shown that, when 0.01 M V(V) solutions contain phosphate ions, unidentified phosphovanadates are formed. Preliminary experiments showed that phosphorus is dissolved from the soils during the 72-h equilibration period. That is why we also checked if any signs of phosphovanadates could be detected in the filtrates. The NMR spectra recorded after equilibration at the natural pH of each soil revealed that these spectra did not differ from those obtained for pure V(V) solutions with corresponding pH and V(V) concentration, so that no phosphovanadates were formed during the 72-h period.

It is now possible to try to explain retention of different ionic species from 10^{-5} M V(V) solution. At every test point and for each adsorbent, the adsorption envelope can be presented as a sum of adsorbed ionic species:

$$A = A[VO_2^+] + A[H_3VO_4] + A[H_2VO_4^-] + A[HVO_4^{2-}] \quad (1)$$

where *A* is absorbed V in µg g^{-1}, and the terms in the sum denote adsorption of the fractions, present in the solution as VO_2^+, H_3VO_4, $H_2VO_4^-$, and HVO_4^-, respectively. Figure 4a–c shows the test points (each point shows one sample) and, as curves, retention of different ionic species. These curves have

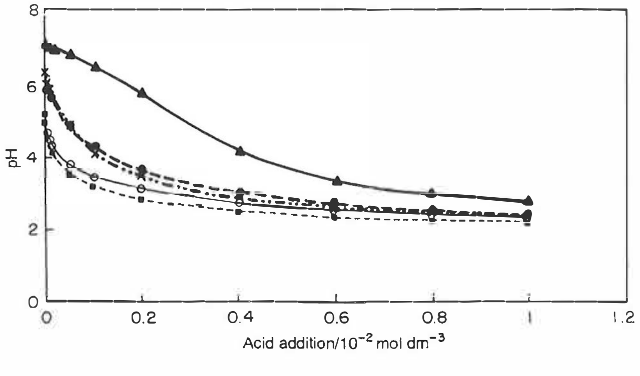

Fig. 2. Ability of the soils to raise pH during the 72-h adsorption period after different acid additions. H$^+$ addition 10^{-2} mol dm^{-3}; ■, solution; ▲, soil 1; ×, soil 2; ●, soil 3; ○, kaolin.

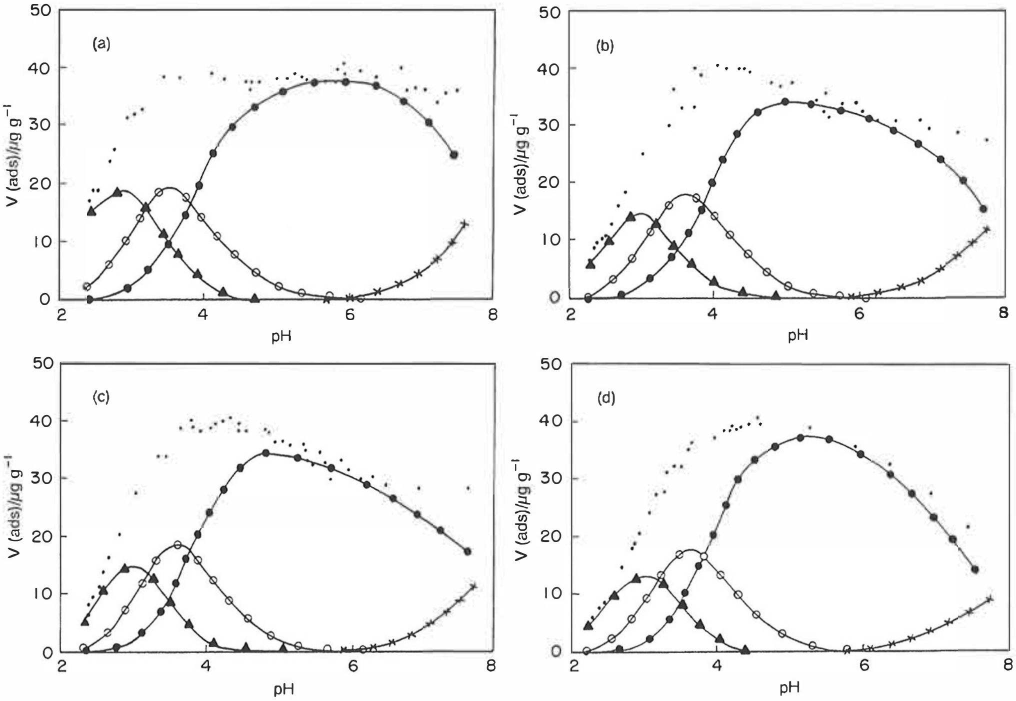

Fig. 4. Test points for adsorption of V from 10^{-5} M solutions. Adsorption of different V(V) ionic species; (a) soil 1, (b) soil 2, (c) soil 3, (d) kaolin. ▲, VO_2^+; ○, H_3VO_4; ●, $H_2VO_4^-$; ×, HVO_4^{2-}; ·, data points.

