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**Soil-water partition coefficients
for some trace metals.**

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Preface

This report contains results of research carried out in the framework of the project 'Setting integrated environmental quality objectives'. The results have been discussed in the 'Setting integrated environmental quality objectives advisory group'. Members thereof are J.H.M. de Bruijn (Ministry of Housing, Physical Planning and the Environment), J.H. Canton (National Institute of Public Health and Environmental Protection), C.A.J. Denneman (Ministry of Housing, Physical Planning and the Environment), J.W. Everts (Ministry of Transport, Public Works and Water Management, Tidal Waters Division), M.P.M. Janssen (Institute for Forestry and Nature Research), P. Leeuwangh (Winand Staring Centre for Integrated Land, Soil and Water Research), E.J. van de Plassche (National Institute of Public Health and Environmental Protection), P.B.M. Stortelder (National Institute of Inland Water Management), J. Struijs (National Institute of Public Health and Environmental Protection), M. Vossen (National Institute of Inland Water Management), and J. van Wensem (Technical Committee on Soil Protection).

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Samenvatting

In het kader van het project Integrale Normstelling (INS) zijn partitievoëfficiënten voor de distributie van stoffen in bodems en sedimenten (K_p 's) afgeleid voor de sporenelementen: Ba, Be, Co, Mo, Se, Tl, Sb, Sn en V. Daartoe is een literatuurevaluatie uitgevoerd met betrekking tot adsorptie-experimenten met bodems en sedimenten. De K_p 's kunnen gebruikt worden voor de afleiding van Maximaal Toelaatbare Risiconivo's (MTR's) voor bodem en sediment uit ecotoxicologisch onderbouwde MTR's voor water als er geen toxicologische gegevens voor bodem- of sedimentorganismen beschikbaar zijn. Verder kunnen de partitievoëfficiënten gebruikt worden voor het op elkaar afstemmen van de MTR's voor de verschillende compartimenten (bodem, sediment, poriewater, en oppervlaktewater). De toepassing van deze zogenaamde evenwichtspartitiemethode voor sporenmatalen wordt besproken. Er werd geconcludeerd dat voor de toepassing van deze methode K_p 's afgeleid uit schudproeven de voorkeur verdienen boven K_p 's bepaald met behulp van andere experimentele technieken. Voorgesteld werd om deze K_p 's te gebruiken voor het berekenen van het geadsorbeerde metaalgehalte dat correspondeert met de MTR voor water en om bij dit gehalte een schatting van het onuitwisselbare metaalgehalte van bodems en sedimenten op te tellen. Dit laatste gehalte kan in eerste instantie ruwweg worden benaderd met het achtergrondgehalte van metalen in bodems en sedimenten.

Voor de adsorptie van Ba, Be en Sn aan bodems waren geen experimentele gegevens beschikbaar. Aangenomen werd dat partitie van de elementen vergelijkbaar is met respectievelijk Ca, Mg en Pb. Aangezien in de literatuur geen schudproeven met sedimenten voorhanden waren, werden de K_p 's voor sedimenten afgeleid uit metingen van de metaalgehalten van gesuspendeerd materiaal uit rivieren. Deze K_p 's bleken aanzienlijk hoger te zijn dan die van bodems. Het verschil werd vooral toegeschreven aan de verschillende adsorptie-eigenschappen van bodems en sedimenten, het feit dat een deel van de metalen onuitwisselbaar gebonden is en aan verschillen in fysisch-chemische eigenschappen zoals de pH, deeltjesconcentratie en de opgeloste concentraties.

Summary

In the frame of the project Quality objectives and risks, partition coefficients (K_p 's) were derived for the partitioning in soils and sediments of: Ba, Be, Co, Mo, Se, Tl, Sb, Sn, and V. For that purpose a literature review with respect to adsorption experiments with soils and sediments was carried out. The K_p 's can be used to derive quality objectives for soils and sediments from ecotoxicologically based quality objectives for water when toxicity data for soil or sediment organisms are not available. Furthermore, according to the equilibrium partitioning theory, the K_p 's can be used to gear quality objectives for different compartments (soil, sediment, interstitial water and surface water) together.

The application to trace metals of this so called equilibrium partitioning method is discussed. It was concluded that in the framework of this method batch experiments should be preferred over other experimental techniques for the determination of K_p 's. It is proposed that K_p 's are used to estimate the adsorbed metal content that corresponds with the quality objectives for water and that an estimation of the unexchangeably bound metal content of soils and sediments is added to this content. The latter might be approximated with the background content of metals in soils and sediments.

Selected K_p 's for soils are presented. Experimental data for Ba, Be, and Sn were not available. Partitioning of these metals in soils was assumed to be comparable with Ca, Mg, and Pb respectively. For sediments no studies were found where adsorption was tested in batch experiments. Therefore, K_p 's for sediments were derived from measurements of the metal content of riverine particulate matter. These K_p 's were much higher than the soil K_p 's. The differences are attributed to differing characteristics of the sorbent, the effect of the unexchangeably bound metal content on the K_p and to different physical-chemical conditions for adsorption like the pH, the particle concentration and the aqueous metal concentration.

1 Introduction

1.1 Objective and framework

In 1989 the project 'Setting environmental quality objectives' started arising from action item A-35 of the National Environmental Policy Plan running as follows. [1] Goal of this project is to derive integrated quality objectives for air, water, and soil for a great number of compounds based on the risk philosophy of the Ministry of Housing, Physical Planning, and the Environment. [2] The project is carried out by the National Institute of Public Health and Environmental Protection. The first sub-project 'MILBOWA' resulted in the report 'Desire for levels'. [3] In this report a methodology was proposed for deriving these objectives for several compounds like heavy metals, chlorophenols, pesticides and polycyclic aromatics. Based on this report integrated environmental quality objectives for water and soil were proposed by the Minister of the Environment from The Netherlands for several compounds. [4] The second sub-project was called 'exotic metals'¹. Goal of this project was to derive integrated quality objectives for water, sediment, and soil for antimony, barium, beryllium, cobalt, molybdenum, selenium, thallium, tin, and vanadium. For deriving these quality objectives almost the same methods are used as described in 'Desire for levels'. This means that maximum permissible concentrations (MPC) for the three compartments are determined using extrapolation methods based on toxicity data, and that these MPC's for the different compartments are coordinated using the equilibrium partitioning method. Therefore the following had to be done:

1. derivation of MPC's for water, sediment, and soil based on ecotoxicological data. Also secondary poisoning had to be taken into account.
2. derivation of partition coefficients in order to apply the equilibrium partitioning method,
3. gathering information about background levels in soil, groundwater, and surface water,
4. proposing integrated quality objectives.

¹ These metals are denoted 'exotic metals', because they were only relatively seldom subject of environmental studies. Although selenium and antimony are strictly speaking not metals but metalloids they are denoted trace metal or 'exotic metal' in this report.

It was decided by the National Institute of Public Health and Environmental Protection and the Ministry of Housing, Physical Planning, and the Environment to publish separate reports about these four aspects. This report contains the ecotoxicological data and the calculation of MPC's using extrapolation procedures based on these data.

1.2 Equilibrium partitioning

The equilibrium partitioning method (EP method) was originally proposed by Pavlou and Weston (1984) to develop sediment quality criteria. The method attempts to model the tendency of a chemical to move from one environmental compartment to another. This concept has been described in detail by Mackay (1979), Mackay and Paterson (1981, 1982) and Shea (1988). Potential biological effects of a certain contaminant concentration in the sediment can be estimated using appropriate water quality criteria and the partition coefficient for the contaminant between the aqueous phase and sediment phases. In this manner sediment quality criteria can be derived from water quality criteria.

When the EP method is applied it is assumed that toxic effects are largely caused by exposure to pore water and hardly or not at all by uptake from particles (Van Leeuwen et al., 1992). Those opposing the EP method stress that this is not always valid (Landrum and Robbins, 1989).

Van de Meent et al. (1990) extended the equilibrium partitioning method to soils to compensate for the lack of toxicity data for soil organisms.

A validation of the equilibrium partition method for the derivation of MPC's for soils and sediments using literature data and field measurements is beyond the scope of this report, but will be undertaken by the National Institute of Public Health and Environmental Protection in the near future.

1.3 Approach

In order to collect the scarce data concerning the mobility of the "exotic metals" in the environment, literature was selected from the Chemical Abstracts Data System. Relevant titles were selected using the following key words in combination with the full name of the metal: "adsorption", "desorption", "partitioning", "partition", "distribution",

"complexation", "Langmuir", "Freundlich", "bio-availability", "complex formation", "fractionation", "precipitation", "coprecipitation", "remobilization", "interaction", "liquid", "solid", "suspended matter", "suspended particulate", "sediment", "sludge", "soil", "particulate matter", "solid phase", "liquid phase", "suspended solid", "suspended material", "interstitial water", "porewater", and "groundwater". Abbreviated metal names were not used as key words, because this would result in a large number of false hits (the abbreviated names often form a part of arbitrary words in the title). As a consequence literature that did not mention the full name of the metal in the title were missed. This was partly overcome by manually selecting titles from recent review articles, relevant handbooks and journals.

Sometimes data concerning the mobility of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn were included in this report, because comparison with these data facilitates the drawing of conclusions concerning the mobility of the "exotic metals". This holds especially when the "exotic metals" are tested together with the other metals in one experiment. Such comparisons and physical-chemical theory considering soil processes have determined which data were finally selected as the most appropriate and reliable.

It is well known that under anoxic conditions metals can form insoluble sulfides in soils or sediments. Therefore, it is expected that fixation of trace metals in anoxic sediments containing sufficient sulfur will lead to a decreased toxicity. Recent experiments with marine sediments contaminated with Cd (Di Toro et al., 1990) showed that LC50's for amphipods were highest for sediments with a high "acid volatile sulfide" (AVS) content. It was concluded that AVS is the reactive pool of solid phase sulfide in sediments that is available to bind with metals and that this phase determines the LC50 for Cd in the sediments tested. The experiments were conducted for Cd only, but the authors expect that the results apply to all other potentially toxic metals whose sulfides are less soluble than iron sulfide (e.g. Ni, Zn, Pb, Cu, Hg). However, the question should be posed whether sediment dwelling organisms actually benefit from anoxic conditions in sediments, because normally such organisms will ensure that they are surrounded by oxic water to allow respiration. Anoxic conditions have not been considered in this report, they remain a subject of further

investigations by the RIVM. Possibly these investigations will include the determination of trace metals in interstitial water and the acid volatile sulfide content of Dutch sediments. Because all partition coefficients presented in this report were determined under aerobic conditions, it is possible that the mobility of some trace metals is overestimated in the case of anoxic conditions that are fairly common for sediments.

