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IVL Swedish Environmental Research Institute

Investigations on methods for site
specific determination of the partition
coefficient - K_d , for contaminants in soil
Thesis work with additional comments

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Sammanfattning/Summary The aim of this work was to find a method for a site specific determination of the partition coefficient K_d , which describes whether a substance is situated in the soil particles or in the soil water. This coefficient is used to calculate guideline values for contaminants in soil. Currently, a theoretical coefficient and some basic assumptions regarding soil qualities are used in the calculations. The difficulty in determining a representative K_d -value is to measure contaminant concentrations in the soil water. A review is presented here where the advantages and disadvantages of existing methods is concluded from a perspective where the quality of the soil water extract is the most important parameter, followed by the parameters time and cost. Finally, centrifugal extraction was determined to be one appropriate method. Laboratory research aimed to solve these issues by wetting soil samples from the bottom in their centrifuge cylinders, which would keep sample yield at a maximum and assure that all cylinders were fully saturated. Investigations were performed on a sandy moraine contaminated with chrome, copper and arsenic.	
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Foreword

This paper is based on a degree project in Physical Geography, 20 points, at Umeå University. IVL, Swedish Environmental Research Institute Ltd. constitutes project owner. The study was performed during September 2004 until February 2005, both at IVL in Stockholm and at Umeå University.

Johan Strandberg has performed most of the work, as the thesis for his studies. Uwe Fortkamp who also has been supervisor at IVL has added some information and discussion comments. The original thesis work is available from Umeå University.

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1 Introduction

1.1 Background

For the remediation of contaminated soils in Sweden a generic guideline value calculated by the Swedish Environmental Protection Agency (SEPA) is commonly used as a limit for contaminant concentrations in the remediated soil (SEPA 1997). There are three levels for this guideline value, the choice of which depends on the future land usage of the contaminated site. The model used to calculate a contaminant concentration can be divided into two parts: one that considers how dangerous the contaminant is (eco- and human toxicology) and one that estimates the risk of exposure (transportation).

To make an assessment of the contaminant transport in the water phase, the soil-water (pore water) concentration (C_w) of the contaminant is derived using the following expression:

$$C_w = \frac{C_s}{K_d + \frac{\theta_w + \theta_a H}{\rho_b}} \quad (\text{Equation 1})$$

Where:

C_s is the contaminant concentration in soil (mg/kg dry weight)

K_d is the distribution coefficient water:soil (l/kg)

θ_w is the soil water content (dm³ water/dm³ soil)

θ_a is the soil air content (dm³ air/dm³ soil)

H is Henry's constant (unitless)

ρ_b is the dry soil bulk density (kg/dm³)

The coefficient K_d by definition describes a linear partition of a contaminant between the soil solution and the soil particles (Langmuir 1997). A K_d over 1 means that a majority of the contaminant is sorbed, while a value under 1 means that a majority is solved. This is important because if the contaminant mainly sticks to the soil particles then the concentration in the pore water will be low. That will in turn decrease the risk for further transportation of the contaminant. As can be seen, Equation 1 is a development of this basic relation to give a more realistic C_w .

The result of equation 1 is a soil-water concentration, which is used in equations later on in the Swedish guidelines to calculate how much of a contaminant that will reach ground- and surface waters (SEPA 1997). Of the factors in equation 1 only C_s is

empirical. The other parameters are made from assumptions based on typical Swedish soils in order to be able to use the guidelines in the whole country, but can of course be chosen site specific. K_d is chosen from literature values, which sometimes varies hundred-fold. If there is an error in one of the parameters of equation 1, this will be inherited by the equations made later on. This is why realistic numbers are so important in equation 1.

A basic assumption regarding the K_d -value, is that the relationship between C_w and C_s is linear and the contaminant is in equilibrium with the solid phase (soil). Alexander and McKinley (1996) criticised the use of K_d in risk assessments, meaning that the theoretical linear behaviour that K_d describes does not correspond to the real behaviour of a contaminant in soil. They suggested that deviation from this expression in nature would lead to an underestimation of contaminant mobilisation. Alexander and McKinley pointed out effects like precipitation and saturation, which are not taken into consideration when using the K_d -value, as examples of situations where theory will deviate from practice.

To determine the K_d of a contaminant at a specific site C_s and C_w are measured; assuming a system in equilibrium, K_d is the quotient of the two concentrations. In order to make adequate risk estimations for a specific site, there is a need for a better estimation of the concentration in the soil water. If correct measurements are presented for C_w equation 1 will be unnecessary, which will in turn enhance the quality of the guideline value. The expression in the denominator of equation 1, i.e., a refined K_d is, however, used further on in several toxicological calculations in the SEPA model. This is where the criticism of Alexander and McKinley (1994) must be considered, since the model for the Swedish guidelines relies on the fact that K_d is linear (SEPA 1996).

There are examples of theoretical models that describe the distribution of a substance in an environment, i.e., fugacity models. But when dealing with systems of such complexity as a soil, it is very hard to account for all deviations. It is therefore easier to estimate the coefficient K_d empirically from concentrations in pore water and solid soil, even though sampling and analysis present several difficulties. There is no method today that gives a 100% accurate measure of a solute concentration in the pore water. But through a standardised method concerning sampling and analysis, it is possible to know the sources of error and it is therefore possible to compensate for them.

1.1 Study aims

There are several methods available today for extraction of pore water. The first aim of this work is to present a review of adequate existing methods, including both field methods and laboratory methods. This also includes some benchmarking to gain some knowledge from other countries regarding this issue. No other countries are known to

have introduced a site-specific determination of K_d, but OECD, EC and the UN have created directives for the measurement of K_d, although they are mostly made for chemical testing. To understand the dynamics of soil water and possible parameters that the proposed method should be able to cope with, theories on soil water chemistry and physics will be presented first.

The second aim of this study is to develop a method for contaminant concentrations in soil water and in extent site specific determination of the partition coefficient, K_d in the unsaturated zone, which preferably can be performed in two days and is possible to standardise. In order present a reliable method a review is presented of important environmental factors, and of current methods and how they reflect these environmental factors.

One limitation of this study is that it concentrates on the K_d value and pore water concentrations for one study site. The presented method will not necessarily be applicable for VOC:s since these are difficult to sample, nor for clay soils, which are difficult to extract water from. The study will also not discuss the accuracy of using K_d in risk assessment models, it only aims to improve the accuracy of the existing use in site specific assessment.

1.2 Materials and methods during literature study

The literature study was conducted between September and November 2004, using the Internet search engine Google and the article database Web of Science. Multiple search words and cross references were used in order to find articles that matched the requirements of this study.

2 Physical and chemical properties affecting mobilisation and transport of contaminants

The partition coefficient K_d in this thesis applies mostly to the unsaturated zone, even though it is a coefficient that can be used under saturated conditions as well. In this section the characteristics of the unsaturated zone, from both a chemical and physical point of view, are explained, particularly, how these characteristics affect the transportation of contaminants. Figure 1 shows some of the properties explained in this section.

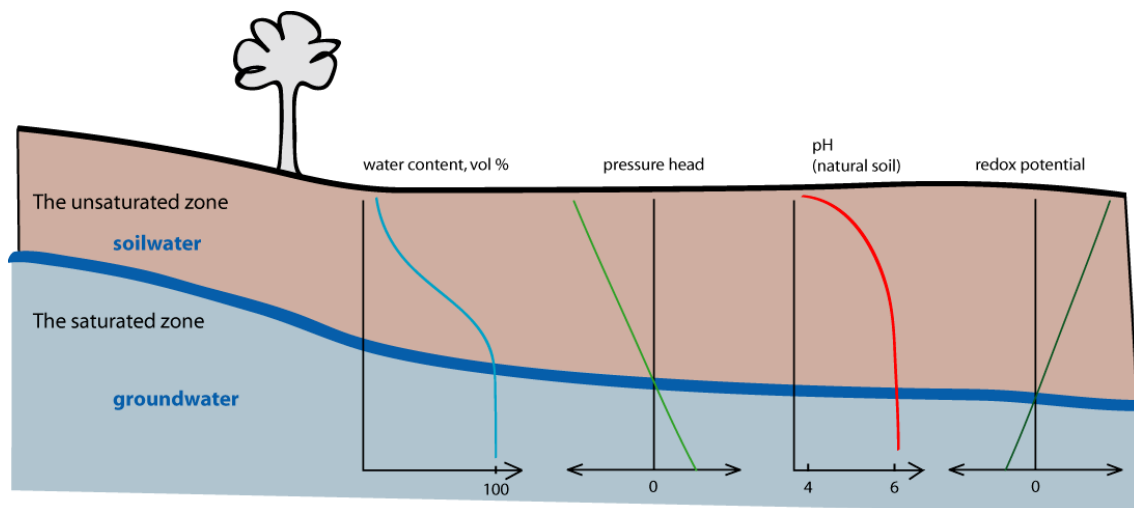


Figure 1. Characteristic properties of a soil profile (Grip and Rodhe 1994, Essington 2004).