been obtained by computer calculations, in which the amount of V(V) adsorbed at each sample pH has been divided into fractions using the information shown in Fig. 3. To make the figure clearer, the single calculated points have not been drawn, but the results are shown as curves fitted to the groups of points. Figure 5a–c gives the corresponding information for desorption.

At both concentration levels, adsorption reaches a maximum at pH 4, where about 70–80% of the added V is adsorbed by each soil. In 10^{-4} M solutions, decavanadate anions occur at pH 3–4 (Pope, 1983) and these may have been adsorbed instead of H_3VO_4. At pH > 4.5, a 10^{-4} M solution contains only monomeric species, and thus V is adsorbed mainly in the $H_2VO_4^{2-}$ form. At pH < 3, V is poorly retained by soils 2 and 3, whereas soil 1 is also able to retain V effectively on the acidic side. At pH > 5, soil 1 adsorbs much higher amounts of vanadium than the other soils. A likely explanation for this is that, immediately after acid addition to the mixture of soil 1 and vanadate solution, the pH of the suspension falls to *c.* 3, but it rises slowly towards pH 7. At pH *c.* 4, a larger amount of V is adsorbed and, during the pH increase in the suspension, the adsorbed V does not begin to dissolve. It is also possible that OH^- ions, which had to be added to suspensions of soils 2 and 3 to get a desired final pH > 6, have occupied some adsorption sites and prevented adsorption of vanadate ions. Soil 1, a limed clay, needed no addition of OH^- ions for the final pH > 6.

Soil 1 seems to bind the retained vanadium more tightly than the other soils, as can be seen from the desorption envelopes. Although the ability of soils 2 and 3 to adsorb vanadium is almost identical, vanadium is leached more easily from soil 3. The desorption curve of kaolin in Fig. 1b shows that V(V) adsorbed at pH < 4.5 is more easily desorbed than from soils.

When adsorption from 10^{-4} M and 10^{-5} M solutions is compared, it can be seen that soils 2 and 3 adsorb relatively more at pH > 5 if the solution is not very concentrated, and the vanadium adsorbed from the 10^{-4} M solution can be washed away more easily than that adsorbed from the more dilute solution.

Most of the retained V is so tightly bound that it cannot be leached by a 17-h treatment with 0.02 M KCl. The relationship between pH(1), the measured pH of the soil suspension after a period of 72 h, and pH(2), the pH after a shaking of 17 h with 0.02 M KCl, is presented in Fig. 6a and b. Re-adsorption of