2 Application of the equilibrium partitioning method to trace metals

The EP method is based on the premise that the distribution of the contaminants in an environmental phase (e.g., sediment) is controlled by a continuous exchange with other environmental phases (water and biota) (Shea, 1988). These bio-geochemical exchange processes must be sufficiently rapid and reversible to have reached equilibrium (or steady state) at the time of sample collection.

The EP method normally involves the use of partition coefficients for the prediction of aqueous concentrations from contents of the solid phase and vice versa. Here it is assumed that the relation between the metal content of the solid phase and aqueous concentrations is approximately linear for the range of concentrations considered. This might be true for partitioning of metals controlled by adsorption processes, but it is certainly not true for partitioning controlled by precipitation processes. Metal concentrations that are controlled by precipitation reactions depend only on the solubility of trace metal containing minerals. They are independent of the trace metal content of the soil or sediment. Therefore, precipitation processes should be treated as special cases of trace metal immobilization where the EP method does not directly apply.

The total concentration of any element, C_{total} , in a soil or sediment is equal to:

$$C_{total} = C_{fixed} + C_{bound} + C_{water} \quad (1)$$

where:

C_{fixed} = concentration of fixed element comprising part of the structure of minerals

C_{bound} = concentration of element adsorbed or precipitated onto the surface of minerals and onto organic matter exchange sites

C_{water}^2 = concentration of element in interstitial water (expressed as mg soluble element/kg soil or sediment)

Because part of the trace metal content of soils and sediments is enclosed in mineral grains (C_{fixed}), trace metals are only partly exchangeable with the water phase. Furthermore, a part of C_{bound} might be irreversibly bound on the surface of particles. Consequently, the unexchangeably bound metal content of soils and sediments equals to C_{fixed} plus the fraction of C_{bound} that is irreversibly bound.

Partition coefficients apply only to the fraction of the element that can exchange with the water phase. This fraction could be approximated with C_{bound} , but is in fact smaller because part of the elements present on the surface of soil or sediment particles might be irreversibly bound.

From the foregoing it is clear that the K_p 's used for the EP method should be based on experiments where adsorption processes control aqueous metal concentrations. The metal concentrations should be at equilibrium or in a steady state situation. The K_p 's should be based on the fraction of the metal content that can actually exchange with the aqueous phase and not on the total metal content. Normally it can be shown, or it is reasonable to assume, that these conditions are fulfilled in batch experiments. In column experiments, "in situ" measurements and measurements of interstitial water or particulate matter these conditions are generally not fulfilled (see 3.8). Furthermore, K_p 's from the latter experiments are usually based on total metal contents of the solid phase, whereas the EP method applies only to the exchangeable fraction of the trace metal.

For the purpose of deriving soil and sediment quality criteria for trace metals from water quality criteria and for the purpose of intercompartmental harmonization, it is proposed that the EP method is used in the following manner:

²Simple calculations show that the trace metal content of interstitial water contributes normally only very little to the total metal content of soils or sediments.

- K_p 's derived from batch experiments are used to estimate the adsorbed metal content that corresponds with the water quality criteria
- and to the adsorbed metal content an estimation of the unexchangeably bound metal content is added.

K_p 's derived for soils and sediments are presented in Chapter 5.

Extractions of uncontaminated Dutch reference soils performed by Aalbers et al. (1992) showed that the major part of the trace metal content of these soils is unexchangeably bound. Therefore, it is concluded that it is reasonable to assume that the unexchangeably bound fraction of trace metals in soils can be approximated with the natural background content of trace metals in soils. The background contents of the "exotic metals" in soils will be reported in a separate report to be published by De Bruijn and Denneman (1992).

To estimate the unexchangeably bound metal content of sediments it is necessary to evaluate the results of desorption experiments. Lietz and Galling (1989) showed that a large fraction of the metal content of uncontaminated sediments is firmly bound. River sediments from Germany were investigated relative to their desorption characteristics of Zn, Cd and Pb. The sediments contained 2297 mg/kg Zn, 78 mg/kg Cd and 293 mg/kg Pb. TA mixture of sediments and water was put in dialysis pipes. From the medium surrounding the pipes samples were taken for analysis after 44 hours of equilibration. Desorption reached a maximum of 1.96 % Pb, 0.31 % Cd and 0.02 % Zn. Addition of 1 μ M EDTA or NTA (complexing agents) to enhance the uptake capacity of the medium raised Zn values 28 fold, Cd and Pb were enhanced by a maximum 5-fold. The authors concluded that more than 90 % of the three metals was firmly bound to the sediment.

Van der Weijden et al. (1977) carried out desorption experiments with particulate matter from the Rhine. Aliquots of particulate matter were resuspended in distilled water, and various seawater solutions. Metal contents of the particulate matter were (in mg/kg): Cr 495, Mn 935, Fe 42020, Ni 65, Cu 405, Zn 1505, Cd 28. Desorption was at maximum in seawater at pH 7.5 (expressed as percentage of the total metal content): Cr 0.2, Mn 17, Co

8, Ni 14, Cu 5, Zn 21, Cd 80. It was demonstrated that complex formation of the metals with ligands from the seawater enhanced the desorption process. The results of Van der Weijden et al. suggest that for some metals only a minor fraction of the metal content of particulate matter can exchange with the aqueous phase, but that this fraction is considerably higher for others (e.g. Cd).

The observations of Lietz and Galling (1989) and Van der Weijden et al. (1977) reveal that the unexchangeably bound metal content of sediments varies considerably as a result of characteristics of the sediment, the metal and differing experimental conditions. As a first coarse approximation it seems reasonable to assume that this fraction can be approximated with the natural background content of trace metals in sediments.

3 Mobility of trace metals

The mobility of trace metals in soil and sediments is controlled by their concentration in the soil solution or interstitial water. The aqueous metal concentration is determined by adsorption, complexation and precipitation of the metal ion. In the most simple treatment of adsorption processes it is usually assumed that the adsorbed metal concentration (C_s) is approximately proportional to the aqueous equilibrium concentration (C_e). The partition coefficient (K_p) is the corresponding equilibrium constant:

$$K_p = \frac{C_s}{C_e} \quad (2)$$

The precipitation of metal ions can be modelled using the solubility products of minerals. The complexation of metal ions is dependent on the composition of the interstitial water and can be modelled using equilibrium constants for the formation of metal complexes.

In the remainder of this chapter a short outline is given concerning physical-chemical factors that determine the mobility of trace metals.

3.1 Adsorption

3.1.1 Electrostatic and specific interactions

Many trace metals, though not all, exist in interstitial water as cations. The adsorption of these metals is partly determined by electrostatic interactions between the metal ions and the surface of the soil particles. In most soils a major part of the soil particles have a negative surface charge (clay minerals, organic matter). This electrostatic charge is counterbalanced by a thin, diffuse layer of the soil solution that contains an increased number of cations compared to the bulk soil solution. The distribution of the cations near the charged surface is determined by the search for a minimal potential energy (the cations approach the negatively charged surface as close as possible) and the search for maximal entropy (a homogenic distribution of the cations in the soil solution) (Bolt, 1978). The resulting distribution of ions is a "diffuse" accumulation zone near the charged surface. The concentration

distribution of cations in the zone obeys the Boltzmann equation:

$$\frac{C_1}{C_2} = e^{\frac{-(E_1-E_2)}{kT}} \quad (3)$$

Here E_1-E_2 is the difference in potential energy of the ions in the attractive field, comparing two arbitrary positions 1 and 2, while kT is the (thermal) kinetic energy of the ion. The distribution of charge and concentration of cations as described above is often called the "Diffuse Double Layer".

Adsorption based on electrostatic interactions is reversible. Selectivity for certain cations is based on the charge of the cation, modified to some extent by geometric factors like the distance of closest approach (Bolt et al. 1978). Cations with a high charge might displace lower charged ions from the Diffuse Double Layer. Cations that easily lose their surrounding water molecules (high hydration enthalpy) can approach the charged surface closer, and are therefore, more strongly adsorbed.

"Specific adsorption" is a second term that is often used when describing adsorption processes. Specific adsorption involves the formation of chemical (covalent) bonds with ligands on the surface of the soil particle. Characteristic for specific adsorption is that the ions are only partially released if a surplus of non specific adsorbing ions is added to the soil solution.

Concentrations of trace metals found in the environment are always considerably lower than concentrations of cations like Ca^{2+} , Mg^{2+} , K^+ and Na^+ . It is shown experimentally that in spite of the very large surplus of the latter cations in soil solution, trace metals are often adsorbed very well in soils. This shows that the adsorption of trace metals in soils cannot be explained by using relatively simple electrostatic models (such models would predict that the large concentrations of the major-cations of the soil solution would displace the trace metals from the diffuse double layer). Therefore, it is concluded that specific interaction processes determine the adsorption of trace metals in soils to a great extent. It can be imagined that electrostatic attraction influences the mobility of trace metals mainly in an indirect way; the electrostatic

attraction enables the cation to approach the surface of soil particles closely, thus allowing the formation of a chemical (covalent) bond with chemical groups located on the surface.

Brummer (1986) gives the following order for increasing affinity of specific adsorption: $Cd < Ni < Co < Zn \ll Cu < Pb < Hg$. This order is only a first, coarse approximation, as will be shown in the remainder of this chapter. The true affinity for adsorption does not depend only on characteristics of the metal, but also on physical-chemical characteristics of the soil particles and the composition of the soil solution.

3.1.2 Clay minerals

Silicate minerals in general and therefore clay minerals as well, possess a negative electrostatic surface charge. Clay minerals are very well capable of adsorbing metal ions, because of this negative charge and their large specific surface area. Beside the negative charge clay minerals sometimes possess some positive charge at the edges of the clay plates.

Certain cations (e.g. K^+ , Cs^+) can be fixed by clay minerals in the crystal structure where they are irreversibly bound.

3.1.3 Fe-, Al-, Mn-(hydr)oxides

Hydroxides of iron, aluminium and, to a lesser extent, manganese always occur in soils, often as a coating of clay minerals and quartz. The micro-crystalline hydroxides have a large specific surface (in general larger than clay minerals). The hydroxides stay most reactive when they are periodically reduced and subsequently oxidized, e.g. after a rainshower that induces local anaerobic conditions (Chardon, 1984). In seawater Fe- en Mn-hydroxides are the major control mechanisms for metal concentrations.

Hydroxides possess a pH-dependent surface charge. At low pH's the surface is mainly occupied by protons, at higher pH's the occupation of acid surface groups decreases and the surface is increasingly negatively charged. At a neutral pH most surfaces of metal hydroxides that occur in soils (except siliceous hydroxides) possess a positive surface charge. Adsorption of trace metals at hydroxides is

strongly pH-dependent, partly because of the varying surface charge. Cation adsorption increases with an increasing pH.