2.1 Flow of water and contaminants in unsaturated soil

Some contaminants that are introduced into a soil will spread using the soil water as a medium, others (non aqueous-phase liquids, NAPLs) form bulges that travel more or less independent of the soil water, while others use colloids as carriers. All of them are affected in one or another way by the flow of soil water. This section addresses the physical aspects of how a contaminant is transported in the soil, which includes both flow of soil water and ways that contaminants migrate. It is important to understand how soil water behaves in natural systems and what mechanisms are responsible for the transportation of contaminants. Since this thesis aims to work on a method for assessment of mobilisation of contaminants, it is important that the analysis results of the suggested method render realistic answers.

The unsaturated soil is that part of the soil between the soil surface and the groundwater surface. The most important characteristics of the unsaturated zone can be summed up in three points (Freeze and Cherry 1979). First, the soil pores are only partially filled with water, which means that the moisture content is less than the porosity, i.e., pores are filled with water and air. Second, the fluid pressure is less than atmospheric pressure, i.e., the pressure head is less than zero. Third, the hydraulic conductivity and the moisture content are both functions of the pressure head.

2.1.1 Soil water retention

Water in the unsaturated zone can be divided into three different classes, depending on how it is bound by the soil (Grip and Rodhe 1994). *Sorptive bound water* is a result of both chemical and physical interactions (described further in section 2.2.3). *Capillary bound water* is affected by capillary forces in-between soil particles. When pores become too big they will not exert any capillary attraction on the water; this water is called *bulk water*. This knowledge is essential to have in mind when it comes to soil solution extractors that rely on applied vacuum, pressure or centrifugal forces. These applied forces are meant to overcome the binding forces of the soil and thereby extracting the solution. This section will therefore describe the different conditions that the soils will have a demand for.

The portion of water that is bound sorptive increases as soil particle size decrease, because the specific surface area and also charge density increase (Hillel 1998). Capillary water is retained harder by smaller pores than larger ones. The total water retaining characteristics of a specific soil are described by the water retention curve in Figure 2, where pressure is plotted against water content.

The clay soil in Figure 2 contains small, charged particles that will retain the biggest portion of sorptive bound water of the three soils, because both surface area and charge favour sorption (Hillel 1998, Wiklander 1976). The pores in the clay are small, which means that the capillary forces are strong. The sorted sandy soil does not sorb water to any significant degree as compared to clay. The sandy soil contains pores of uniform size, which are larger than the pore spaces in the clay. Since capillarity is dependent on pore size most water will be held at similar forces. This is why the curve flattens out at a certain pressure. Some capillary water will remain where the particles are in contact with each other, because these contact surfaces create larger capillary pressures.

The unsorted soil in Figure 2 will be the least porous, have the smallest pores and therefore the lowest water content of the three soils. Retention characteristics in this soil type will be dependent on the clay content, since this fraction has superior retention properties. In addition to this, the range of pore sizes will vary more in this soil, which will result in a curve that is lacking the flat areas seen for the sandy soil. Because of the heterogeneity inherent in an unsorted soil, the retention characteristics can differ substantially between soil samples.

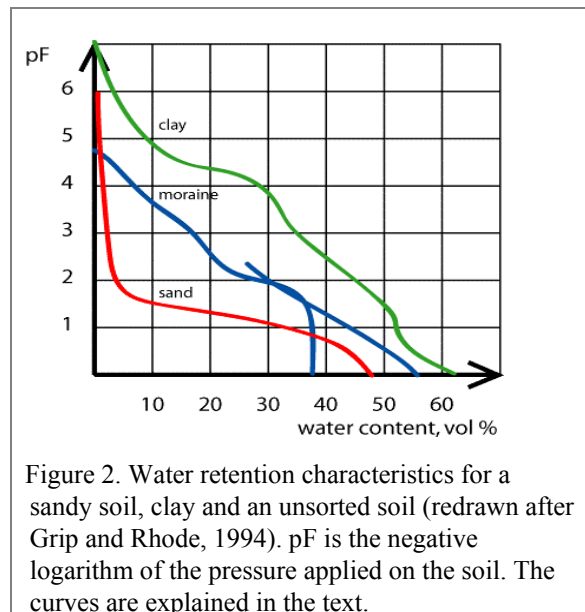


Figure 2. Water retention characteristics for a sandy soil, clay and an unsorted soil (redrawn after Grip and Rhode, 1994). pF is the negative logarithm of the pressure applied on the soil. The curves are explained in the text.

The unit pF is the logarithm of the negative pressure (compared to atmospheric pressure) applied on a soil, for which there are several important values. pF 2 is the field capacity of the soil, or in other words, the water holding capacity for a soil exerted to free drainage (Wiklander 1976). pF 4.2 is the wilting point, where plants can no longer assimilate water. At this pressure water is extracted from pores of 0.2 μm in diameter. pF 7 represents the conditions of a soil dried at 105°C, which is a common water content point of zero. At pF 7 water is increasingly retained by chemisorption (See also section 2.2.2.1). There are no sharp limits between different attraction forces. The extreme points of the water retention curve are, according to some authors, not to be strongly relied on (Bachmann and van der Ploeg 2002, Groenevelt and Grant 2004). This may be a result of the sorptive bound water being held by different forces depending on the involved minerals.

2.1.2 Distribution of water

The sum of gravitational forces and pressure, called pressure head, will determine the direction of a water molecule in soil (Freeze and Cherry 1971). Gravitation drags water down while pressure created by hydraulic forces pulls water up. For a water molecule to travel upward, the pressure has to overcome gravitation. The possible direction of a water molecule is, however, not just up or down; for example, the pressure head can also cause water to travel horizontally into small pores with larger under-pressure.

The distribution of water in the unsaturated zone is not only depending on the pressure head, it also depends on hydraulic conductivity of the soil (the resistance in the soil matrix). This is probably the most important difference between groundwater flow and unsaturated flow (Hillel 1998). Conductivity in a saturated soil is dependent on pore

size, where large pores will have the highest conductivity (Grip and Rodhe 1994). A tube with a 1-mm radius will have the same water transporting capacity as 10 000 tubes of 0.1-mm radius because the friction against the walls of the tube has a greater effect on the water in the smaller tubes.

At lower moisture contents large pores will be depleted of water one by one because the flow is the highest in these pores (Grip and Rodhe 1994). Then they decrease significantly in conductivity, since water does not travel easily in air-filled pores. Smaller pores high in water content are therefore a more important route for water, even though the saturated conductivity is lower. Water flow under unsaturated conditions can also occur as so-called film creep, where water creeps along the walls of wide pores (Hillel 1998, Or and Tuller 2003). The influence of water content on conductivity means that which pores are involved in the transportation depends on the water content. This phenomenon is called fingering, because the dominating flow paths appear as fingers in the soil. Even though velocity is very low in small pores, which means that contaminants in these are retarded by flow velocity, there is an exchange of water and also substances. A small pore may be neighbouring a large pore with larger conductivity, which can be supplied by the small pore and thus sets the contaminant free. This means that soil water from small pores can not be excluded in from the risk assessment.

A result from pores having different flow rates is that oxygen saturation varies greatly in a soil (Essington 2002). Small pores that are hardly ever emptied will be undersaturated with respect to oxygen, while larger pores in the same soil are saturated (see also section 2.2.3). The larger specific surface of smaller pores also results in different pore-water chemistry than in larger ones (Nissinen et al 2000). These findings make it clear that the conditions in the unsaturated zone vary both spatially and temporally, which makes it hard to totally characterise a soil.

Three conclusions concerning the extraction of soil water are drawn with respect to the findings in this and the previous section:

- 1) All pore sizes are of interest.
- 2) It is desirable to keep the natural soil matrix.
- 3) Conclusion 1 and 2 will mean that variance in-between individual samples will increase which leads to the conclusion that multiple samples are needed.

2.1.3 Movement of contaminants in the unsaturated zone

There are four different ways that a contaminant can travel in the soil: advection, diffusion, colloid-mediated transport, and mobility as non-aqueous phase liquids, each of which are described in this section.

The most important mechanism for contaminant transport is advection, which means that the contaminant goes with the flow (Freeze and Cherry 1979). In a homogenous material and with a molecule that is not influenced by attraction from particles, the contaminant has exactly the same speed as the bulk fluid. This means that undisturbed advection is not probable under natural conditions and definitely not under unsaturated conditions except on a small scale. With the concept of fingering in mind, advective transport occurs in different pores and therefore at different speeds, depending on the water content of the soil.

Ionic or molecular constituents can move under the influence of their own kinetic activity (Freeze and Cherry 1979). The process is self-supporting without any bulk fluid movement. It is driven by the concentration gradient for a substance, where it moves from an area of high concentration to an area of low concentration. The diffusion rate of a porous medium is lower than in pure water and even lower in an unsaturated porous medium (Freeze and Cherry 1979), because of adsorption on particles (see also section 2.2.2.1) and the significantly longer distance that the substances have to travel around the particles in the soil matrix. Laboratory experiments conducted on saturated porous mediums have shown that the velocity decreases from 2 to 100 times as compared to pure water. Diffusion is most probably a very small contributor to contaminant transport in the unsaturated zone; nonetheless, diffusion can contribute to dispersion of the contaminant.