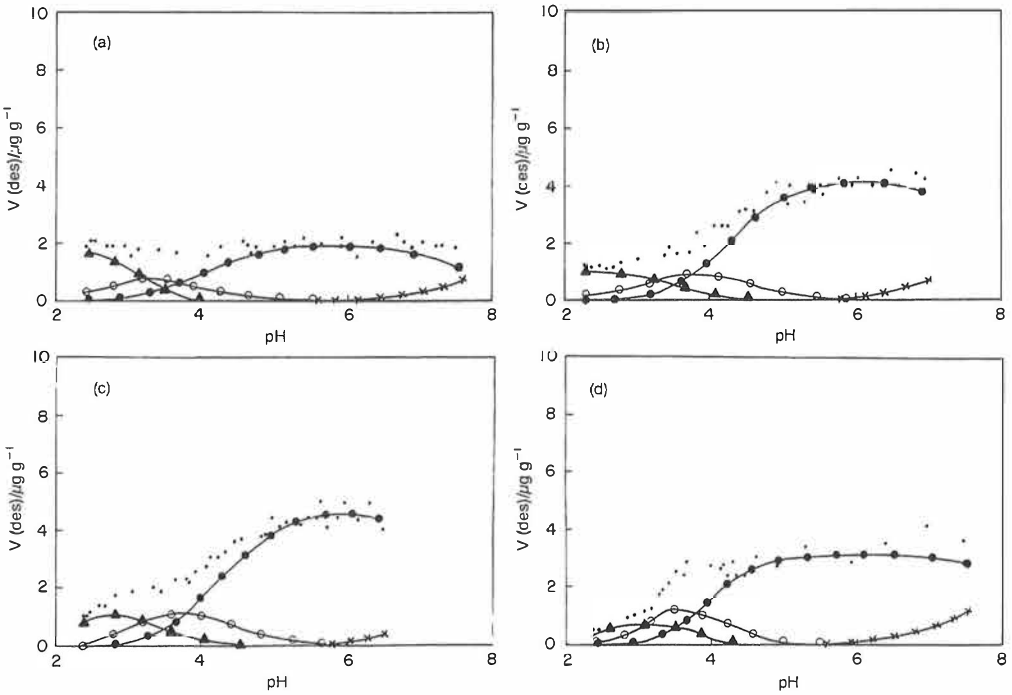

Fig. 5. Test points for desorption of V adsorbed from 10^{-5} M solutions. Leachability of different V(V) ionic species. pH denotes the acidity at the end of the 72-h adsorption process. (a) soil 1, (b) soil 2, (c) soil 3, (d) kaolin. ▲, VO_2^+; ○, H_3VO_4; ●, $H_2VO_4^-$; ×, HVO_4^{2-}; ·, data points.

leached V(V) species may have occurred during the 17-h shaking.

These results are in good agreement with those obtained by Tyler (1978), who used artificial rainwater acidified to pH values of 4.2, 3.2 and 2.8 for leaching of heavy-metal ions from two forest soils. The leachability of V in organic soil increased with pH, at least in the pH interval 4–6 of the percolate. The present results are also parallel with those obtained for retention of Mo(VI) by these same soils (Mikkonen & Tummavuori, 1993*b*).

Mo(VI) is adsorbed rapidly during the first hours of equilibration (Kyriacou, 1967; Gonzalez *et al.*, 1974; Motta & Ferreira de Miranda, 1985; Cruywagen & De Wet, 1988). Our experiments on adsorption of V(V) by the test soils from 10^{-4} M solution without any acid or base addition at the beginning showed that only about 30–45% of the total amount adsorbed in 72 h was retained during the first three hours. The measurements were performed after equilibration of 3, 5, 22, 29, 46 and 70 h, respectively.

On the basis of the adsorption results, it can be concluded that the organic matter content of soil or the texture alone plays an insignificant role in the adsorption of vanadium from a dilute solution. Soil 2, which has the coarsest texture and lowest humus content, retains identical amounts compared with soil 3 with a finer texture and higher humus content. Neither does it seem that the adsorption process can be explained by the amounts of Fe and Al oxides alone.

Because it was difficult to explain adsorption of V by the soils using the information of Table 1, we also measured the amounts of soluble phosphorus in the filtrates after equilibration of 3, 5, 22, 29, 46 and 70 h, and noticed that there seemed to be an almost linear correlation between soluble P and adsorbed V. It could be possible that the $H_2VO_4^-$ ion predominating at pH 5–7 is adsorbed effectively on the same sites of soil particles from which phosphate has been displaced. This assumption is not, however, valid at $pH < 4$, because in acid conditions the filtrates contain large amounts of soluble P.

Our adsorption envelopes show that retention of vanadate differs from that of molybdenum at $pH > 4$ (Mikkonen & Tummavuori, 1993*b*). Adsorption of molybdate decreases strongly as the pH increases, but adsorption of vanadate remains at a high level. In conditions where molybdenum added to soil would be readily available for plants or leached by rain water, a large amount of added vanadium would still be adsorbed by soils.