3.1.4 Organic matter

It is now thought that organic particles, because of the very high specific surface area and the negative surface charge, contribute most to the functional groups regarding metal adsorption in aquatic systems (Morell, 1983). Organic matter occurs as free particles (living organisms, dead remains, condensed humic material) or in the form of organic coatings on inorganic particles (e.g. clay minerals and oxides). Organic matter is a major constituent of particulate matter (Morell, 1983).

The affinity for adsorption of trace metals to organic matter differs for each metal (e.g. Cu is adsorbed strongly by soils rich in organic matter).

On average organic matter in soils is decomposed at 1-3 % a year depending on the type of organic matter and soil conditions. In the long term trace metals bound to organic matter remain bioavailable due to the degradation of organic matter.

Low organic matter contents are often found in sediments being rich in sand. This partially explains the usually weak adsorption characteristics of sandy sediments (see 3.1.5).

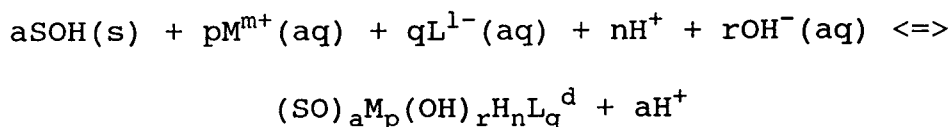
3.1.5 Exchangeability and texture

All trace metals including the exotic metals are found in natural, unpolluted soil and surface- or groundwater. The contents usually are low. Trace metals in soils are partly enclosed in the crystalline structure of minerals (e.g. quartz or clay minerals). It is obvious that this part of the trace metal content cannot exchange with the interstitial water and is, therefore, unavailable for organisms. Natural background values for most trace metals are usually lowest in soils with a coarse texture (sand soils). This is mainly a result of the fact that these soils chiefly consist of quartz which generally contains less trace metals than clay minerals.

Soils rich in clay usually adsorb trace metals more strongly than sandy soils. This is partly a result of the fine texture of the clay soils (with decreasing size of soil particles the specific surface area increases and therefore adsorption is increased). Texture affects adsorption also in an indirect way. In clay soils a low pH is encountered relatively seldom, whereas low pH's are common for sand soils. The low pH values in sand soils result in low adsorption coefficients for cations (see 3.1.6).

3.1.6 pH

The adsorption of metal cations is often represented by reaction equations like:



Where SOH(s) represents an reactive adsorption site on an oxide or hydroxide solid, M^{m+} is a metal cation, L^{l-} is a ligand and d represents the valence of the solid phase product formed. The exact stoichiometry and the number of adsorption sites are usually not known. However, the reaction illustrates that an increase of the pH results in a decrease of the aqueous concentration of the metal ions; the proton competes with metal ions for adsorption sites.

Chardon (1984) investigated the pH-dependent adsorption of Cd using 12 Dutch soils brought to pH's between 4 and 7 with HCl and $\text{Ca}(\text{OH})_2$ solutions. For 10 soils K_p increased when the pH was raised; for the remaining two soils the increase of the K_p halted at pH 6, after which it decreased. On average the K_p increased with a factor 3 when the pH was raised one unit.

Figure 1 shows that metal adsorption at riverine particulate matter and fine sediments is strongly enhanced by a high pH. A rise of the pH from 6 to 7 results in an increase of the Co-adsorption from approximately 65% to 90% (steepest part of the curve). It is difficult to estimate the pH-effect for partitioning in the field, because it depends on the pH-range, the metal, the composition of the interstitial fluid and the nature of the adsorbing surface. Furthermore, Kinniburgh and Jackson (1982) showed that so called adsorption edges for iron hydroxides (these resemble

the sigmoid curves shown in Figure 1) shift to progressively higher pH values when the surface of the oxide becomes increasingly occupied with Zn.

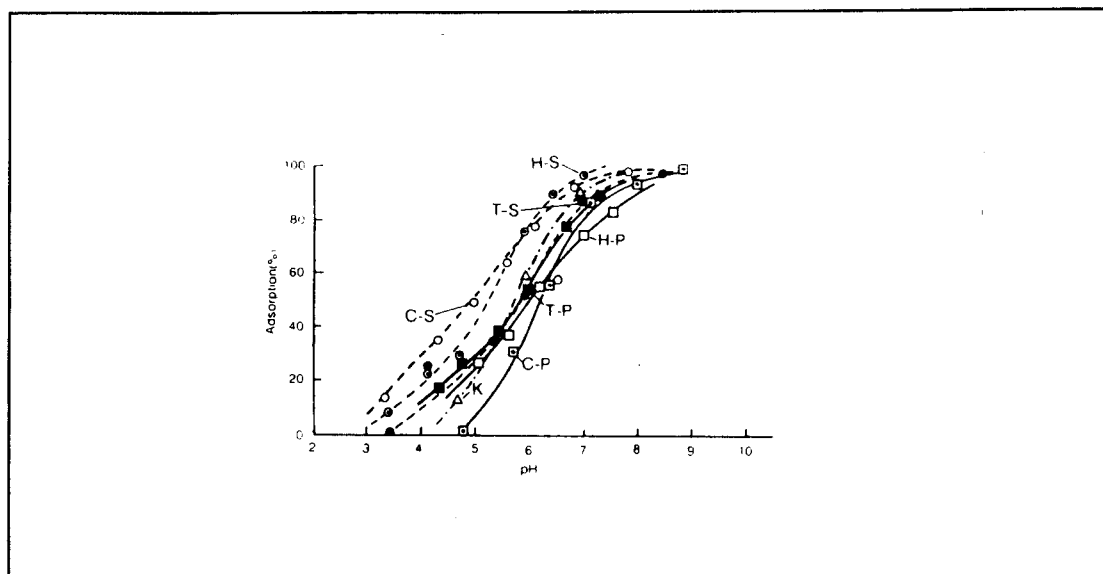


Figure 1 pH dependent adsorption of Co(II) to fine riverine sediments (H-S, T-S, C-S) and particulate matter (H-P, T-P, C-P) from Japan. After Osaki et al. (1990)

3.1.7 Concentration dependency

In many experiments it was shown that the K_p for the adsorption of metals is not constant, but dependent upon the equilibrium concentration of the aqueous phase; for high concentrations K_p 's are usually lower than for low concentrations. In other words the adsorbed amount of the compound increases if the equilibrium concentration increases, but the increase becomes smaller at high equilibrium concentrations. If we assume that specific adsorption is the major adsorption process, the foregoing can be explained considering that sites on the surface of soil particles that are favourable for adsorption are gradually filled up with an increasing supply of metal ions. To describe the deviation from linearity of the adsorption process, several equations called adsorption isotherms were developed. Often experimental adsorption data are fitted using the Freundlich isotherm:

$$C_s = K_f C_e^{(1/n)} \quad (4)$$

Where:

- C_s is the metal content adsorbed to the solid phase per kg solid phase [kg/kg]
 C_e is the aqueous equilibrium concentration of the metal [kg/m³]
 $1/n$ is a dimensionless exponent
 K_f is the Freundlich constant [$m^{(3/n)}kg^{(-1/n)}$]

Experimental adsorption data can always be easily fitted by this isotherm because both K_f and $1/n$ can be varied to adjust the shape of the curve.

The Freundlich isotherm is entirely empirical, in other words its validity is not supported by physical-chemical understanding of adsorption processes or experimental proof. Extrapolations of K_p 's to concentrations outside the range where they were actually determined are therefore very questionable and the resulting K_p 's are unreliable.

When adsorption data from the literature are compared it is important to realize that K_f is in general not equal to K_p . This is only true in the case of linear adsorption ($1/n$ equals 1). If the value of the exponent differs from 1 it follows that K_p is only equal to K_f if the equilibrium concentration (C_e) is 1 (in the unity that was originally chosen for aqueous concentrations e.g. mg/l or M). The values for $1/n$ found in the literature vary mostly between 0.7 and 1.1, therefore, K_p usually differs considerably from K_f .

From Equation 4 it follows that the unit of K_f depends on the value of $1/n$ (dimensionless) and the units chosen for C_s and C_e . Because values for $1/n$ can vary considerably and because authors use different units for C_s and C_e (e.g. kg/kg, mg/kg, ug/kg, mole/kg) literature values for K_f cannot generally be compared directly. In literature the unit for K_f is often not given or is erroneously stated (e.g.: $m^{(3)}kg^{(-1)}$ instead of $m^{(3/n)}kg^{(-1/n)}$).

To derive K_p 's from adsorption data reported in the form of Freundlich isotherms the following approach was chosen in this report. From the Freundlich isotherm and the initial

metal concentrations the actual aqueous equilibrium concentrations and the corresponding K_p 's are calculated. Because environmental metal concentrations are usually very low, K_p 's for low equilibrium concentrations are most relevant in the framework of this report. Therefore, only the K_p corresponding to the lowest equilibrium concentration of the isotherm is reported and used for the calculation of an average K_p .

3.1.8 Particle concentration effect

K_p 's and adsorption isotherms should be, according to the present theoretical knowledge on interactions at solid-solution interfaces, independent of the particle concentration (C_p). Experiments have shown however that K_p 's determined in systems with low C_p 's are larger than in systems with high C_p 's (Honeyman and Santschi, 1988; Chardon, 1984). Two schools of thought have evolved over the interpretation of this so-called C_p effect. One holds that it is essentially an experimental artefact. Colloids can only be partly separated from the aqueous phase and because these particles adsorb large quantities of trace metals the concentration of the trace metal in the aqueous phase is overestimated. At high C_p 's when the concentration of colloids in the aqueous phase is high this overestimation is largest. This results in a low K_p . The other opinion is that the C_p -effect is a consequence of particle-particle interactions (formation of aggregates) which increase with an increase of the C_p . Particle-particle interactions would lead to decreased adsorption, because the formation of aggregates limits the accessibility of particle surfaces for metal ions.

Honeyman en Santschi (1988) tried to quantify the C_p -effect. It was shown that there was a linear relationship between $\log K_p$ and $\log C_p$. The relationship was linear for 2 to 7 magnitudes of variation of C_p , but the slope of the curve differed for each metal ($\delta \log K_p / \delta \log C_p$ varied from -2 to -0.4). For the metal cesium, K_p was independent of C_p . In nature $\log C_p$ (kg/l) varies from ≈ -5 in typical surface water (Rijkswaterstaat/RIVM, 1986) to ≈ 0.7 in a soil with 30% water-filled pores.