Normally, strongly sorbing contaminants are retarded by soil surface charges, but through colloid carriers they can be transported at significant rates (Grolimund et al 1996). It can in fact become the dominant transport pathway for strongly sorbing contaminants, especially since the preference of heavy organic carbons (HOCs) for colloidal dissolved organic carbon (DOC) is very high.

Kretzschmar et al (1999) lists four key conditions that must be met for colloid-facilitated transport to become environmentally significant. First, mobile colloidal particles must be present in sufficiently large concentrations. Second, the particles must be transported over significant distances through uncontaminated zones of the porous medium. Third, the contaminants must sorb strongly to the mobile particles and desorb only slowly. In many cases, the contaminant exerts a hazard only when the bonds to the colloid are broken, but if they are broken too early the contaminant will not be transported at all. Fourth, the contaminant must be highly toxic so that even trace

concentrations in groundwater cannot be tolerated. In addition to this, the persistency of the contaminant should be of importance, because the contaminant will be retarded for some time during which a non-persistent contaminant will be deteriorated. Since the releasing of the contaminant can be dependent on the colloid being broken down the contaminant must survive this, which also takes persistence.

Colloids are very small particles in the range of 1 nm to 1 µm in radius, which may include clay minerals, metal oxides, humic acids, viruses and bacteria (Kretzschmar et al 1999). Their size gives them some important properties: first, the specific surface area is >10 m²/g; and second, particle transportation through diffusion can actually be faster than by sedimentation. Colloids stay suspended in the water mass for a long time because the gravitational forces are less than the attractions in the solution. Colloidal particles in groundwater were long regarded as a sampling artefact due to, e.g., well installation and they were therefore removed through filtration (Backhaus et al 1993). There are several sources of colloids. The most important is in situ mobilisation, which occurs through changes in solution chemistry (Roy and Dzombak 1996, Ryan and Elimelech 1996). Studies have shown that high pH, high Na⁺ saturation and low ionic strength favour dispersion and release of particles in most soils (Seta and Karathanasis 1996). Contaminants sorbed by the colloid generating medium will then be released together with the colloids. McCarthy and Degueldre (1993) found that colloid concentrations in natural undisturbed groundwater are below 1 mg/l, but can be increased by human activity.

In an unsaturated soil, colloids are transported less effectively (Wan and Wilson 1994). A larger fraction is deposited in the soil because the velocity of the bulk water is reduced in this situation. It is also shown that colloids are deposited at the gas-water interface – larger air content results in more interfaces, which in turn increases deposition. Another important factor is that hydrophilic colloids are more mobile than hydrophobic.

The two groups of chemicals for which colloids have the greatest importance for transportation are radionuclides (Champ et al 1982) and hydrophobic organic compounds (Chiou et al 1979). The first group has a high affinity for clay mineral colloids and the latter for natural dissolved organic carbon. Roy and Dzombak (1997) showed that hydrophobic organic carbons (HOC) are only partially mobilised from low organic sands because of colloid release, based on leaching measurements following application of colloid-rich water to a soil saturated with HOC. They suggested that the colloids are not strong enough sorbents to affect the overall transport. An environmental change that increases the colloid production outside the contamination site will have a small effect on the total contamination transport.

Colloids are, however, of interest when the production increases at the site, which means that they should be included in the extracted soil water. The choice of filter size used to filter soil water is a historical heritage from the time when colloids were looked upon as sampling artefacts. Another possibility is the fact that DOC colloids were defined as smaller than 0.45 µm. With new knowledge of colloids (even inorganic) being transporters of contaminants it seems realistic to include them into the analysis of soil water. A common objection to including colloids in the samples is that contaminants sorbed by colloids are less toxic than free contaminants; bioavailability is significantly reduced and the contaminant is therefore “disarmed”. Although the effects of interacting contaminants are not clearly understood, the previous argument of disarmed contaminants is the current understanding. Colloids are transported very efficiently since they do not stick to soil particle surfaces. They are instead in the middle of the stream where the velocity is highest. This is why contaminants sorbed on colloids can travel long distances in a short time. The final destination of the colloid may therefore differ (in for example pH, redox or microbial population) from the point where it sorbed the contaminant. This change of environment can cause desorption of the contaminant or even deterioration of the colloid. Even though the contaminant is sorbed at one place it does not necessarily have to be disarmed forever. A change of conditions may be all that takes to “rearm” it.

Non-aqueous phase liquids (NAPLs) are divided into two different groups: light (LNAPLs) and dense (DNAPLs) depending on whether they sink or float in water (Khachikian and Harmon 2000). Since they do not mix with water their behaviour is somewhat different than contaminants described above (Suthersan 2002). LNAPLs can accumulate near the ground surface, excluding water from this area, and DNAPLs can penetrate the groundwater and form pools along geologic layers. Both types can be trapped in soil pores. Although NAPLs form pools, they dissolve slowly and contaminate the groundwater that flows through the pools (Khachikian and Harmon 2000), creating a dissolved contaminant plume. The dissolution rate can be so slow that it may take decades or centuries to entirely dissolve the NAPL.



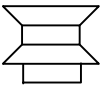
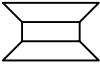
2.2 Surface chemistry and sorption reactions

Many of the chemical reactions in a soil take place on surfaces, which makes soil chemistry more complex than classical inorganic solution chemistry. An important concept in surface chemistry is sorption, which is a term that includes both adsorption, where a substance is attracted to a surface, and absorption, where the substance is incorporated into the absorbing medium. The specific mechanisms concerning the incorporation of contaminants in soils are often unclear, which explains why the less-specific term sorption is often used. It is important to understand the uncertainty introduced by this when choosing a method to determine the K_d-value for a soil.

2.2.1 Specific area and surface charge of minerals

The two single most important factors for the reactivity of soils are specific surface area and charge (Wiklander 1976). Surface area depends on particle size and shape — small particles have a larger surface area per volume and a perfectly round particle has a smaller area than one of irregular shape. Basically, more area means more reaction possibilities (Table 1). Thus, secondary clay minerals have superior sorbing capacities, because they are rectangular, very small and often more charged than other particles (Wiklander 1976, McBride 1994, Essington 2001).

Table 1. Basic properties of some common secondary clay minerals, where the right angled shapes are alumina layers and the non-right angled silica layers (McMurry 1991 and Yong et al 1992).

Clay Mineral	Specific surface area (m ² /g)	Cation exchange capacity (CEC) (cmoles/kg)	Source of charge	Charge characteristics
Kaolinite 	5-20	1-15	Edges, broken bonds, (hydroxylated edges)	Variable and fixed charges
Illite 	80-150	10-40	Isomorphous substitution, some broken bonds at edges	Mostly fixed charges
Vermiculite 	300-700	100-150	Isomorphous substitution	Mostly fixed charges
Montmorillonites 	800	80-100	Isomorphous substitution, some broken bonds at edges	Mostly fixed charges

This results in a positive correlation between the clay content of a soil and specific surface area, independent of what the remaining fractions may be (Petersen et al 1996). There is also a positive correlation between clay content and cation exchange capacity (CEC). In Swedish soils with low clay content, DOC plays an important role in the absence of clays (see section 2.2.2.2).

The permanent surface charge of a soil particle depends on two different mechanisms (McBride 1994). Permanent surface charge is developed at the time when the mineral is formed and it is a property that cannot be altered by the environment once the mineral has crystallised. Permanent charge is a result of isomorphic substitution, which means that during formation one ion in a crystal lattice is substituted by another ion similar in size when there is a deficit of the original ion. If the charge of the new ion differs from the original this will disturb the structure. For example, when Mg^{2+} is substituted for Al^{3+} or Al^{3+} for Si^{4+} this results in a deficit of the positive charge required for balancing the O^{2-} and OH^- ions in the mineral. This will yield a net negative charge. Permanent charge development is specific for the phyllosilicates, where clay minerals are included (Table 2). These charges are not affected by changes of pH in soil solution (Wiklander 1976). Table 1 shows that there is a strong correlation between surface area and CEC, although vermiculite shows a discrepancy to that pattern. Vermiculite has a high permanent charge density, which is explained by its high structural charge that makes it possible to attract large amounts of cations.

Table 2. Point of zero charge (pH_{PZC}) values for selected soil minerals (Sverjensky and Sahai, 1996 and Sahai and Sverjensky, 1997)

<i>Mineral</i>	<i>pH_{PZC}</i>
Quartz	2.9
Amorphous silica	3.5
Kaolinite	4.7
Rutile	5.8
Magnetite	6.9
Muscovite	7.5
Gibbsite	8.9
Goethite	9.0

There can also be a pH-dependent surface charge. If a mineral is equipped with surface hydroxyl groups (denoted $\equiv SOH$, where $\equiv S$ represents a metal bound in the crystal) it will, in contrast to the minerals mentioned above, change surface charge depending on the environment that surrounds it (Essington 2001). This change arises from the protonation or deprotonation of the functional group (-OH). Hydroxyl groups are commonly found on phyllosilicates, metal oxides, hydroxides and oxyhydroxides. These minerals are also primary minerals. When there are an equal amount of negative and positive sites on the mineral surface the point of zero charge is reached (Table 2). When the pH is below the pH_{PZC} the mineral will have a net positive charge. Minerals with low pH_{PZC} have a greater ability to attract cations over a broader pH range.