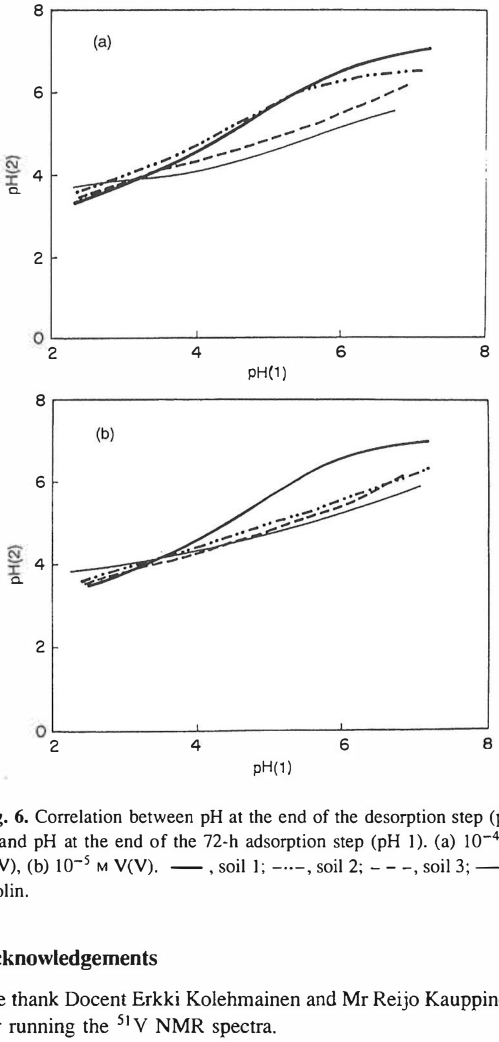

Fig. 6. Correlation between pH at the end of the desorption step (pH 2) and pH at the end of the 72-h adsorption step (pH 1). (a) 10^{-4} M V(V), (b) 10^{-5} M V(V). ——, soil 1; -··-, soil 2; - - -, soil 3; ——, kaolin.

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References

Allen, M.B. 1956. Photosynthetic nitrogen fixation by blue-green algae. *The Scientific Monthly*, **83**, 100–106.

Arnon, D.I. & Wessel, G. 1953. Vanadium as an essential element for green plants. *Nature*, **172**, 1039–1040.

Benemann, J.R., McKenna, C.E., Lie, R.F., Traylor, T.G. & Kamen, M.D. 1972. The vanadium effect in nitrogen fixation by *Azotobacter*. *Biochimica et Biophysica Acta*, **264**, 25–38.

Berrow, M.L., Wilson, M.J. & Reaves, G.A. 1978. Origin of extractable titanium and vanadium in the A horizons of Scottish Podzols. *Geoderma*, **21**, 89–103.

Bloomfield, C. & Kelso, W.I. 1973. The mobilization and fixation of molybdenum, vanadium, and uranium by decomposing plant matter. *Journal of Soil Science*, **24**, 368–379.

Bortels, H. 1933. Kurze Notiz üner die Katalyse der biologischen Stickstoffbindung. *Zentralblatt für Bakteriologie*, **87**, 476–477.

Burns, R.C., Fuchsman, W.H. & Hardy, W.F. 1971. Nitrogenase from vanadium-grown *azotobacter*: isolation, characteristics, and mechanistic implications. *Biochemical and Biophysical Research Communications*, **42**, 353–358.

Butler, J.R. 1953. The geochemistry and mineralogy of rock weathering, I. The Lizard area, Cornwall. *Geochimica et Cosmochimica Acta*, **4**, 157–178.

Cannon, H.L. 1963. The biogeochemistry of vanadium. *Soil Science*, **96**, 196–204.

Cruywagen, J.J. & De Wet, H.F. 1988. Equilibrium study of the adsorption of molybdenum(VI) on activated carbon. *Polyhedron*, **7**, 547–556.

Cruywagen, J.J., Heyns, J.B.B. & Visagie, J.L. 1989. Vanadium(V) protonation and condensation equilibria in the pH range 7–10 (NaCl medium, 25°C); a potentiometric and spectrophotometric study. *Polyhedron*, **8**, 1800–1801.

Davis, R.D., Beckett, P.H.T. & Wollan, E. 1978. Critical levels of twenty potentially toxic elements in young spring barley. *Plant and Soil*, **49**, 395–408.

Dean, J.A. (ed.) 1985. *Lange's Handbook of Chemistry*, 13th edn. McGraw-Hill, New York.

Fay, P. & De Vasconcelos, L. 1974. Nitrogen metabolism and ultrastructure in *Anabaena cylindrica*. II. The effect of molybdenum and vanadium. *Archives of Microbiology*, **99**, 221–230.

Goodman, B.A. & Cheshire, M.V. 1975. The bonding of vanadium in complexes with humic acid: an electron paramagnetic resonance study. *Geochimica et Cosmochimica Acta*, **39**, 1711–1713.