3.2 Precipitation

When precipitates are formed the mobility of trace metals is no longer solely determined by adsorption processes;

mobility is now at least partially determined by the solubility of compounds containing the trace metal. Unfortunately solubility calculations only give a rough idea of precipitates that are formed, because only few thermodynamic data for minerals containing trace metals are available and the available data often are of poor quality. Furthermore, much depends on the poorly understood kinetics of precipitation- and dissolution reactions.

3.2.1 Aerobic conditions

Under aerobic conditions trace metals can precipitate as precipitates, (hydr)oxides, sulphates or phosphates. Whether precipitation actually takes place depends to a large extent on characteristics of the trace metal, pH, and the concentration of the anions involved. Precipitation of metal hydroxides, hydrous oxides, or oxides is enhanced by a high pH.

3.2.2 Anaerobic conditions

Under anaerobic, reducing conditions SO_4^{2-} is converted into S^{2-} . Most trace metal sulfides are practically insoluble. If the availability of SO_4^{2-} in the soil or sediment is high enough anaerobic conditions may lead to the precipitation of trace metals. The mobility and, consequently, the biological availability of the metals are dramatically lowered by this process (Di Toro et al., 1990).

3.3 Speciation

Adsorption and precipitation of metals are influenced by speciation. The term speciation stands for coincidence of different forms of an element in the aqueous phase. Forms that can occur are: different valences of the element (e.g. Se(IV) or Se(VI)) or different complexes of the metal. Cd for example can occur in soil solutions as: Cd^{2+} (free Cd), CdSO_4^0 , CdCl^+ and CdHCO_3^+ (Lindsay, 1979).

Apart from inorganic compounds there are a large number of soluble organic compounds that can form complexes with metal ions. The occurrence of a certain species (or complex) depends on its chemical stability and the concentration of the trace metal and the complexing ligand.

Each species has a different affinity for adsorption to soil particles. In general, free (not complexed) metal ions adsorb better than complexed species. Chardon (1984) showed that the binding strength of soils for Cd, with the exception of soils with a high pH, was lower when Cl^- was present in the soil solution instead of NO_3^- or SO_4^{2-} ; between the latter two there was no significant difference. The decrease of the K_p could be explained very well using equilibrium constants for the formation of CdCl-complexes.

The solubility of compounds that contain trace metals depends on the speciation of the metal. If the fraction of complexed metal ions increases, the thermodynamic activity of the free metal ion decreases. Due to this the solubility of the metal containing compounds is increased resulting in higher aqueous metal concentrations.

3.4 Ionic strength

An increase of the ionic strength of the soil solution results in a decreased chemical activity of the metal ions and therefore their solubility is increased (see 3.2). Beside this the increased ionic strength results in a increased competition for adsorption sites and consequently in a decrease of the adsorption of metal cations.

3.5 Anaerobic conditions/redox potential

Anaerobic (reducing) conditions influence the solubility and speciation of trace metals (see 3.2 en 3.3). Therefore, the mobility of redox sensitive trace metals (e.g. As, Cr, Mo, Se, Sb, Tl, and V) under anaerobic conditions usually differs considerably from the mobility under aerobic conditions.

When soil or water contains much organic matter, anaerobic conditions can lead to the formation of organic acids that increase trace metal mobility by means of complexation (see 3.3). This situation can occur for example underneath rubbish dumps.

Fe- en Mn-hydroxides are dissolved under anaerobic conditions, because of reduction of ferric and manganese ions. Trace metals adsorbed to these minerals are liberated. If the metals are not re-adsorbed, this process leads to the mobilisation of trace metals.

3.6 Kinetics

Adsorption processes that take place in the field might take more time than in adsorption experiments performed in the laboratory. Honeymann en Santchi (1988) state that adsorption- and desorption rates in the field are often lower than what could be expected from physical-chemical models.

3.7 Anions

Some of the trace metals occur under normal Eh and pH conditions of soils and sediments mainly as anionic hydroxo-complexes (As, Cr, Mo, Sb, Se, Tc en V). These metals probably adsorb chiefly to Fe-, Mn- and Al-(hydr)oxides (these soil particles possess a positive electrostatic charge at near to neutral pH values). The adsorption of the metal anions usually increases with a falling pH.

Summarizing it may be said that in general:

- the adsorption of metal cations to hydroxides and organic matter seems to be more significant than fixation to clay minerals,
- a high pH will probably reduce the mobility of trace metal cations, on the other hand an increased ionic strength will lead to an increased mobility,
- the presence of inorganic ligands and dissolved organic matter can increase trace metal mobility,
- and trace metals that occur mainly as negatively charged hydroxo-complexes adsorb chiefly to Fe-, Mn- and Al-hydroxides. The mobility of these metals decreases with a fall of the pH,
- under anaerobic conditions precipitation of trace metal sulfides may result in a decreased mobility.

3.8 Experiments found in literature

Partitioning of metal ions are often studied using the following experimental techniques (discussed in the indicated paragraphs):

- 3.8.1 batch experiments (eventually using tracers)
- 3.8.2 column experiments
- 3.8.3 "in situ" measurements
- 3.8.4 separation of the soil solution (through centrifugation or compression)
- 3.8.5 centrifugation or filtration technique for particulate matter

3.8.1 Batch experiments

Batch experiments involve the shaking of soil, sediment or particulate matter with an aqueous solution containing the adsorbent. After a certain equilibration period the suspension is either centrifugated or filtered and the aqueous concentration of the metal is then determined. The adsorbed fraction is calculated from the decrease of the aqueous metal concentration. To derive an adsorption isotherm, the adsorbed fraction is measured for at least 4 to 5 initial metal concentrations. To determine the period required for equilibration of the adsorption process the progress of the adsorption should be determined. This is often done in a preliminary experiment.

To perform adsorption experiments at the very low aqueous concentrations that are usually found in the environment, it usually is necessary to use a radioactive tracer. The experiment is more or less performed as described above, but now a radioactive isotope of the trace metal is added to the aqueous phase together with the stable metal ions. The adsorbed fraction of metal ions is determined from the decrease of radioactivity in the aqueous phase after equilibration. It is assumed that the radioactive metal ions partition in the same manner between solid and aqueous phases as stable ions. Commercially available tracers possess a very large specific radioactivity (often they are called "carrier free"), therefore, it is possible to utilize very low aqueous concentrations. The concentration of the tracer solution is often so low that addition results only in a negligible concentration increase of metal ions.

Experimental conditions for batch experiments should be chosen in such a way that reliable K_p 's or adsorption isotherms are derived. For batch experiments this means that experimental conditions resulting in nearly complete

or nearly no adsorption should be avoided. In these cases small analytical errors of the aqueous metal concentration will lead to a considerable error in the K_p . This is shown in Figure 2. Initial concentrations and particle concentrations should be chosen in such way that adsorption will lie approximately between 20 to 80%.

3.8.2 Column experiments

The leaching and degradation of chemicals in soils is usually tested in column experiments. Usually the chemicals are applied at the top of a soil filled column and subsequently the column is sprinkled for a certain period with water. At the bottom of the column the drain water is collected at given time intervals for analysis. From the progress of concentration in the drain water usually a so called retention factor (R_f) is calculated. A K_p can be calculated from the retention factor using the following formula:

$$K_p = (0.286/R_f) - 0.286 \quad [l/kg]$$

Column experiments have advantages and disadvantages over batch experiments for the determination of trace metal mobility. In general terms it can be said that physical-conditions in column experiments reflect actual soil conditions better than in batch experiments. For example, particle concentrations in batch experiments are considerably lower than actual particle concentrations of soils (the effect of the particle concentration on K_p has already been discussed in Chapter 3.1.8). However, from results of column experiments it usually is not possible to derive whether the adsorption processes have reached an equilibrium situation. Most of the time this will probably not be the case. Therefore, in this report K_p 's derived from batch experiments are preferred over those derived from column experiments.

3.8.3 In situ measurements

Measurements of the distribution of metal ions in soils and sediments under field conditions can give valuable information about actual concentration distributions. Unfortunately, existing data are very scarce or difficult to interpret, partly because they are not necessarily

related to an equilibrium situation. As stated in Chapter 1.2 a validation of the EP method is beyond the scope of this report, but will be undertaken by the RIVM in the near future.

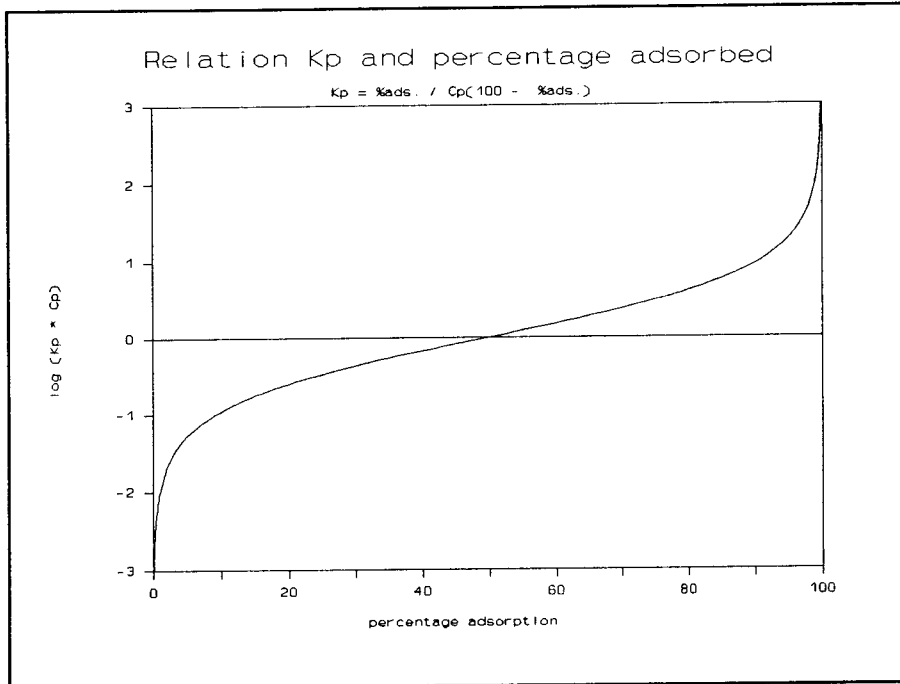


Figure 2 The relation between adsorption expressed as percentage adsorbed and the partition coefficient (calculated). Partition coefficients determined in experiments where adsorption is less than $\approx 20\%$ or more than $\approx 80\%$, are very sensitive to small experimental errors and analytical uncertainties (steep parts of the curve).

3.8.4 Separation of the soil solution

Using centrifugal filtration techniques or a pore water press, soil solutions can be obtained from soil and sediment samples. For anoxic samples this should be done in a glove box under a nitrogen atmosphere.