Illites are the quantitatively most important clay mineral in Sweden, which contributes to the low CEC in Swedish soils (Wiklander 1976). Exceptions are the montmorillonites which are common in Baltic clay moraines located in the Uppsala area and Skåne. Vermiculites can be found in shale primary rock moraines in Skåne, which further increases the CEC of this area. Kaolinites, which are important for the sorption of non-polar substances, can be found in low concentrations in most soils. Table 1 and Table 2 show that not only particle but also mineral types must be accounted for when

estimating the K_d-value for a soil contaminant in contrast to a site specific measurement where these factors are “included”.

2.2.2 Sorption and desorption of polar compounds

Adsorption can be divided into two types: physical and chemical adsorption. Strong forces are indicative of chemisorption, in which a covalent or short-range electrostatic bond (Coulombic forces) is formed between the molecule and the surface. This bond is typically in the range between 80 and 400 kJ/mol and will pull the attracted ion close to the particle (Hillel 1998). Physical adsorption (i.e., van der Waals forces and London forces) is weaker, typically less than 20 kJ/mol, but takes less or no energy to form. The attracted ion is not as closely connected to the particle as in chemisorption. The sorption to a surface is an exothermic reaction, which is favoured by lower temperatures (Suthersan 2002). A rise in temperature increases desorption. This imposes a problem, because temperatures differ between soils at different depths. A contaminant that leaches down into deeper soil layers may be sorbed there due to the lower temperature. Another problem may be the temperature at the lab. If you bring cold soil samples into a warm lab, desorption will increase and the solution concentration will be overestimated.

Ion exchange is a very important mechanism when it comes to the understanding of contaminant behaviour. The charged surface of a soil particle attracts counterions, which will swirl around the particle in a cloud, loosely held by the charges. These ions can be exchanged for other ions that are introduced into the soil solution. Since the sum of charges must remain constant (electroneutrality), an ion with a lower affinity must be desorbed if an ion with a stronger affinity is sorbed by the particle surface. This mechanism creates the ion exchange that both adsorbs and desorbs ions to particles and mobilizes ions into solution. In nature this change is often slow, which can create a net positive or negative charge for some time. This may appear as only sorption or desorption.

Ion exchange is a basic mechanism that can be seen in plants and also the human body. For soil contamination, ion exchange is an important mechanism that is responsible for buffering (sorbing) the contaminant.

2.2.2.1 Cation exchange of inorganic soils

Minerals that have a negative charge are surrounded by cations to balance the negative surface charge. This adds an ion coating onto the particle; the composition of this coating depends on the mineral and its surroundings. Ions are sorbed by strong physical sorption or chemisorption. This zone around the mineral is neither mineral nor bulk solution. The coating is actually so closely connected such that, if you could imagine

that you could see the minerals, it would in fact not be the mineral surface rather you saw, but rather the water molecules and the ions that surround the mineral.

The theory of the electric double layer describes a soil particle and its surrounding. This concept has evolved over time from the first Helmholtz and Gouy-Chapman models to the Stern electric double layer model, which incorporates both of these models (McBride 1994). The Stern model is depicted in Figure 3. Another model that is frequently used today is the triple model (Westall 1986). This is a refinement on the double model, although the basic principle is pretty much the same.

A chemical definition of the double layer theory (McBride 1994) is that the double layer is situated where the ion concentration of the solution surrounding the particle differs from the concentration in the bulk solution. This means that the diffusive layer surrounding a negative particle is where the cation concentration is higher than in the bulk water.

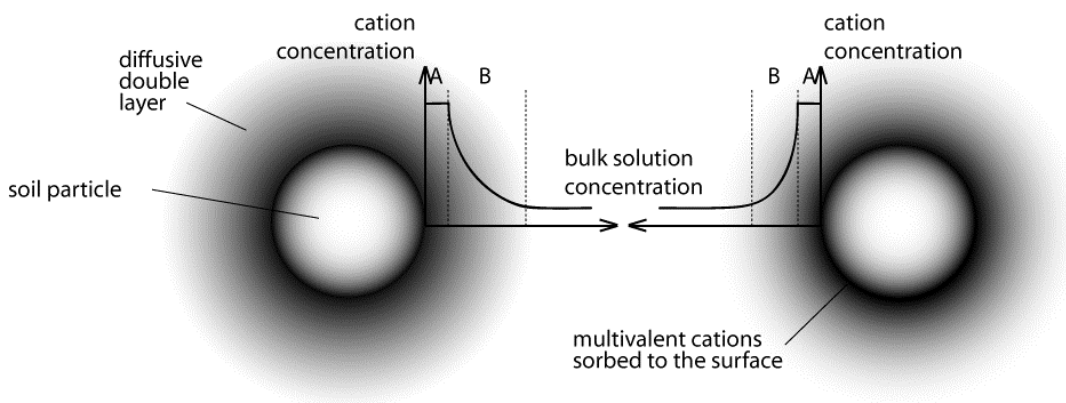


Figure 3. The electric double layer model and the effect of cations bound to the surface, shielding the charge (redrawn after Luckner and Schestakow, 1991; Essington 2001).

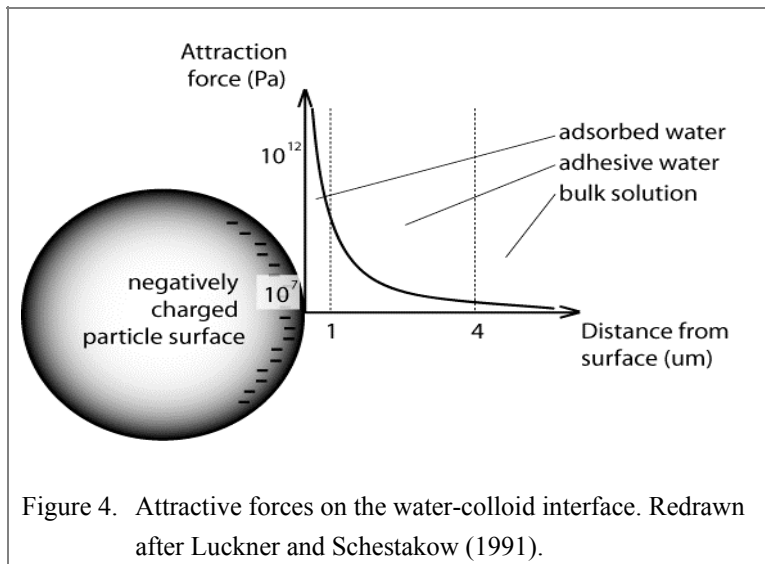
Hillel (1998) defines the double layer from a physical point of view:

The double layer is a result from two opposing tendencies: “(1) the electrostatic attraction of the negatively charged surface of the positively charged ions, which tends to pull the cations inward so as to attain the minimum potential energy level; and (2) the kinetic motion of the liquid molecules, inducing the outward diffusion of the adsorbed cations in a tendency to equalize the concentration throughout the solution phase, thus maximizing entropy”.

The solid surface itself is negatively charged. The first layer (Figure 3) is called the Helmholtz layer (A), which is bound by both chemisorption and physical sorption. The second layer (B) is held by physical sorption and is therefore less stable.

If a negatively charged particle were introduced into pure water, the particle would attract water molecules, where a water molecule's positive side is orientated towards the negatively charged particle and the negative side of the water molecule is oriented outwards towards the bulk solution. This layer is called vicinal water. Outside this layer an opposite layer of water molecules would form, facing the other way. A clay particle is typically able to attract 5-8 layers of water molecules in this fashion (Luckner and Schestakow 1991, Grip and Rhode 1994).

Natural water is not composed only of water molecules; it also contains ions that are attracted by the electrostatic forces of the soil surfaces. These surface charges are only partly balanced by the counterions in the inner sphere. This results in a diffusive layer of cations and anions that exists in the outer sphere. Cations are also able to stick to the vicinal water because the negative part of the water molecule is facing the bulk water. The charge density is highest close to the particle, where ions of high valence are likely to be found, and declines with distance until the bulk solution composition is reached. The thickness of the double layer decreases with increasing ionic strength in the solution.



The border between sorptive and bulk water is not definite. There will be an ongoing change of ions in the sphere of the double layer all the time. Some authors here suggested that all ions will be exchanged (Wiklander 1976). It's just a question of time, although the probability of an ion bound by chemisorption to be exchanged is lower than an ion in the outer spheres.

An interesting definition was made by Luckner and Schestakow (1991), whereby the actual binding forces of a particle are determined (Figure 4). It is unlikely that this force is the same for all types of particles because charge densities can differ, particularly between clay minerals and bigger particles.