Gonzalez, R., Appelt, H., Schalscha, E.B. & Bingham, F.T. 1974. Molybdate adsorption characteristics of volcanic-ash-derived soils in Chile. *Soil Science Society of America Proceedings*, **38**, 903–906.

Gough, L.P., Shacklette, H.T. & Case, A.A. 1979. Element concentrations toxic to plants, animals, and man. *U.S. Geological Survey Bulletin*, **1466**, 55–56.

Heath, E. & Howarth, O.W. 1981. Vanadium-51 and oxygen-17 nuclear magnetic resonance study of vanadate(V) equilibria and kinetics. *Journal of the Chemical Society, Dalton Transactions*, 1105–1110.

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. *Journal of Soil Science*, **23**, 177–192.

Holm-Hansen, O. 1968. Ecology, physiology, and biochemistry of blue-green algae. *Annual Reviews of Microbiology*, **22**, 47–70.

Jacks, G. 1976. Vanadium in an area just outside Stockholm. *Environmental Pollution*, **11**, 289–295.

Kabata-Pendias, A. & Pendias, H. 1985. *Trace Elements in Soils and Plants*. CRC Press, Boca Raton, FL.

Koljonen, T. (ed.) 1992. *A Geochemical Atlas of Finland. Part 2, Till*. Geological Survey of Finland, Espoo.

Kyriacou, D. 1967. The pH dependence of adsorption of metallic oxyanions by ferric oxide powder. *Surface Science*, **8**, 370–372.

Le Riche, H.F. & Weir, A.H. 1963. A method of studying trace elements in soil fractions. *Journal of Soil Science*, **14**, 225–235.

McKenna, C.E., Benemann, J.R. & Traylor, T.G. 1970. A vanadium containing nitrogenase preparation: implications for the role of molybdenum in nitrogen fixation. *Biochemical and Biophysical Research Communications*, **41**, 1501–1508.

Mikkonen, A. & Tummavuori, J. 1993*a*. Retention of vanadium(V), molybdenum(VI), and tungsten(VI) by kaolin. *Acta Agriculturae Scandinavica, Section B, Soil and Plant Science*, **43,** 11–15.

Mikkonen, A. & Tummavuori, J. 1993*b*. Retention of molybdenum (VI) by three Finnish mineral soils. *Acta Agriculturae Scandinavica, Section B, Soil and Plant Science*, **43,** 206–212.

Mikkonen, A. & Tummavuori, J. 1993*c*. Retention of tungsten(VI) by three Finnish mineral soils. *Acta Agriculturae Scandinavica, Section B, Soil and Plant Science*, **43,** 213–217.

Motta, M.M.G. & Ferreira de Miranda, C. 1985. Adsorption of molybdate by clay minerals. *Revista Portuguesa de Quimica*, **27,** 505–510.

Nicholas, D.J.D. 1975. The functions of trace elements. In: *Trace Elements in Soil–Plant–Animal Systems* (eds D.J.D. Nicholas & A.R. Egan), pp. 181–198. Academic Press, New York.

Parker, R.D.R., Sharma, R.P. & Miller, G.W. 1978. Vanadium in plants, soil and water in the Rocky Mountain region and its relationship to industrial operations. In: *Trace Substances in Environmental Heath 12* (ed. D.D. Hemphill), pp. 349–350. University of Missouri, Columbia, MO.

Pope, M.T. 1983. *Heteropoly and Isopoly Oxometalates*. Springer-Verlag, New York.

Pratt, P.F. 1966. Vanadium. In: *Diagnostic Criteria for Plants and Soils: Riverside* (ed. H.D. Chapman), pp. 480–483. University of California, Riverside, CA.

Szalay, A. & Szilagyi, M. 1967. The association of vanadium with humic acids. *Geochimica et Cosmochimica Acta*, **31,** 1–6.

Taylor, B.M. & Giles, J.B. 1970. The association of vanadium and molybdenum with iron oxides in soils. *Journal of Soil Science*, **21,** 203–215.

Tyler, G. 1976. Influence of vanadium on soil phosphatase activity. *Journal of Environmental Quality*, **5,** 216–217.

Tyler, G. 1978. Leaching rates of heavy metal ions in forest soil. *Water, Air and Soil Pollution*, **9,** 137-148.

Wallace, A., Alexander, G.V. & Chaudry, F.M. 1977. Phytotoxicity of cobalt, vanadium, titanium, silver, and chromium. *Communications in Soil Science and Plant Analysis*, **8,** 751–756.