3.8.5 Centrifugation or filtration technique for particulate matter

In order to estimate the load of metals transported by rivers to the oceans, the metal content of particulate matter is sometimes studied. Using either a continuous-flow centrifuge or by filtering large volumes of water,

particulate matter is collected from riverine or marine water samples. When both particulate matter and filtered water samples are analyzed a concentration distribution can be calculated.

4 Qualitative description of the mobility of the "exotic metals"

Much of the information in this Chapter concerning the valence of the metals and their solubility is derived from so called Eh-pH stability graphs published by Dragun (1988).

4.1 Barium

Barium is an alkaline-earth metal. It is chemically similar to other alkaline-earth metals, in particular Ca and Sr. In the environment Ba occurs only in a 2+ valence. Ba forms insoluble salts with arsenate, carbonate, oxalate, chromate, fluoride, sulphate, and phosphate ligands. Cartwright et al. (1978) studied the chemical control of Ba solubility and showed that for most water samples, Ba concentrations were controlled by the amount of sulphate in the water. Ba can form aqueous complexes with inorganic and organic ligands. The complexing properties of Ba-ions are comparable to those for Ca (Smith and Martell, 1976).

Probably, electrostatic adsorption of Ba by soils is somewhat stronger than for Ca, because of Ba's relatively high hydration enthalpy (see 3.1.1).

Lagas et al. (1984) performed column experiments with soils and wastes amended with Ba salts. They observed that leaching of Ba was retarded because of the precipitation of BaSO_4 and BaCO_3 . Nevertheless, high aqueous Ba-concentrations were measured (up to 1800 mg/l). This was remarkable considering the low solubilities of BaSO_4 and BaCO_3 (respectively 10^{-10} and $10^{-8.3}$, Smith and Martell, 1976). The high mobility was explained by assuming complexation of Ba with fatty acids from the waste.

The US EPA (1984) states that Ba-compounds can partly dissolve under acid soil conditions.

4.2 Beryllium

Be is an alkaline-earth element. In the environment Be occurs only in a 2+ valence. Be is the lightest of all stable solid elements. Some of Be's chemical characteristics are similar to those of Al, particularly its high affinity to oxygen. On the surface of metallic Be a film of BeO is formed, that is resistant to corrosion,

water and acids. Sintered berylliumoxide is very stable and possesses ceramic properties. Cationic Be salts are hydrolysed in water and react to form insoluble (hydr)oxides or aqueous hydrated complexes at pH values between 5 and 8, and beryllates above a pH of 8 (Reeves, 1986). At environmental pH ranges of 4 - 8, beryllium (hydr)oxide is highly insoluble, thus preventing mobilization in soil (IPCS, 1990). Furthermore, Be is strongly adsorbed by fine sediments, clays, iron hydroxides, and organic substances (Izmerov, 1985).

Asami en Fukazawa (1985) analyzed over a 100 Japanese soil samples. The distribution of Be in soil profiles reflected leaching processes; the Be-contents increased with depth in the profile. The observed leaching shows that under certain circumstances Be can be mobile in soils.

Griffitts et al. (1977) state that because of the low solubility of beryllium oxides at normal aqueous pH's only very low concentrations of Be are found in the form of chloride, fluoride, chloro, carbonate or organic complexes.

4.3 Cobalt

In the environment Co occurs only with a 2+ valence or as metallic Co. The solubility of various Co (hydr)oxides strongly decreases at pH's above 8, consequently reducing the mobility. At a high pH and under reducing conditions metallic Co is thermodynamically stable.

Several authors state that soil Co is for a major part incorporated or associated with Mn-hydroxides (Anderson and Christensen, 1983; Tiller et al., 1969).

4.4 Molybdenum

Mo shares some chemical characteristics with Cr and W (tungsten) that are in the same column of the periodic system.

Mo can occur in 5 valences (6+, 5+, 4+, 3+ en 2+). In the environment Mo occurs mainly as Mo(IV) or Mo(VI). In soil solutions only anionic Mo occurs, above pH 5 - 6, MoO_4^{2-} ions dominate, whereas, below pH 5-6 HMoO_4^- ions dominate (Scheffer et al., 1984; Jarell et al. 1980). Under reducing soil conditions and a low pH molybdate might be reduced to Mo(IV) or Mo(III). Mo(IV) is probably precipitated as MoO_2 .

Mo(III) can occur as Mo^{3+} ions that are probably strongly adsorbed (Jones 1990).

Adsorption of molybdate ions mainly takes place at soil Fe-(hydr)oxides. Al-(hydr)oxides, organic matter and clay minerals adsorb molybdate as well, but to a lesser extent than Fe-(hydr)oxides.

Soil Mo is usually associated with Fe-, Mn- and Al-(hydr)oxides or organic matter (Jones 1990). In soils the mobility of Mo is strongly pH-dependent, it increases with an increasing pH because of competition of hydroxyl ions for adsorption sites. It is illustrative that addition of chalk to agricultural soils can increase Mo availability for plants. In poorly drained soils the mobility is often high because of the high pH's that often occur there (Jones et al. 1990). Precipitation of calcium molybdate at high soil pH's was not observed until now (Jarell et al. 1980). In acid soils Mo can precipitate as ferro-molybdite ($\text{Fe}_2(\text{MoO}_4)_3 \cdot 8\text{H}_2\text{O}$). At a higher pH precipitation of wulfenite (PbMoO_4) could be of importance.

4.5 Antimony

The chemical characteristics of Sb resemble those of As, which is in the same column of the periodic system as Sb. Sb can occur in several valences: -3, 0, +3, and +5.

Sb(III) and Sb(V) hydrolyse in water to hydroxo-complexes. The exact structure of these aqueous species is unknown, however, it is generally assumed that only Sb(III) can occur as a cation. Under oxic conditions $\text{Sb}(\text{OH})_6^-$ or SbO_3^- are probably the major aqueous species. Under slightly reducing conditions $\text{Sb}(\text{OH})_3^0$ might be the dominant aqueous species and precipitation in the form of Sb_2O_3 might occur. Under very reducing conditions metallic Sb becomes thermodynamically stable.

Sb oxides (Sb_2O_5 , Sb_2O_3) are well soluble. Consequently, Sb concentrations will mostly be too low to allow precipitation of these minerals. Under reducing conditions precipitation of stibnite (antimony sulfide) might occur.

Callahan et al. (1979) stated that Sb is adsorbed by clay and other minerals. Furthermore, they state that Sb can co-precipitate with Fe-, Mn-, or Al-(hydr)oxides and that this process can determine Sb concentrations in the environment.

Coprecipitation of As with soil hydroxides is a well known process.

4.6 Selenium

The chemical characteristics of Se resemble those of S; both elements are in the same column of the periodic system. Consequently, Se is often associated with S minerals. In the environment Se can occur in several valences: -2, 0, +4 or +6. Under Eh-pH-conditions that can occur in soils, the following Se-species are thermodynamically stable: Se (s), selenite (SeO_3^{2-} , HSeO_3^- , H_2SeO_3), selenate (SeO_4^{2-} and HSeO_4^-). At high pH and redox potential selenate species dominate. At a lower pH and lower redox potential selenite species dominate. Under anoxic conditions metallic Se is thermodynamically stable. Under these conditions aqueous HSe^- and H_2Se can also be stable (Neal, 1990).

Most authors conclude that selenite is more strongly adsorbed by soils than selenate (e.g. Deverel en Millard, 1988 en Neal, 1990), often no adsorption of selenate is observed. This is sometimes explained by stating that selenite can form strong covalent ('innersphere') bounds with soil surfaces, whereas selenate can only form relatively weak ('outersphere') bounds where a water molecule remains present between the ion and the soil surface. Sulphate en phosphate compete with selenate and selenite for adsorption sites. Neal (1990) proposes the following order in affinity for adsorption:

phosphate > arsenate ≥ selenite ≥ silicate ≥ sulphate
 ≥ selenate > nitrate > chloride

4.7 Tin

Sn can occur in the valences 2+ or 4+. In the environment probably only Sn(IV) occurs. SnO_2 or Sn(OH)_4 are very insoluble minerals, consequently the mobility of Sn is probably very low.

Gerritse et al. (1982) investigated the mobility of a number of metals in soils. For sand and loam soils they showed that Sn is a relatively immobile metal. The mobility of Sn increased after the addition of a sewage sludge solution. This was explained assuming that Sn ions were complexed with dissolved organic matter. The enhanced ionic

strength of the soil solution might have increased the mobility as well.

Resuming it can be said that the scarce literature indicates that Sn is a relatively immobile metal, comparable with Pb, or even less mobile.

4.8 Thallium

Tl occurs in nature in the valences +1 and +3. Under normal Eh and pH conditions for natural waters, Tl occurs mainly as Tl^+ cations (Callahan et al., 1979). In very oxidizing waters, however, Tl^{3+} may be present with $TlOH_3^0$ as the predominant species in fresh water, and $Tl(OH)_3^0$ and $TlCl_4^-$ may predominate in seawater (Baes and Mesmer, 1976; Callahan et al., 1979; Cotton and Wilkinson, 1972). Tl^{3+} cations hydrolyse to insoluble $Tl(OH)_3$ (s). The Tl^+ ion resembles alkali metals, e.g. complexation of Tl^+ usually does not occur (comparable with Na^+ and K^+).

4.9 Vanadium

V can occur in the environment in the following valences: 3+, 4+ and 5+. In natural waters both cationic and anionic V species may occur: VO_2^+ , $VO(OH)^+$, $H_2VO_4^-$, $H_2VO_4^-$, HVO_4^{2-} , VO^{2+} , $HV_2O_5^-$, V^{3+} , VOH^+ , VO^+ . Wehrli and Stumm (1989) stated that VO^{2+} , $VO(OH)^+$, $H_2VO_4^-$, and HVO_4^{2-} occur primarily in natural waters.

V(V) is stable over a wide pH range, under mild reducing conditions it can be reduced to V(IV). The vanadyl ion (VO_2^+) may form many complexes, of which most are anionic. Furthermore, V(IV) may precipitate as V_2O_4 . V(III) species occur probably only at low pH's and low redox potentials. V(III) may precipitate as V_2O_3 .

Wehrli and Stumm (1989) showed that vanadate ions ($H_2VO_4^-$ and HVO_4^{2-}) are strongly adsorbed by Al- and Ti oxides.

5 Partition coefficients

As expected, data for most of the "exotic metals", particularly Ba, Be, Tl, and Sn, were scarce. K_p 's for the "exotic metals" are presented together with data for As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn from the same experiments if available. This allows comparison with these relatively well-studied metals. Cd, Ni and Zn are generally seen as relatively mobile metals, whereas Cr, Cu, Hg, and especially Pb, are usually considered immobile. As occurs in interstitial water as oxyanions that are well adsorbed by soils rich in Fe-(hydr)oxides with a low pH.