An extension to the discussion regarding exclusion of water from small pores (section 2.1.2) is whether sorptively retained water should be included. This will have an impact on the useage of extraction methods which can apply a high force on the soil solution. Wiklander (1976) meant that all compounds will be resuspended from the mineral surface and that it is just a matter of time. Whether an ion will be desorbed or not is determined by the attraction forces between the ion and the mineral. The closer to the mineral the ion gets, the stronger the forces involved and the probability of desorption is lower. Luckner and Schestakow (1991) stated that ions sorbed onto the surface are attracted by $>10^{12}$ Pa. This depends on the mineral, the ion and the surrounding. The attractive force in the outer sphere of the diffusive double layer is 10^7 Pa (\sim pF 5, which is well over the wilting point of pF 4.2), although this is dependent on the ion concentration in the bulk solution. This agrees with Wiklander (1976), who considered that water retained by pF 7 ($\sim 10^9$ Pa) is both physical and chemical sorption. It is known that water retained less than pF 4.2 circulates through biota uptake. The question is whether water that is more strongly retained is to be included. The definition of Luckner and Schestakow (1991) is in favour of using higher pressures, since 10^7 Pa is pF 5. An objection to this statement may be that these forces may have been calculated for clay particles and that a coarser particle of different chemical constitution retains its adsorptive water by weaker forces. This is true, but the diffusive forces from the surrounding bulk solution should still be the same according to the definition of Hillel (1998). A coarser particle of lower charge density has practically no diffusive layer, because the diffusive layer is a result of diffusive forces.

The information about the double layer provided by different authors shows that compounds in the diffusive double layer can be mobilised quite easily. Depending on the scenario to be investigated they have to be included in the measurement for the partition coefficient, i.e. forces would have to be applied to guarantee that these are set free.

2.2.2.2 Cation exchange by soil organic matter (SOM)

Humic acid, that soil organic matter (SOM) to a great deal consist of, can be approached as a common acid with a pK_a of approximately 5, with exchangeable ions on the surfaces. The negatively charged surface of SOM can be looked upon as a weak field exchanger (Figure 5). Actually, the variability of pH is a cation exchange (McBride 1994). The hydrogen ion (H^+) is a cation that can be exchanged as well as any metal cation. So, this means that metal ions will compete with the hydrogen ion for the exchange sites. This makes SOM more efficient as a cation exchanger when the H^+ concentration is low, i.e., when pH is high (McBride 1994; Lee et al 1996). When the concentration of H^+ is high then H^+ will outcompete the metal ions and a leakage of metals from the soil occurs. For this type of ion exchange, radius and charge are the factors that are selective for the exchange. Large cations displace small cations. The

order of selectivity for alkali and alkaline earth metals is: Cs⁺ > Rb⁺ > K⁺ > Na⁺ > Li⁺ > Ba²⁺ > Sr²⁺ > Ca²⁺ > Mg²⁺.

In addition to the electrostatic forces that affect metal ions, humic acids are effective sorbents through chemical absorption of several metal ions. Lee et al (1996) showed that among all soil properties, organic matter plays the most important role in controlling Cd (II) sorption to soils. Dörr and Münnich (1991) studied the transport of cesium and lead in European forest soils and found that lead was so tightly bound to organic matter that the transport of lead is due to the sedimentation of organic material only. They also concluded that the residence time of Pb and Cs in organic rich soils is limited more by the turnover time of the organic matter than by inorganic chemical exchange reactions. The affinity of cesium for humic matter is lower than the affinity of lead, which leads to some vertical dispersion due to other mechanisms than organic material turnover (Comans et al 1998). The turnover of carbon in organic and mineral soils in a Canadian study was found to be 6-1600 years and >3000 years respectively (Trumbore and Harden 1997).

SOM can form stable chelates and mercury and several more metals show very high affinities to sulfides in the organic matter (Essington 2001, Skyllberg et al 2003, Ravichandran 2004). These complexes are commonly suggested to decrease bioavailability (Suthersan 2002). Although clay minerals generally determine the characteristics of a soil, clay-rich soils are not common in Sweden, and SOM instead becomes the dominating sorption regime. Consequently, it can be expected that CEC will correlate better to SOM content than to particle size. Therefore, the estimation of 0.2% organic content made in the model of SEPA (1997) can lead to incorrect estimations of the sorption characteristics of a soil.

A relevant question is how contaminants sorbed to SOM are to be accounted for. When doing risk assessments, the assumption is that a sorbed substance is immobilised and therefore not dangerous to the environment. Obviously, all SOM will eventually be dissolved into DOM and colloids in foreseeable future. Maybe the same arguments as for colloids being included in the C_w-term in the K_d-equation, would apply to SOM, which really constitutes the source of organic colloids.

2.2.2.3 Cation exchange selectivity

The most important factor deciding the adsorption/desorption mechanisms of an ion is its valence (Bohn et.al 2001). Divalent ions are generally more strongly retained than monovalent ions. Quadrivalent ions such as thorium (Th⁴⁺) are practically irreplaceable by an equivalent amount of KCl, which means that thorium can be considered as a part of the particle. Soils with high cation exchange capacity (CEC) generally have the

greatest preference for highly charged ions (Bohn et.al 2001), which means that a pH rise will lead to changed cation selectivity, where polyvalence ions are preferred.

Another important property that influences the exchange selectivity of ions is the hydration energy of the ion (McBride 1994). Water molecules surround all particles. If the ion has a high hydration energy it is more likely to be trapped in the water layer outside the particle. With valence and hydration energies in mind, it makes it possible to predict how a substance will act in the ground with regard to exchange selectivity. There are exceptions though, for example, where certain colloids exhibit unusually high preferences for specific cations. These colloids and other exceptions are not addressed in this paper.

The relative ion replaceability of ions is called the lyotropic series, where lithium is most easily disconnected from the soil and thorium is the most strongly bound: $Li^+ \approx Na^+ > K^+ \approx NH_4^+ > Rb^+ > Cs^+ \approx Mg^{2+} > Ca^{2+} > Sr^{2+} \approx Ba^{2+} > La^{3+} \approx H(Al^{3+}) > Th^{4+}$ (Bohn et.al 2001).

A simple electrostatic model to describe the cation exchange is the Eisenman model (McBride 1994). This model isolates three types of situations that can occur in the interaction between particles and ions (Figure 5):

1. No water molecules present.
2. Water present on a weak field exchanger, such as most clay minerals. Strongly hydrating ions will not be attracted strongly enough by the surface to overcome the forces of hydration. First row transition metals (Vo^{2+} , Cr^{3+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) and the heavy metals (Cd^{2+} , Hg^{2+} and Pb^{2+}) will form so-called inner-sphere complexes, where the ion is bound directly onto the surface, with no water molecules between.
3. Water present on a strong field exchanger. No strong field permanent charge clay minerals are known, even though studies of ferrous oxides have revealed such behaviour. The structural charge is not negligible so all ions are attracted to the surface. This will create the inner sphere association.

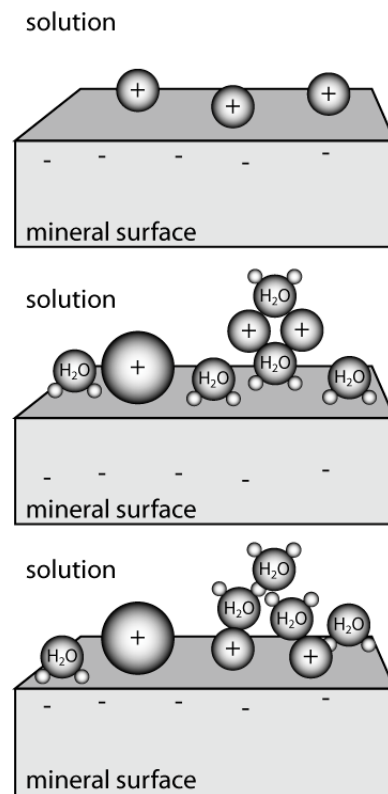


Figure 5. Three limiting cases of ion exchange on mineral surfaces (redr. after McBride, 1994).

The presence of several contaminant species will affect the K_d -value of the individual contaminant in different matters, depending on its affinity for soil compared to the competing species. This makes it harder to predict the behaviour of the contaminant. This means that chemical testing performed as described in section 3.3 using one chemical at a time poorly describes the nature. Furthermore, a contaminant sorbed by soil particles can, due to the introduction of a contaminant of higher affinity, be remobilized. An extraction of the actual soil water will, however, deal with these problems.

2.2.2.4 Anion exchange

Even though anion exchange is commonly considered as less important than cation exchange, it exists. Anion exchange is primarily electrostatic, just like cation exchange (Bohn et al 2004). The attraction is weak and the exchange is fast, which makes anions more mobile than cations. The anion exchange capacity (AEC) of a soil is highly affected by the degree of weathering and pH, which is why the modestly weathered soils of Sweden have a CEC that greatly exceeds the AEC.