Wanty, R.B. & Goldhaber, M.B. 1985. A method for the determination of vanadium and iron oxidation states in naturally occurring oxides and silicates. *Talanta*, **32,** 395–398.

Welch, R.M. 1973. Vanadium uptake by plants. *Plant Physiology*, **51,** 828–832.

Welch, R.M. & Cary, E.E. 1975. Concentration of chromium, nickel, and vanadium in plant materials. *Journal of Agricultural and Food Chemistry*, **23,** 479–482.

Wells, N. 1956. Soil studies using sweet vernal to assess element availability. Part 2. Molybdate ion fixation in New Zealand soils. *New Zealand Journal of Science and Technology, A: Agricultural Research*, **37,** 482–502.

PAPER 5

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

ANNELI MIKKONEN and JOUNI TUMMAVUORI

MIKKONEN, A. & TUMMAVUORI, J. 1994. **Desorption of phosphate from three Finnish mineral soil samples during adsorption of vanadate, molybdate, and tungstate**. Agricultural Science in Finland 3: 481–486. (Department of Chemistry, University of Jyväskylä, P.O.Box 35, FIN-40351 Jyväskylä.)

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 AYLMORE 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 oxysalt 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 phosphate 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 $Mo(OH)_6$, $HMoO_4^-$, and MoO_4^{2-}, the last one being predominant at pH > 4.5. At concentrations > 10^{-4} mol/l, polyanions, such as $Mo_7O_{24}^{6-}$ and its protonated forms, may be present at pH ≤ 5. In V(V) solutions, at pH ≤ 5, polyionic decavanadate species $HV_{10}O_{28}^{5-}$ and $H_2V_{10}O_{28}^{4-}$ 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, Maksimovskaya 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 $(H^+)_p(MoO_4^{2-})_5(HPO_4^{2-})_2$, p = 8,9,10 (Pettersson et al. 1985) and tetra-decavanadophosphate $HPV_{14}O_{42}^{8-}$ (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 $HClO_4$ + 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); 1 g: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

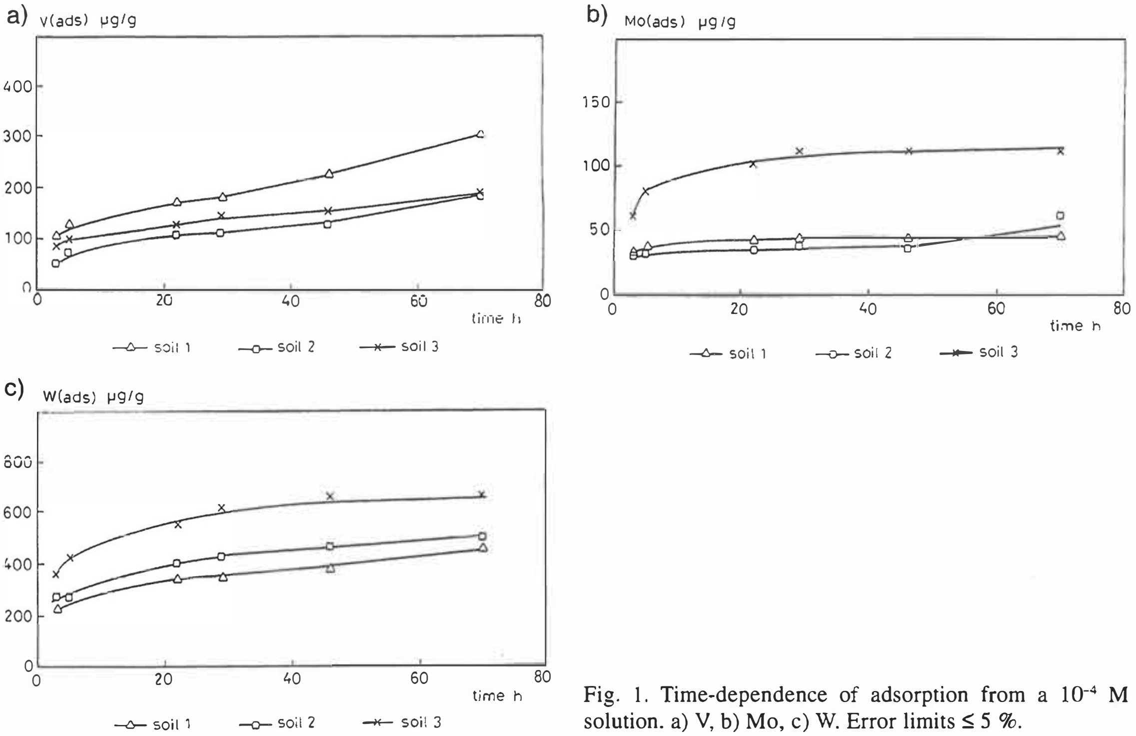

Fig. 1. Time-dependence of adsorption from a 10^{-4} M solution. a) V, b) Mo, c) W. Error limits ≤ 5 %.