5.1 Partition coefficients for soil

5.1.1 Summary of data from 2 batch experiments

Buchter et al. (1989) studied the retention of 15 elements by 11 soils (pH: 4.3-8.5, clay: 0.5-54.7 %) from the USA. Batch experiments were performed for 10 initial concentrations between 0.01-100 mg/l (for Hg 8 initial concentrations were used). C_p was 0.100 kg/l. The equilibration period was 18 hours. The data were fitted with the Freundlich equation. The calculated K_f and $1/n$ values were presented. K_p 's were deduced from these values for each soil for an equilibrium concentration of 0.01 mg/l (approximately the lowest equilibrium concentrations observed). The logarithmic K_p 's are presented in Table 1

King (1988) performed batch experiments similar to those of Buchter et al. with 21 soil samples (pH: 4.2-6.5, clay: 2-63 %) from the USA. Adsorption was tested for one initial concentration: Cd (20), Co (20), Cr(40), Cu (70), Ni (20), Pb (200), Sb (200), Zn (40 mg/kg). C_p was 0.125 kg/l. The equilibration period was 6 days. The equilibrium concentrations of the trace metals were usually between 1 and 100 mg/l being much higher than environmental concentrations. The metal contents of the soils after equilibration were also rather high. The concave shape of some of the adsorption isotherms for Pb suggests that precipitation of Pb-minerals might have been partly responsible for the fixation of the metal ions. The K_p 's are presented in Table 1.

Table 1 Log K_p 's (l/kg) for soils from the USA (data from Buchter et al., 1989 and King, 1988)

		log K_p												
		As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Se	V	Zn
Buchter	average	2.28	2.30	2.07	2.04	2.99	2.23	2.44	2.08	3.28	-	1.01	2.49	2.20
et al.*	CV (%)	18	33	37	22	12	38	12	33	17	-	-	22	43
(1989)	n	11	11	11	6	11	11	7	11	8	0	1	11	11
King**	average	-	0.60	0.83	1.41	1.33	-	-	0.77	1.88	1.93	-	-	0.85
(1988)	CV (%)	-	100	67	28	46	-	-	71	38	32	-	-	85
	n	0	15	15	15	13	0	0	15	14	10	0	0	15

* For some soils Pb-concentrations were below detection limits. For some soils no sorption of Cr, Mo, and Se, was detected. The values shown are calculated without considering these data.

** For some soils adsorption of Cu, Pb, and Sb resulted in concentrations below detection limits. The values shown are calculated without considering these data.

Kings K_p 's are all significantly lower than those of Buchter et al. The difference usually is one order of magnitude or more. The difference is probably a result of the high equilibrium concentrations in King's experiments (concentration dependency see 3.1.7). These are often 2 - 4 orders of magnitude higher than those of Buchter et al. The K_p 's of King seem to be valid only for trace metal concentrations that are much higher than environmental concentrations.

Results of Chardon's (1984) detailed investigation of Cd-adsorption in 12 Dutch soils were compared with the results of Buchter and King. The average log K_p (l/kg) for Cd was 2.47 (CV = 32 %), the median 2.44, the 25 percentile 1.87 and the 75 percentile 3.43. These values are in good agreement with the data of Buchter et al., but they disagree with King's results. The agreement for Cd supports the use of K_p 's derived from data of Buchter et al.

5.1.2 Remaining data

Cobalt

McLaren et al. (1986a) performed batch experiments with 8 Scottish soils. Details of the soils have been published by McLaren et al (1986b). The native Co-content of the soils ranged from 3.11 to 14.7 mg/kg. Four grams of soil were equilibrated in a 0.01 M CaCl_2 solution for 72 hours with 0 - 0.2 mg/l Co. At the lowest concentrations desorption of

native soil Co was observed. Log K_p 's ranged from 0.30 to 2.30 (l/kg), the average log K_p was 1.26 (l/kg). The corresponding equilibrium concentrations ranged from 0.2 $\mu\text{g/l}$ to 34 $\mu\text{g/l}$.

In relation with Co deficiency of stock Tiller et al. (1969) performed batch experiments with 25 Australian soils. The native Co-content of the soils ranged from 0.18 to 97 mg/kg. Stable Co and a radioisotope of Co were added to the equilibration fluid containing 0.05 M CaCl_2 . C_p was 0.08 kg/l. The soil pH (0.05 M CaCl_2) ranged from 4.2 to 6.9. K_p 's were calculated at an equilibrium concentration of 0.2 mg/kg from parameters of the Langmuir isotherm presented in the article. Log K_p 's ranged from 0.08 to 2.01 (l/kg). The average log K_p was 0.99 (l/kg).

Anderson and Christensen (1983) performed batch experiments at low metal concentrations for Cd, Zn, Ni, and Co (initial Co concentrations ranged from 18 - 118 $\mu\text{g/l}$). 13 Danish soils were used. Adsorption was tested for each soil at 3 pH values. Stable Co and a radioisotope of Co were added to the equilibration fluid containing 1 mM CaCl_2 . C_p was 0.01 or 0.05 kg/l. Mobility of Co was lower than the mobility of Cd, Zn, and Ni. K_p 's were positively correlated with the pH, the Mn oxide content and the organic matter content of the soils. A negative correlation existed for soluble organic matter. The results were presented in the form of regression equations describing the relation between log K_p and soil characteristics. Log K_p was 2.10 (l/kg) for mean values of the soil characteristics ($\text{pH}_{\text{H}_2\text{O}} = 6.2$, lutum = 13 %, O.C. = 9.7 %, CEC = 11.2 meq/100 g). For Cd, Ni, and Zn this value was 2.53, 2.21, and 2.37 (l/kg), respectively.

Molybdenum

Jarell and Dawson (1978) performed batch experiments with 8 soils from western Oregon. Mo was added as molybdate. The pH of the suspensions ranged from 4.8 to 5.3. C_p was 100 g/l. Results were presented in the form of parameters for the Freundlich isotherm. Log K_p 's (l/kg) calculated from these parameters at an equilibrium concentration of 0.03 mg/l ranged from 3.14 to 3.70 with an average of 3.39.

Karimian and Cox (1978) performed batch experiments similar to those of Anderson and Christensen. 5 North American mineral soils were tested. K_p 's were calculated from parameters of the Freundlich equation presented ($C_e = 10$

mg/l Mo). Log K_p 's (l/kg) ranged from 0.43 to 1.62 with an average value of 0.87.

The K_p 's of Karimian and Cox are significantly lower than those of Jarell and Dawson and. The difference usually is one order of magnitude or more and is probably a result of the high equilibrium concentrations in the experiments of Karimian and Cox (concentration dependency see 2.1.6). These are often 3 orders of magnitude higher than those in the experiments of Jarell and Dawson. The K_p 's of Karimian and Cox seem to be valid only for trace metal concentrations that are much higher than environmental concentrations.

Selenium

Singh et al. (1981) performed batch experiments for selenite and selenate with 5 Indian soils (pH = 7.6 - 10.1, C_p = 100 g/l). The samples were equilibrated for 72 hours. Equilibrium concentrations varied from 10 to 21 mg/l Se. Selenate was always adsorbed in higher amounts than selenite. Log K_p 's (l/kg) calculated for the lowest aqueous concentrations varied from 0.75 to 1.66 for selenite and from 0.97 to 1.66 for selenate.

Ylärinta (1983) performed batch experiments with 3 soils for selenite and selenate. pH's were around 5. For selenate no adsorption was observed in any of these soils. Se added in the form of selenite was partly adsorbed. Log K_p 's (l/kg) calculated for the lowest aqueous concentrations (0.34 - 1.35 mg/l) varied from 1.18 for a peat soil to 2.08 for a clay soil.

Elsokarry (1980) performed batch experiments with 3 Egyptian soils (pH = 7.8 - 8.0, C_p = 50 g/l). Se was added in the selenite form. Log K_p 's (l/kg) calculated for the lowest aqueous concentrations (0.7 - 4.0 mg/l) varied from 1.17 to 1.28.

Additional information for Se was derived from "in situ" measurements performed by Fuji and Deverel (1989). They sampled contaminated groundwater in the San Joaquin valley (California) that contained 0.28 - 6.2 mg/l Se. The corresponding soil samples contained 0.6 - 4.2 mg/kg Se.

These results are in agreement with the weak adsorption observed by Buchter (1988). Furthermore, the experiments of

Singh et al. and Ylärinta showed that adsorption of selenite (usually the dominant species in the environment) is stronger than selenate.

Thallium

Magorian et al. (1974) showed that Tl is strongly adsorbed by montmorillonite clay. The $\log K_p$ (l/kg) derived from batch experiments was 4.51 ($C_p = 0.001$ kg/l, pH = 8.1, $C_e = 3$ μ g/l). At pH 4,0 adsorption was less effective.

Callahan et al. (1979) state that in soils Tl is not adsorbed as strongly as Cu and Zn ions under similar conditions.

5.2 Sediment partition coefficients

In the literature almost no studies were found where the adsorption of the "exotic metals" in fresh water sediments was tested in batch experiments. Therefore K_p 's were derived from concentration distributions of the metals in riverine particulate matter and water (see 3.8.5).

Strictly speaking the results of the particulate matter analysis are concentration distributions that are not suited for the EP method because they do not necessarily relate to an equilibrium situation, and because they are based on total metal contents (see Chapter 2). Calculations were performed with data for particulate matter (Cd, Cu, Pb, and Zn) from the Rhine (Rijkswaterstaat/RIVM, 1991) to see whether a correction for the unexchangeably bound metal content would be useful. Analogous to soil the unexchangeably bound metal content of the sediments was approximated with the background content of sediments (Cd 0.25, Cu 13, Pb 21, Zn 68 mg/kg, Salomons, 1983). This estimation of the unexchangeably bound metal content was subtracted from the total metal content of the particulate matter. K_p 's were calculated with this corrected metal content and the aqueous metal concentration. The K_p 's calculated in this manner were not significantly lower than K_p 's calculated on the basis of total metal contents. This resulted from the fact that the background contents were very low compared to the total metal contents of the particulate matter. It was concluded that a correction of K_p 's for particulate matter with background contents is not useful. It remains doubtful, however, whether nearly the whole metal content of sediments is really exchangeable.

Because data on the exchangeability of metals in sediments were insufficiently available, no other approach for the estimation of the unexchangeably metal content was attempted. K_p 's presented in 5.2.1 were derived directly from the total metal content of particulate matter and the aqueous concentrations.