As seen in Table 3, the interaction of anions with soil varies. As with cations, it depends on the radius of the hydrated molecule and the hydration energy. Other factors affecting the anion repulsion include: 1) anion charge and concentration, where repulsion increases with anion charge (valence). A higher concentration of anions in the soil solution increases the number of anions repelled, even though the anion comes closer to the particle before it is repelled. 2) Species of exchangeable cations: cations that are tightly connected to the particle (see previous chapters) render a tighter and more concentrated field around the particle. This will better neutralise the negative forces of the particle, which in turn decreases the repulsion of anions. 3) pH: a low pH increases the amount of positive sites on the particle, which will decrease the repulsion. 4) Presence of other anions: the presence of tightly binding anions such as phosphate ions, occupy the positive binding sites and repulsion will increase. 5) Nature and charge of the soil surface: the greater the negative charge of the surface, the greater the repulsion of anions. Montmorillonite therefore exhibits greater anion repulsion than kaolinite, which contains fewer negative charges at all pH's.

Table 3. Anion and molecular interaction with soil (Bohn et al 2004).

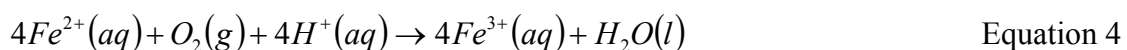
Repelled to weakly retained	moderately retained	strongly retained
NO_3^- , SO_4^{2-} , SeO_4^{2-} , HCO_3^- , CO_3^{2-} , ClO_4^- , Cl^- , Br^- , I^-	H_3BO_3 , $H_2BO_3^-$, F^- , CrO_4^{2-}	$H_2PO_4^-$, $H_2BO_3^-$, H_2S , HS^- , $H_2AsO_4^-$, $HAsO_4^{2-}$, MoO_4^{2-}

Anion repulsion is very important for transport (Gvirtzman and Gorelick 1991). When it is repelled from the particle and its surroundings into the pore water, it can travel at the water front as a concentration bulge. The anions therefore appear to travel faster than the bulk water.

2.2.3 Redox reactions

Since the experimental goal of this study is to calculate a K_d -value for the unsaturated zone, where oxygen supply and therefore the redox potential is varying, it is important to know how redox potential affects a contaminant. Redox conditions in soils can vary widely over short distances, because O_2 must diffuse through pores of different sizes with varying water content (Bohn et al 2001). In wet soils only the largest pores are open to gas diffusion from the atmosphere. This can result in oxygen deficiency inside a soil aggregate, although aerobic conditions exist outside. This change from aerobic to anaerobic conditions occurs within a few millimetres.

Basically, a redox reaction is electron transfer from one substance to another. A medium that are rich in electrons (electron donors) are termed reducing and areas deficient in electrons (electron acceptors) are termed oxidizing (Essington 2004). A redox reaction can be subdivided into a reduction half-reaction and an oxidizing half-reaction, which are then re-combined to make up the redox reaction. The reactions below are examples of an oxidation (Equation 2), a reduction (Equation 3) and a redox reaction (Equation 4):



In this redox reaction oxygen serves as the oxidizing agent and iron as the reducing agent, with the result that iron is oxidized and oxygen is in turn reduced.

Although oxygen is the most important oxidizing agent, or electron acceptor, a substance can be oxidized by any other substance, as long as the electron potential of the oxidizing agent (electron acceptor) is sufficiently higher than the substance that is oxidized (electron donor). Other electron acceptors are not as efficient as oxygen, which is why oxygen supply is important for soil redox reactions. When the dissolved O_2 has been consumed, nitrate takes over the function as electron acceptor and becomes reduced (Luckner and Schestakow 1991). If reducing conditions are maintained, a series of reductions occur in the following order: Mn^{4+} to Mn^{2+} , Fe^{3+} to Fe^{2+} , SO_4^{2-} to HS^{-} , CO_2 to CH_4 and finally N_2 to NH_4 . All of these reactions need an electron donor, which can, for instance, be some kind of organic substance. Many redox reactions are

kinetically slow in natural groundwater, and it is therefore assumed that many reactions never reach their equilibrium (USEPA 1999). A realistic scenario for soils is that ground water level is raised during spring or autumn, which creates reducing conditions in the soil. Cations sorbed by soil particles then changes in valence (are reduced), which decreases the holding capacity since ions of lower valence are more weakly retained by soil. A release of sorbed cations will occur. Since the cations also can sorb contaminants this can cause sorbed contaminants not affected by redox potential to be released as well.

2.2.4 Sorption of hydrophobic compounds

A hydrophobic compound is a compound that does not resemble water, i.e., it is not polar. The more different from water it is the greater the hydrophobic forces will be. When introduced into a soil solution, a non-polar organic compound can adhere to both clay minerals and soil particles, even though these may be charged, because such compounds can be the most hydrophobic substances in that environment (Delle Site 2000). Different types of bonds are involved in the sorption of organic chemicals by clay, while, in the case of soils or sediment, hydrophobic interactions prevail. When sorbing to clay minerals it is suggested that hydroxyl surfaces sorb more effectively than the oxygen surfaces. This results in a decrease sorption in the following order: gibbsite>kaolinite>montmorillonite. Although much research has been addressed to the partitioning of organic contaminants between soil solution and soil solid phase, still little is known about the binding types and mechanisms and about the influence of SOM quality and soil solution composition on PAH sorption (Wilcke 2000). Roy and Dzombak (1997) showed that the leaching of a non-polar hydrophobic compound like phenantrene from a mineral soil column was affected by a change in pH within natural conditions.

Even though minerals can adsorb non-polar organic compounds, the contribution of natural organic matter in sediments and soils are much more relevant than the contribution from other components, such as minerals (Delle Site 2000). The rough estimation of 0.2% organic carbon content in soils in the SEPA model (1997) can therefore be somewhat misleading. Sorption of hydrophobic organic compounds is in general directly proportional to the organic matter content, although a small variation in the sorptivity can arise from diversity in composition and structure. Sorption was found to consist primarily of hydrophobic partitioning into the soil organic matter; adsorption by the soil mineral fraction is relatively unimportant in wet soils because of the strong dipole interaction between soil minerals and water, which excludes the organic compounds from this portion of the soil (Delle Site 2000). The presence of a cosolvent, such as ethanol and methanol that are miscible with water, can drastically increase the solubility of hydrophobic compounds (Suthersan 2002).

2.3 Sorption models

It is important to determine what fraction of a contaminant is solved and how much is sorbed, or in any other way not solved. The solved fraction is transported by soil-water to larger areas, which can complicate remediation; contaminants are also in general more toxic to animals and plants as solved ions (Suthersan 2002). It has therefore been of great interest to predict the partition of a substance between the solid and the liquid phase. According to Douchette (2000) a definition of soil sorption coefficients is: “soil sorption coefficients quantitatively describe the extent to which a chemical distributes itself between an environmental solid and the aqueous phase that it is in contact with at equilibrium”.

All of the models described below suffer from a hysteresis between sorption and desorption. This means that it in fact requires lower concentrations in the solution (stronger diffusive force) for the ion to desorb than it takes for it to sorb, which is not shown in the figures below. The important consequence is that ions are less able to desorb as the concentration of these ions are lowered in the solution (McBride 1994). This imposes a possible problem, because the K_d-value used by SEPA (1994) can have been determined for a sorbing regime, while the desorbing regime may be prevailing at a contaminated site, or the opposite. Further, a soil sample taken in the back of the contaminant plume will show a different K_d than sample taken in the front of the plume, because different regimes are prevailing. This it is important to be aware of the situation to be described when choosing a soil water extraction method for determination of the partition coefficient. This will be further commented in the description of methods.

The model applied by the Swedish EPA (1994) for calculating a generic guideline value relies on the K_d-model when calculating the partition between soil and solution. But there are at least three other types of isotherms that describe different types of interactions between the solid and the substance: Langmuir isotherm (L-type); H-type; and S-type (Figure 6).

The constant partition coefficient model (C-type) is a model that describes a linear relationship between the chemical sorbed by solids and the concentration of the chemical in water. This is the most theoretical model, which is relevant only at small contaminant concentrations (McBride 1994, Langmuir 1999). Equation 5 shows this formulated as an equation:

$$K_d = \frac{q}{c_{eq}} \tag{Equation 5}$$

where q is the equilibrium mass of adsorbed substance per unit mass of sorbent, c_{eq} is the equilibrium mass of the substance in solution per unit volume of solution. K_d has units of volume per mass.

The Langmuir isotherm (L-type) shows a high affinity between the adsorbate and adsorbent at low surface coverage, and is usually held in place by chemisorption (Langmuir 1999). As coverage increases the sorption will increase slower. This is the most commonly encountered type of isotherm in soil chemistry.

The H-type model describes an adsorbate that has an even higher affinity by chemisorption for the adsorbent than in the L-type (McBride 1994, Langmuir 1999). Organic substances rarely follow this isotherm because few of them form strong covalent bonds with soil colloids, but inorganic substances do. The H-type model is often interpreted to indicate the formation of inner-sphere complexes.