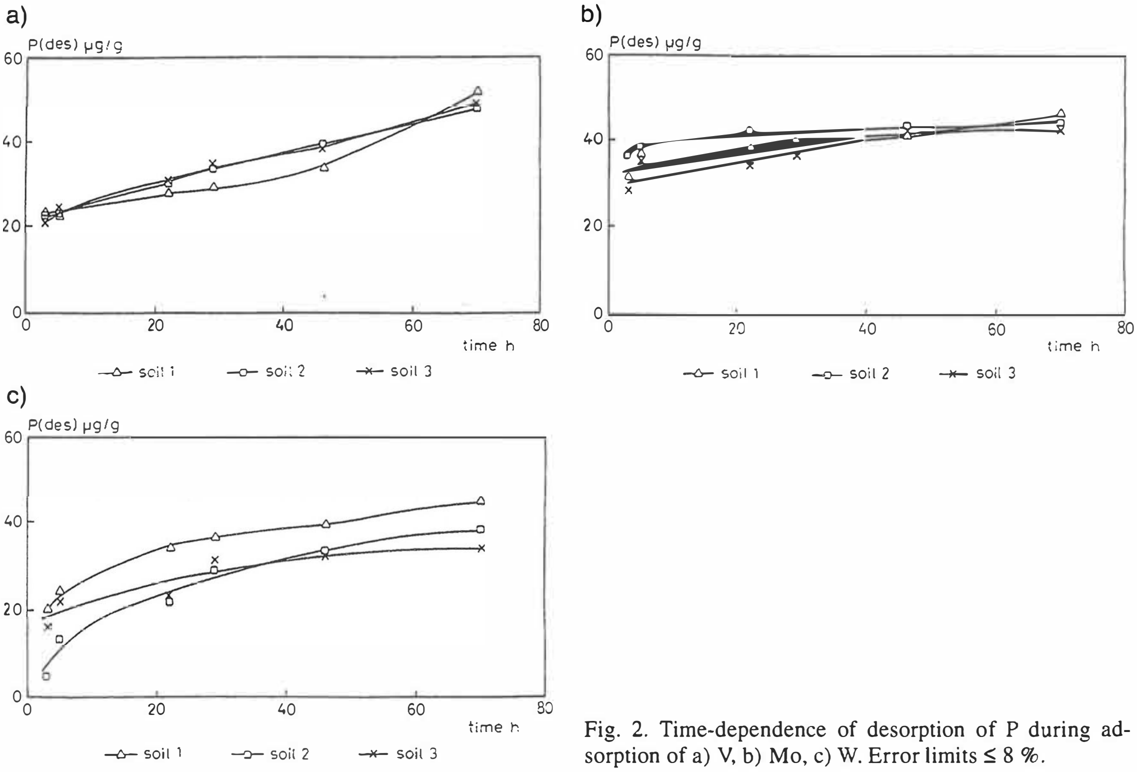

Fig. 2. Time-dependence of desorption of P during adsorption of a) V, b) Mo, c) W. Error limits ≤ 8 %.

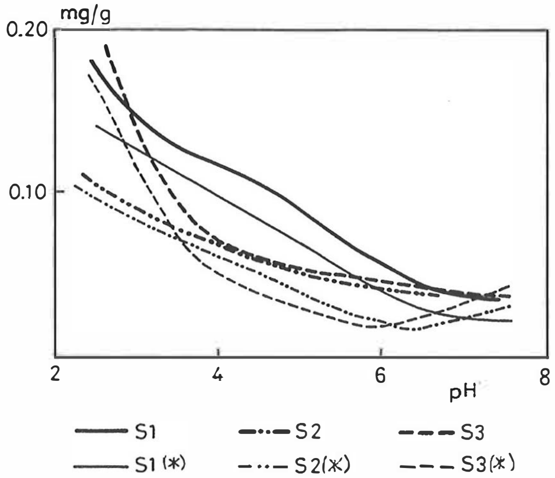

Fig. 3. Mobility of P from the blank samples and changes caused by the addition of 10^{-4} M molybdate. S1 = soil 1, S2 = soil 2, S3 = soil 3; (*) denotes blank samples.