5.2.1 Summary of data for particulate matter

DBW/RIZA (1989) derived K_p 's from data for riverine particulate matter. The database from Rijkswaterstaat/RIVM (1991) containing data for various Dutch rivers and lakes was used. Only samples taken from 1983 to 1986 were considered. The K_p 's calculated by DBW/RIZA are presented in Table 2. The values are medians calculated from averages for various Dutch rivers and lakes. Van de Meent et al. (1990) used these K_p 's to derive sediment MPC's for As, Cd, Cr, Hg, Ni, Pb, and Zn from water MPC's. The K_p 's for these trace metals are included here for comparison with K_p 's for the "exotic metals".

Van der Sloot et al. (1985) measured several oxyanionic metals in water and particulate matter samples from the Dutch Wadden Sea, the North Sea, the estuaries of the Rhine and Scheldt and lake Yssel. K_p 's derived from data for lake Yssel (the only freshwater samples) are presented in Table 2. Sampling of particulate matter involved filtration through 0.45 μm filters. The metal content of the particulate matter was determined after leaching for 18 h with 0.1 N HCl.

Popp and Laquer (1980) determined the concentration distribution of trace metals for water and particulate matter in three rivers (New Mexico, USA). Particulate matter was collected by centrifugation or filtering of large water volumes through 0.45 μm filters. For analysis the samples were dissolved in a HF/HNO₃ mixture. The K_p 's presented in Table 2 were calculated from average aqueous and particulate concentrations of the three rivers.

Li et al. (1984) performed batch experiments with particulate matter from the Hudson River (USA). To unfiltered Hudson river water samples (fresh water, $C_p = 18$ mg/l) 13 radiotracers were added. The spikes did not greatly change the natural concentration of various trace elements, as most radiotracers were carrier free and the amounts of spikes added were small. The samples were shaken

for 20 days at 2 °C. The aqueous radioactivity was determined in subsamples taken at predetermined intervals using a germanium-lithium detector. K_p 's for (unfiltered) Hudson river water and a 4 to 1 mixture with filtered seawater are presented in Table 2 (equilibration period 20 days).

Table 2 Log K_p 's (l/kg) for particulate matter from various aquatic systems. The K_p 's were calculated from the total metal content of particulate matter and corresponding water samples. Data for As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn were added for comparison.

	Log K_p (l/kg)											
	Rhine ¹ Lobith	3 locations Ysselmeer ²			Rio Gran- de ³	Rio Puer- co ³	Rio Sala- do ³	Hudson River ⁴	Hudson River + sea- water ⁴	Solo River ⁵	Wono Kromo River ⁵	Porong River ⁵
As	4.00	3.65	3.72	3.76	3.19	2.64	2.76	-	-	-	-	-
Ba	-	-	-	-	3.91	2.89	2.65	3.78	2.66	-	-	-
Be	-	-	-	-	3.51	2.72	2.64	-	-	-	-	-
Cd	5.11	-	-	-	3.32	2.94	2.63	4.22	3.82	-	-	-
Co	-	-	-	-	3.35	2.55	2.59	5.47	4.93	-	-	-
Cr	5.46	-	-	-	4.69	4.05	4.31	-	-	-	-	-
Cu	4.70	-	-	-	-	-	-	-	-	-	-	-
Hg	5.23	-	-	-	-	-	-	4.76	5.09	-	-	-
Mo	-	<4.21	<4.40	<4.29	3.24	2.43	2.19	-	-	3.75	3.69	3.36
Ni	3.90	-	-	-	3.58	2.73	2.91	-	-	-	-	-
Pb	5.81	-	-	-	3.41	3.00	2.97	-	-	-	-	-
Sb	-	-	3.52	3.64	-	-	-	4.07	4.00	3.17	3.00	3.72
Se	-	<3.31	<3.34	<3.18	3.31	2.50	2.58	-	-	-	-	-
Sn	-	-	-	-	-	-	-	5.55	5.59	-	-	-
Tl	-	-	-	-	-	-	-	-	-	-	-	-
V	-	4.11	4.13	4.13	3.41	3.24	3.07	-	-	3.90	3.83	4.06
Zn	5.04	-	-	-	4.28	4.48	3.43	4.00	3.66	-	-	-

¹ K_p 's based on concentrations in filtered- and unfiltered samples from various Dutch rivers and lakes (after DBW/RIZA, 1989). The values shown are medians calculated from average K_p 's for different rivers and lakes. Samples were taken from 1983 - 1986.

² Van der Sloot et al. (1985): Dutch lake. Average distribution (geometric mean) for 3 water and 3 corresponding particulate matter samples. Mo- and Se-contents of the particulate matter were below detection limits. pH Ysselmeer \approx 8.3 (Rijkswaterstaat/RIVM, 1986);

³ Popp and Laquer (1980): North American Rivers. K_p 's calculated from average aqueous concentrations (8-12 samples, geometric mean) and metal contents of particulate matter (around 8 samples); pH not stated

⁴ Li et al. (1984): North American Rivers. Tracer experiment with unfiltered Hudson river water ($S \approx 0 \text{ ‰}$) and a 4 to 1 mixture of Hudson River water and filtered seawater ($S \approx 6 \text{ ‰}$). pH = 7.5

⁵ Hoede et al. (1987): Indonesian rivers. Average distribution (geometric mean) for 8 water and 8 corresponding particulate matter samples. Mo in particulate matter was sometimes below detection limits. Averages were calculated without these values. All K_p 's for the Wono Kromo and the Porong River are based on only one sample pair.

Hoede et al. (1987) determined metal concentrations of particulate matter and Indonesian river water. Sampling of the particulate matter involved continuous flow centrifugation of 50 l water. Particulate matter was obtained in two size/density fractions. The metal content of the particulate matter was determined using neutron activation analysis (NAA). The metal concentrations of the water samples (0.45 μM filtered) were determined with NAA after a preconcentration procedure. For the calculation of the K_p 's presented in Table 2 the average metal content of the two size fractions was used.

The K_p 's presented in Table 2 should be lowered by a factor 1.5 to account for the lower adsorption of the metals by sediments as compared to particulate matter (DBW/RIZA, 1989). The relatively strong adsorption of metals by particulate matter is probably a result of the relatively high organic matter and clay content (size fraction smaller than 2 μm).

5.2.2 Remaining data

Antimony

Brannon and Patrick (1985) determined Sb concentrations in interstitial water phase of 10 North American sediments. Sediments were kept under anoxic conditions. Five fresh water sediment samples were mixed with cellulose (1% weight/weight) to enhance reduction of the sediment. Sb(III) was added (75 mg/kg, sediment dry weight) in the form of an antimony potassium tartrate solution. The containers were sealed and incubated for 45 days under a nitrogen atmosphere at 20 °C. After this period interstitial water from the sediments was collected by centrifugation of the sample under a nitrogen atmosphere. All aqueous concentrations for unamended sediments were below detection limits. Log K_p 's (l/kg) calculated from the total Sb-content of 5 fresh water sediments (native Sb-content and added Sb) and the corresponding interstitial concentrations ranged from 2.82 to 3.64. The average log K_p was 3.32 (l/kg).

Molybdenum

Runnels (1977) analyzed relatively acid groundwater that was in contact with sediments that contained 800 mg/kg Mo. They found that the aqueous concentrations were smaller

than 0.2 mg/l. The derived log K_p is 3.2 (l/kg) or greater.

Tin

To estimate fluxes of Sn to the sea, Byrd and Andrea (1986) measured dissolved and particulate Sn in several rivers worldwide. Dissolved concentrations were extremely low: usually tenths of pM. Particulate Sn was collected by means of filtering river water through 0.45 μ M filters. Log K_p 's (l/kg) for the Rhine (Bergenz), Tejo (estuary, Portugal), Guadalquivir (Spain), Mississippi (Port Allen) and the river Delaware (Wilmington) were 6.95, 6.40, 6.26, 6.26, and 6.88 respectively.

Thallium

Günther et al. (1981) performed desorption experiments with contaminated river sediments (21 mg/kg Tl). At pH 3 the aqueous concentration was 1.04 mg/l (log K_p = 3.30), at pH 5.6 the concentration was 0.67 mg/l (log K_p = 3.50).

5.2.3 Partition coefficients for marine sediments

Physical-chemical conditions for the adsorption of trace metals in seawater differ considerably from conditions in freshwater. Consequently, K_p 's for marine particulate matter or sediments might differ from those for freshwater.

The pH of seawater is about 8 whereas in freshwater considerably lower pH's may occur. This may lead to high K_p 's for cationic metals and low K_p 's for oxyanionic metals in seawater (see 3.1.6 and 3.7). The high ionic strength of seawater may lead to decreased adsorption and increased solubility of trace metals (see 3.4). High concentrations of ions in seawater that readily form complexes with trace metals (e.g. Cl^- and SO_4^{2-}) may lead to low K_p 's (see 3.3).

The question arises whether the derivation of MPC's for marine sediments requires different K_p 's than for freshwater sediments. Therefore, K_p 's derived from data for marine particulate matter and seawater were compared with K_p 's derived from freshwater particulate matter. For the "exotic metals" such a comparison was possible with the data published by Van der Sloot et al. (1985) and Hoede et al. (1987) (see 5.2.2). Regarding the data of Van der Sloot et al. it was found that the average K_p 's for Sb, V, Mo, and As were higher in seawater than in freshwater. A brief

examination of the data of Hoede et al. showed the same result for Sb and V.

The results obtained with the data of Van der Sloot et al. and Hoede et al. are surprising because for the oxyanionic metals they tested not a higher but a lower K_p would be expected in seawater (theoretically a high pH, more complexation and a high ionic strength would result in low K_p 's for oxyanionic metals). This surprising result shows that it is difficult to predict K_p 's for seawater from freshwater K_p 's with a theoretical approach. More research is needed to explain these observations.

Experiments of Li et al. (1984) (see 5.2.2) with riverine suspended matter that was equilibrated with seawater showed that K_p 's for Cd, Zn, and Ba are lower in seawater than in freshwater. However, K_p 's for Fe, Sn, Bi, Ce, and Hg were higher in seawater than in freshwater.

The findings of Li et al. (1984) show that the difference between freshwater and seawater K_p 's depends on the metal regarded. Furthermore, it was already concluded that theoretical predictions for the K_p 's in seawater are difficult to make. This holds especially for the "exotic metals" for which only few data are available. In the framework of this report it is concluded that sufficient data are lacking to propose well-founded K_p 's for the "exotic metals" in seawater. For the moment the assumption is made that the K_p 's for the "exotic metals" metals in seawater are equal to the K_p 's reported for partitioning in freshwater. However, more research on this subject is necessary.