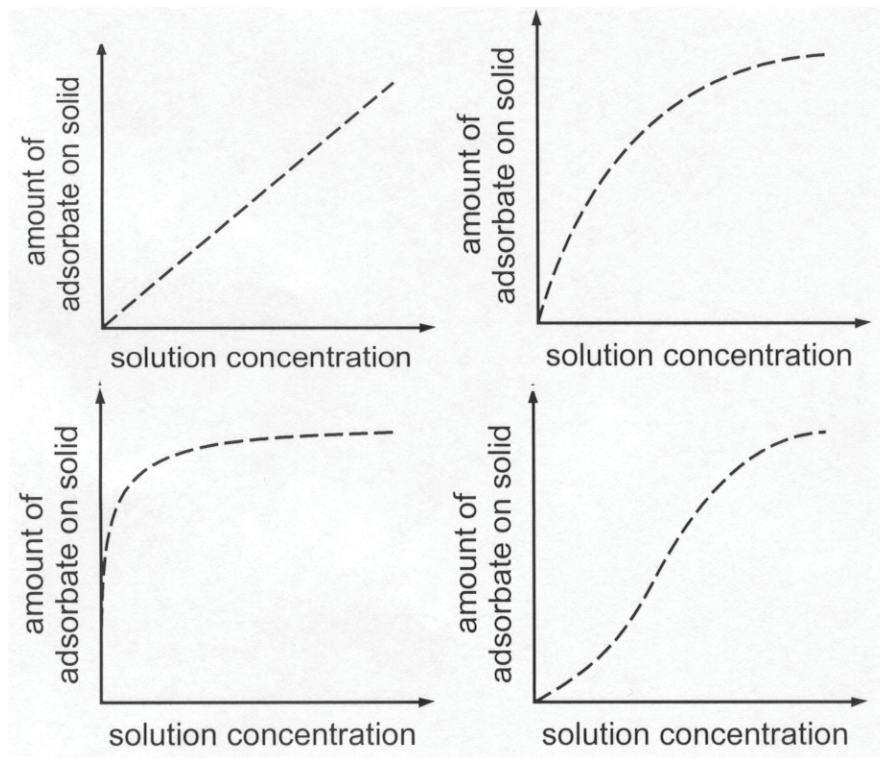


Figure 6. Sorption models. From upper left to lower right: constant partition model; the Langmuir model; the H-type; the S-type (redrawn after Langmuir, 1997; McBride, 1994).

A shallow slope at low concentrations that increases with adsorbate concentration characterizes the isotherm of an S-type model (McBride 1994, Langmuir 1999). In this model the interactions between the chemical in solution are stronger than the attractions from the surface. At high concentrations, the S-type model resembles the previous isotherms. The adsorption of trace elements by soil is often described by the S-type isotherm, particularly when the soil solution contains large concentrations of DOC.

2.4 Summary of factors influencing the sorption coefficient and its determination

The sorption of compounds or contaminants in soil is very complex; however, three major sources of errors for the determination of the partition coefficient can be identified. First, a source of error is connected to the method. Every method has its weak points, which can introduce an error early in the process. There is always a risk that undesirable interactions will occur between the laboratory equipment and the chemical species of the soil water (Baes and Sharp 1983). A more detailed description of different methods follows in the next section. Second, the K_d-coefficient is a ratio between two concentrations (Baes and Sharp 1983). When the concentrations are low, a small error (but relatively seen large) in either soil or solution concentration produce a large error in the results. The relative error increases rapidly with increasing K_d. The third factor is really a number of factors, all concerning the environment and the soil. These factors are summarized in Table 4 (the explanation to each factor is found in previous sections, which are given in the table). If one of these factors changes, it can create an error compared to the calculated K_d-value. However, only some of the listed factors are subject to change. Some of them are most likely to be constant or at least has a small effect on desorption of the contaminant if they are introduced to an old contamination.

As seen in Table 4, pH and redox potential would be desirable to alter in order to make a better risk assessment. A report from the Swedish Geotechnical Institute (2004) suggests the use of NH₂OH/HCl, which is both reducing and pH-lowering, to simulate a high groundwater level and an acidous spring flood. That is a sound method if the wish is to develop the model even further, in order to simulate natural processes.

Table 4. Some environmental factors influencing the magnitude of sorption and desorption of a compound in soil and the probability and consequences of them changing.

Environmental factor (<i>explanation is found in chapter</i>)	Influence on polar compounds	Influence on non-polar compounds	Probability of change	Consequences of a change
<i>Surface area</i> (2.2.1)	Increased surface area of the sorbent increases the sorption.	Increased surface area of the sorbent increases the sorption.	Constant feature of the soil	
<i>Mineral surface properties</i> (2.2.1)	More charge on the surface increases sorption.	Less charged surface increases sorption. Hydroxyl groups sorb better than oxides.	Charge of pH-sensitive minerals will change at change of pH.	
<i>Solubility</i> (2.2.3)	Polar compounds are soluble in water	Low solubility of the compound increases the sorption.	Constant property of the contaminant	
<i>Temperature</i> (2.2.2)	Decreased temperature increases sorption because sorption is exothermic.	Relatively independent	Small effect on mobilisation.	A high temperature could release contaminants
<i>pH</i> (2.2.1)	A high pH favours sorption of cations while a low pH favours sorption of anions.	If pH reaches pH_{pzc} sorption increases.	Probable change at for example spring flood.	Affects different colloids, certain contaminants and certain minerals.
<i>Salinity</i>	High salinity decreases sorption (Suthersan 2002).	Can show an increased sorption at high salinity (Suthersan 2002).	Not likely. Areas exposed to seaspray probably suffer from high salinity from the start. New salt in reasonable amounts will therefore not affect contaminants.	
<i>Cosolvents</i> (2.2.3)	Polar compounds are seen as soluble in water	Presence of cosolvents decreases sorption.	Only a threat if new contaminants are introduced.	Would release contaminants with affinity for the cosolvent
<i>Dissolved organic matter (DOM)</i> (2.2.2.2 and 2.2.3)	High concentration increases sorption for some species.	High concentration drastically increases the sorption.	Feature of the soil. The probability of new DOM is not likely.	
<i>Colloids</i> (2.1.3)	Sorbs radionucleids efficiently, but may not retard them.	Colloids in the form of DOC sorbs HOC:s efficiently, but may not retard them.	Small effect on old contaminants.	Can show effects at changed pH
<i>Competitive sorption</i> (2.2.2.3 and 2.2.1)	Compounds of high affinity to soil decreases sorption of others.	Compounds of higher affinity to soil will decrease sorption of others.	Only a threat if new contaminants are introduced.	Would release contaminants with lower affinity to the soil
<i>Redox conditions</i> (2.2.3)	Redox sensitive cat ion species decreases sorption at low pE if the ion is reduced.	Not influenced.	Probable change at for example spring flood or autumn near groundwater outflow.	A lower redox potential will release redox sensitive contaminant species and affect binding capacities of colloids.

3 Methods for estimation of partitioning coefficient

Extensive research has been done to find a method that gives a “true” partitioning coefficient. Certain methods have advantages in particular situations, but there is no method that works for all situations. The problem is that you try to measure a system, but when measuring it, you alter the system by applying the analysis tools or taking your sample, so the outcome is often a disturbed coefficient. Another issue is the fact that the concentrations of contaminants are very small, so any disturbance from sampling devices etc. will be of great importance. This section reviews current methods, which includes a description of each method, along with a discussion of its pros and cons. During this section, one or more methods are to be found, that fulfils the demands that were specified in the previous section.

3.1 In situ soil water samplers

The basic principle of in situ samplers is to collect a water sample from an undisturbed soil, which is assumed to contain natural soil water. The composition of this undisturbed soil water is the one wanted for the K_d -analysis; because it is an empirical coefficient, real soil-water is the most relevant to use. But, there are questions as to how natural this extracted soil water really is, because water chemistry and properties can vary depending on sampling method.

3.1.1 Vacuum lysimeters

Pore water extraction using vacuum lysimeters is a very common method (Morrison and Lowery 1990, Dorrance et al 1991, Ludwig et al 1999, Essert and Hopmans 1997, Essington 2004). The apparatus consists of a porous cup (Figure 7) that is connected with a hose to a suction device, through which you create a vacuum. The application of a vacuum affects soil pores in different ways (Morrison and Lowery 1990). Since capillary forces hold the water in the smallest pores strongly, this water will be the hardest to extract. Because, in order to extract water from the pores a greater hydraulic force must be applied in the lysimeter than the existing capillary forces that hold the water in the pore spaces. Morrison and Lowery (1990) investigated the sampling of a common porous ceramic cup and found that the sampling radius in medium-grained sand is in the order of centimetres.



Figure 7. Vacuum lysimeter
(Soilmoisture Corp, 2004).

The “efficiency of sampling”, i.e., how much of a known compound that is sampled, decreased with distance from the cup, which implies that the applied force is not enough for small pores further away. Morrison and Lowery concluded that “the liberal use” of vacuum lysimeters should be evaluated carefully given their limited sampling radius.

There are three different ways of applying a vacuum (DEPA 2001: 1) sudden tension, where you apply the vacuum when a sample is wanted. 2) Continuous tension, when a vacuum is created after sampling. It is not continued after that, but the low pressure remains until next sampling, although the pressure will drop. This results in faster sampling in the beginning of the sampling cycle and therefore extraction from a larger spectrum of pore sizes than in the end. 3) Variable tension, when the suction is regulated to be just above the soil tension. This results in a fairly constant water sampling and relatively undisturbed hydraulic conditions in the soil, although it is more difficult to operate.