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 µg/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

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 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 µg/g) and desorbed P (in µg/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

References

BARBER, S.A. 1984. Soil nutrient bioavailability. A mechanistic approach. John Wiley & Sons, New York. 398 p.

BARROW, N.J. 1974. On the displacement of adsorbed anions from soil: 1. Displacement of molybdate by phosphate and by hydroxide. Soil Science 116: 423–431.

– 1989. Testing a mechanistic model. IX. Competition between anions for sorption by soil. Journal Soil Science 40: 415–425.

CRUYWAGEN, J.J. & VAN DER MERWE, I.F.J. 1987. Tungsten(VI) equilibria: A potentiometric and calorimetric investigation. Journal of Chemical Society, Dalton Transactions: 1701–1705.

GOLDBERG, S. & TRAINA, S.J. 1987. Chemical modeling of anion competition on oxides using the constant capacitance model-mixed-ligand approach. Soil Science Society of America Journal 51: 929–932.

GORLACH, E., GORLACH, K. & COMPAŁA 1969. The effect of phosphates on the sorption and desorption of molybdates in the soil. Agrochimica 6: 506–512.

HARRISON, A.T. & HOWARTH, O.W. 1985. Oxygen exchange and protonation of polyanions: a multinuclear magnetic resonance study of tetravanadophosphate(9–) and decavanadate(6–). Journal of Chemical Society, Dalton Transactions: 1953–1957.

LINDSAY, W.L. 1979. Chemical equilibria in soils. Wiley-Interscience, Brisbane. 449 p.

MAKSIMOVSKAYA, R.I. & BURTSEVA, K.G. 1985. ^{17}O and ^{183}W NMR studies of the paratungstate anions in aqueous solutions. Polyhedron 4: 1559–1562.

MIKKONEN, A. & KOLEHMAINEN, E. 1994. ^{51}V NMR studies on aqueous solutions of V(V) and V(IV). Department of Chemistry, University of Turku, Research Report No 1/1994, p. 77.

– & TUMMAVUORI, J. 1993a. Retention of vanadium(V), molybdenum(VI) and tungsten(VI) by kaolin. Acta Agriculturae Scandinavica, Section B. Soil and Plant Science 43: 11–15.

– & TUMMAVUORI, J. 1993b. Retention of molybdenum (VI) by three Finnish mineral soils. Acta Agriculturae Scandinavica, Section B, Soil and Plant Science 43: 206–212.

– & TUMMAVUORI, J. 1993c. Retention of tungsten(VI) by three Finnish mineral soils. Acta Agriculturae Scandinavica, Section B, Soil and Plant Science 43: 213–217.

– & TUMMAVUORI, J. 1993d. Retention of vanadium(V) by three Finnish mineral soils. European Journal of Soil Science (In press)

MURALI, V. & AYLMORE, L.A.G. 1983. Competitive adsorption during solute transport in soils; 3. A review of experimental evidence of competitive adsorption and an evaluation of simple competition models. Soil Science 136: 279–290.

PETTERSSON, L., ANDERSSON, I. & ÖHMAN, L.-O. 1985. Multicomponent polyanions. 35. A ^{31}P NMR study of aqueous molybdophosphates. Acta Chemica Scandinavica A 39: 53–58.

POPE, M.T. 1983. Heteropoly and isopoly oxometalates. Springer-Verlag, Berlin. 175 p.

ROY, W.R., HASSETT, J.J. & GRIFFIN, R.A. 1986a. Competitive interactions of phosphate and molybdate on arsenate adsorption. Soil Science 40: 203–210.

–, HASSETT, J.J. & GRIFFIN, R.A. 1986b. Competitive coefficients for the adsorption of arsenate, molybdate, and phosphate mixtures by soils. Soil Science Society of America Journal 50: 1176–1182.

–, HASSETT, J.J. & GRIFFIN, R.A. 1989. Quasi-thermodynamic basis on competitive-adsorption coefficients for anionic mixtures in soils. Journal of Soil Science 40: 9–15.

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

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