6 Discussion and conclusions

K_p 's for sediments and particulate matter are usually very large compared to soil- K_p 's (compare Table 1 and 2). K_p 's for sediments were often 1 to 3 orders of magnitude higher than for soils. Five plausible explanations can be given for the observed differences.

- The pH of sediments and particulate matter is often higher than the pH of the soils; in the experiments presented here the average difference was about 2.5 units. For cations the relatively high pH might lead to high K_p 's (see 3.1.6). Furthermore, a high pH normally enhances the precipitation of cationic metals thus lowering the aqueous concentration.
- C_p 's in aquatic systems are much lower than in soils. Mostly experimental C_p 's for soils are above 10^{-3} kg/l. Experimental C_p 's for sediments and particulate matter lie mostly between 10^{-6} to 10^{-3} kg/l (see 3.1.8).
- The adsorption experiments with sediments and particulate matter presented here were all performed at very low aqueous concentrations (see 3.1.7).
- The composition of particles in sediments and particulates differs from soil particles, therefore, they possess different adsorption properties. Furthermore, the texture of sediments is often finer than that of soils resulting in a higher specific surface area (see 3.1.5).
- The K_p 's for sediments are based on total metal contents of particulate matter, whereas the K_p 's for soils are based on the adsorbed metal content determined in batch experiments. The adsorbed metal content is only a fraction of the total metal content of soils and sediments. Consequently K_p 's based on total metal contents are higher than K_p 's based on adsorbed metal contents (see Chapter 2).

In 3.7 it was shown that the K_p 's of trace metals that occur mainly as oxyanions usually decrease when the pH increases. Nevertheless, the high K_p 's for oxyanions occur in waters with high pH's. Thus the pH-effect is outweighed by other factors. Consequently factors like the C_p , the

aqueous metal concentration, the texture and the unexchangeability of the metals must have a considerable influence on the K_p for trace metals.

The five plausible explanations given above indicate that the large difference in K_p 's for sediments and soils result from different adsorption characteristics of the adsorbing material and different physical-chemical conditions. Furthermore the difference results at least partly from the different determination of the metal content of the adsorbing material (total metal content versus adsorbed metal content). The question arises to what extent the different K_p 's reflect actual differences in the distribution of trace metals in soils and sediments and to what extent the differences depend on "experimental artifacts". Differences in the physical-chemical conditions that actually occur in soils and sediments (pH, C_p , texture, organic matter content, aqueous concentrations) all point towards strongest adsorption of trace metals by sediments (the only exception is the influence of the pH on the adsorption of the oxyanionic trace metals that points towards weaker adsorption by sediments). Therefore it is thought that the large differences in K_p 's for soils and sediments reflect actual differences in the distribution of trace metals in the environment. Differences resulting from the testing method applied are considered less important. However, only field research involving the measurements of chemicals in interstitial water, can show how well experimental K_p 's can predict actual concentration distributions. Research involving analysis of interstitial waters will be undertaken in the near future by the RIVM.

The K_p 's presented in this chapter can be used to estimate the metal content of soils and sediments corresponding with ecotoxicologically based water quality criteria as proposed by Van de Plassche et al. (1992). It should be kept in mind that K_p 's, that must apply to a wide range of soils and sediments that differ considerably in their physical-chemical characteristics, can never be very accurate. On the basis of the statistic parameters shown in Tables 1 and 2 and adsorption data presented by Chardon (1984) it is estimated that a coefficient of variation of about 30 % applies to the logarithmic K_p 's presented in this chapter.

K_p 's for the "exotic metals" in seawater might differ considerably from K_p 's for freshwater sediments. However, sufficient data are lacking to propose well-

founded K_p 's for the "exotic metals" in seawater. For the moment the assumption is made that K_p 's for the "exotic metals" metals in seawater are equal to the K_p 's reported for partitioning in freshwater.

6.1 Selected partition coefficients for soil

Selected K_p 's for Co, Mo, Sb, Se, and V are shown in Table 3.

Literature indicates that precipitation of $BaSO_4$ salts might control Ba concentrations (see 4.1). Calculations with the (low) solubility product of $BaSO_4$ (10^{-10} , Smith and Martell, 1976) were performed to estimate at what concentration level Ba mobility could be controlled by precipitation. Assuming a SO_4^{2-} concentration of 1 mg/l Ba concentrations would remain slightly above 1 mg/l. This level is several magnitudes above the MPC (15 μ g/l) for water proposed by Van de Plassche et al. (1992). In other words at these concentration levels mobility of Ba is probably not determined by precipitation processes but by adsorption processes. Thus it is concluded that in the framework of this report partitioning of Ba can be described with a K_p (see Chapter 2). Analogous to Ba, literature indicates that precipitation of hydrolysis products of Be and Sn (BeO and SnO_2) might control aqueous Be and Sn concentrations. Calculations with the solubility products of Be- and Sn oxides analogous to those performed for Ba were not possible, because solubility data were lacking. It is assumed that at the low levels of the MPC's (Be 0.16, Sn 18 μ g/l proposed by Van de Plassche et al., 1992) the mobility of Be and Sn is controlled by adsorption processes and therefore partitioning can be described with a K_p .

In the literature no batch experiments were found where the adsorption of Ba, Be, Sn, and Tl were tested. Therefore, alternatives were sought to derive K_p 's for these metals.

It is reasonable to assume that Ba adsorption is comparable or somewhat stronger than Ca adsorption (see 4.1). Adsorption characteristics of Be are assumed to be comparable with those of Mg (see 4.2). Adsorption characteristics of Sn are assumed to be comparable with those of Pb (see 4.7). Callahan et al. (1979) stated that adsorption of Tl was weaker than for Zn and Cu.

K_p 's for Ca and Mg were derived from data presented by Scheffer et al. (1984). Interstitial waters from two soils (pH = 3.2 and 6.1) were analyzed and the exchangeable Mg and Ca content (extraction with 1 M NH_4Cl) were determined. Adsorption was weakest for the acid soil. Log K_p 's (l/kg) ranged from 1.37 to 2.18 for Ca and from 1.13 to 2.03 for Mg. K_p 's for Cu, Zn, and Pb were already presented in Table 5.1.1.1.

The K_p 's presented for soil can be used to estimate the adsorbed metal content of soils that corresponds with water quality criteria. To this metal content an estimation of the unexchangeably bound metal content should be added. The latter can be approximated with the background level of the metals in soils (see Chapter 2). The background contents of the "exotic metals" in soils will be reported in a separate report to be published by De Bruijn and Denneman (1992).

Table 3 Log K_p 's for soils (l/kg).

	Geom. mean	n	References
Ba	1.78	-	no data available, adsorption of Ba is assumed to be comparable with Ca, data for Ca from Scheffer et al. (1984)
Be	1.58	-	no data available, adsorption of Be is assumed to be comparable with Mg, data for Mg from Scheffer et al. (1984)
Co	1.60	69	Buchter et al. (1989); McLaren et al. (1986a); Tiller et al. (1969); Anderson and Christensen (1983).
Mo	2.94	15	Buchter et al. (1989); Jarell and Dawson (1978).
Sb	1.93	10	King (1988)
Se	1.30	16	Buchter et al. (1989); Singh et al. (1981); Ylärinta (1983); Elsokarry (1980).
Sn	3.28	-	no data available, adsorption of Sn is assumed to be comparable with Pb, data for Pb from Buchter et al. (1989)
Tl	2.20	-	no data available, estimation (more mobile than Zn and Cu), data for Zn from Buchter et al. (1989);
V	2.49	11	Buchter et al. (1989)

6.2 Selected partition coefficients for sediments

In Table 4 average log K_p 's are shown derived from concentration distributions for particulate matter presented in Chapter 5.2. The K_p 's were lowered with a factor 1.5 to account for the weaker adsorption of sediments as compared to particulate matter. No data were found for Tl. Callahan et al. (1979) stated that adsorption of Tl was weaker than for Zn and Cu. Therefore, the log K_p for Tl presented in Table 6.2.1 was chosen below the average log K_p 's of Cu and Zn shown in Table 5.2.1.1.

The K_p 's presented can be used to estimate the metal content of sediments corresponding with water quality criteria. The K_p 's are based on total metal contents, therefore, unlike for soils, no estimation of the unexchangeably bound metal content should be added to this content.

Table 4 Log K_p 's for sediments (l/kg). The values are derived from concentration distributions for particulate matter in various rivers and lakes. It was assumed that K_p 's for sediments are roughly 1.5 times lower than for particulate matter.

	Geom. mean	References
Ba	3.00	Popp and Laquer (1980); Li et al (1984)
Be	2.78	Popp and Laquer (1980)
Co	3.60	Popp and Laquer (1980); Li et al (1984)
Mo	2.93	Popp and Laquer (1980); Hoede et al. (1987)
Sb	3.41	Van der Sloot et al. (1985); Li et al. (1984); Hoede et al. (1987)
Se	2.62	Van der Sloot et al. (1985); Popp and Laquer (1980)
Sn	6.09	Li et al. (1984); Byrd and Andrea (1986)
Tl	3.00	no data available, estimation (more mobile than Zn), average Log K_p for Zn = 3.91 derived from: Rijkswaterstaat/RIVM (1991); Popp and Laquer (1980); Li et al. (1984)
V	3.59	Van der Sloot et al. (1985); Popp and Laquer (1980); Hoede et al. (1987)

7 Recommendations for further investigations

This report indicates several topics concerning the application of the EP method that need attention. In further research special attention may be paid to the following subjects:

- The application of the EP method was extended from sediments to soils. Particularly the validity of the EP method for soils needs to be examined.
- Trace metals can only partly exchange with the aqueous phase. Further research is needed to quantify the unexchangeable metal fraction of soils and sediments.
- In Chapter 6 it was stated that a coefficient of variation of about 30 % applies to the (logarithmic) K_p 's. The results of several experiments (e.g. Chardon, 1984; King, 1988; Buchter, 1989) indicate that this rather large variation results largely from the differences in the pH. Attempts should be made to model the influence of the pH on the partition coefficient of trace metals.
- It is generally accepted that under anaerobic conditions fixation of trace metals in the form of metal sulfides can take place. Anaerobic conditions are very common for sediments. Here partition coefficients cannot be applied. Research is needed to assess whether sediment dwelling organisms profit from this fixation. To assess the mobility of trace metals under anoxic conditions, measurement of the available sulfide content of Dutch sediments is necessary.
- A validation of the EP method with field data should be undertaken. For this purpose concentrations of contaminants in pore waters in combination with the metal contents of the soils and sediments are required.
- K_p 's for particulate matter in seawater should be determined. This may lead to K_p 's for marine sediments that differ considerably from those for freshwater sediments.

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