Extensive developmental research has been done on vacuum lysimeters, so there are several varieties of the device on the market (USEPA 1999). It is known that interactions between the contaminants and the material in the porous cup and hose occur, so attention has been paid to that subject (DEPA 2001). The choice of apparatus is therefore important when interpreting lab results.

3.1.1.1 Pros and cons of vacuum lysimeters

The great advantage of the method is the extensive experience that exists in this area. The knowledge of which cups should be used for certain compounds is detailed, and there are also numerous studies to compare with. The hydraulic contact with the soil solution is important when sampling, which can be a problem if you want to sample the soil water shortly after installing the device. After drilling the hole and putting the lysimeter into it, the space between the cup and the soil has to be eliminated. This can be done in different ways, but a general problem is that it has to equilibrate for some time. The fact that Morrison and Lowery (1990) found a concentration gradient in medium-grained sand is very interesting, since this soil most likely offers favourable hydraulic conditions at saturated conditions. The gradient will therefore be even steeper in a poorly sorted soil. This should result in a false soil solution in most situations.

3.1.2 Zero tension lysimeters

The zero tension lysimeter, or just simply lysimeter, applies no artificial pressure or vacuum on the soil solution (MacDonald et al 2004(1), MacDonald et al, 2004(2), Buczko et al, 2004, Ranger et al, 2001, Essington, 2004). The device can be constructed in many different ways. The basic properties are some type of a collector device that is mounted in a horizontal cavity, a storage vessel connected through a hose that is placed

below the collector and finally a hose that runs from the vessel to the ground surface, which makes it possible to sample water continuously. Since the lysimeter applies no pressure it only collects a sample when there is an intermittent saturation in the soil.

3.1.2.1 Pros and cons of zero tension lysimeters

Zero tension lysimeters are seen as the reference method when it comes to extracting soil water (MacDonald et al 2004(1), MacDonald et al 2004(2), Buczko et al 2004, Ranger et al 2001, Essington 2004). The water and the solutes that are sampled are the ones that finally would reach the groundwater at that moment. It is therefore a *true* measurement in risk assessments. But as in nature, the leakage in the lysimeter varies temporally and spatially and sample extraction will be difficult at low flows. This makes comparison between this method and other methods difficult, because the extracted soil water is not the same as in a forced system. Installation of the lysimeter is complicated and has to be done in good time before sampling can occur in order to reflect natural values. The soil has to equilibrate after this type of operation, which makes this method suitable for research and monitoring, but makes it unsuitable to use in acute contamination situations. It would be a great monitoring device when natural remediation is used.

3.1.3 Ceramic plate extraction

Ceramic plate extraction is similar to the previously described zero tension lysimeter (Marsha et al 1992, Dorrance et al 1991). The installation is exactly the same and the apparatus is also the same except in one aspect: suction is applied on the plate.

3.1.3.1 Pros and cons of ceramic plate extractions

The drawbacks are essentially the same as for the lysimeter. The installation is complicated and has to be done well in advance. The extracted soil water will be of the same quality as the vacuum lysimeter except for the fact that it is possible to extract a larger amount of soil water, which will better represent the sampling area than a vacuum lysimeter. An advantage compared to the zero tension lysimeter is that you can retain soil water whenever wanted. You do not have to trust natural flow.

3.1.4 Filter tip sampler

The filter tip sampler is a development of the vacuum lysimeter. It consists of two parts: the permanently installed filter tip (includes a pointed tip to help with installing, a porous section, a nozzle and a septum) and the replaceable glass sample vial (Dorrance et al 1991). The filter tip is constructed from high-density polyethylene, porous ceramic

or sintered stainless steel. The sample is taken in a similar matter as the vacuum lysimeter (DEPA 2000). It is installed in a predrilled hole. To ensure hydraulic contact it is common to fill out the spaces with “quartz flour”. Once the permanent part is in place, the sample vial is mounted onto it. The vial contains a vacuum, which fills it with soil water. It is unclear if this method is still in use; a search of “filter tip sampler”, for example, using Google’s search engine (www.google.se) only turns up the document by the Danish EPA (2000).

3.1.4.1 Pros and cons of filter tip samplers

According to the Danish EPA (2000) the filter tip sampler is easy to install and does not contaminate the sample because it does not contain connection hoses. The disadvantages are that it is hard to create and uphold the hydraulic contact that is needed and that the sample volume is strictly limited up to 500 ml.

3.1.5 Hollow fibre samplers

Jackson et al (1976) invented a hollow fibre sampler that has been used only under experimental conditions (Dorrance D.W. et al 1991, DEPA 2000). It uses the same principal as the other suction samplers, the difference being the actual sampling part, which consists of a bundle of perforated threads (250µm in diameter) sealed at one end.

3.1.5.1 Pros and cons of hollow fibre samplers

No obvious advantages can be seen using this method instead of the common vacuum lysimeter. Holes of approximately the same size have to be made and suction radius is the same. The aim when creating the device was probably to increase the hydraulic conductivity by making small fibres that “blends in”. The disadvantage of that is the fragility that probably follows.

3.1.6 Rhizon sampler

The Rhizon sampler (Figure 8) is another variation to the vacuum lysimeter, which is increasing in use (Giesler, personal communication; Tiensing et al, 2001). It consists of a 4.5-mm thick, 9-cm long sampler that is inserted into the soil (Eijkelkamp agrisearch equipment, www.eijkelkamp.com). A vacuum is created by a syringe, a vacuum flask or a pump, depending on the desired sample volume or possible serial connected samplers. The Rhizon soil moisture samplers are, according to the manufacturer, very suitable for pot-, cylinder-, column- and field research. Rhizon samplers are used when several soil solution samples are needed of the same soil volume in the study of plant uptake of soluble nutrients as nitrate, solubility of metals in soil, transport of soluble components in soil,

accumulation of salts and environmental research. According to Tiensing et al (2001) the Rhizon sampler mimicks the physical aspects of plant uptake and is therefore more suitable than centrifugation when determining the bioavailable fraction of metals in soils.

3.1.6.1 Pros and cons of Rhizon samplers

The method requires less work than the common vacuum lysimeter, since the sampling probe can be driven into the soil without predrilled holes. It also leaves the soil rather unaffected which is an advantage if you want to return to the same sampling site. Simplicity is a strong argument for the device, because the simpler construction the less probability of material artefacts and breakage. On the negative side, the sample yield volume must be accounted for. Similar to the vacuum lysimeter, only a limited volume can be extracted at a time. If larger aliquots of solutions are needed numerous insertions have to be made or extraction over a longer time.



Figure 8. Rhizon sampler with vacuum flask (Eijkelkamp, 2004).

The fact that numerous samples must be taken repeated is not necessarily a drawback. Since the sample radius of a rhizon sampler is small, in accordance with similar findings on lysimeters, a composite sample is probably more representative for an area. If the installation is simple, this may not be a big inconvenience.

This method is relatively new and testing has not been extensive. It is therefore too early to assess the practical utility of this method, but it is the most promising field method today. Depending on the vessel that contains the extracted soil solution this method can be conducted without large-scale alterations on the soil. A commercially interesting application would be if a vacuum flask, with adequate negative pressure, was produced that is easy to mount onto the sampler. The flask or vessel would then, after extraction, be dismantled and sent to lab. This would minimize the involved steps to a minimum. Similar to the filter tip sampler, the negative pressure of the vessel is the limiting factor. Since several samplers can be connected to one suction device, this should solve the sample volume problem.

3.2 Laboratory methods

Although the aim of extraction is to resemble natural soil water, there are advantages to conducting the whole procedure in the laboratory. Controlled environmental conditions and handling are easier to establish, which serves for good replication, an important

factor when comparing results from different sites. The same question as in field methods is to be answered here: is this natural soil water?

3.2.1 Batch equilibration (BE)

According to the USEPA (1999) batch studies represent the most common laboratory method for determining K_d values. It is both used at contaminated sites and for predicting the behaviour of a chemical in soil (OECD 2002). This section is restricted to describing the first case. For a more detailed description of the latter case see section 3.3.

The batch equilibration method is simple. You mix the contaminated soil with a known amount of liquid, usually non-ionised water. Common procedures include a 1:2 soil:solution dilution. The mix is shaken into a slurry and allowed to equilibrate for an adequate time (typically 24-48 h). To separate the solution, the slurry is normally transferred to a centrifuge tube and centrifuged. This leaves the solution, called supernatant, on top of the soil, which is thereafter removed, often filtered and thereafter analysed. There are several variations to this general procedure.

3.2.1.1 Pros and cons of batch equilibration

Research by Dahlgren (1993) and Ludwig et al (1991) showed that water extractions described above resulted in low ionic strengths in the solutions. USEPA (1999) means that this is a common phenomenon often encountered by investigators. It is called “particle concentration effect” or “solids effect” (Yin et al 2002) and there are two different main hypotheses for where this effect derives from. It either depends on “real” physical/chemical processes or on experimental artefacts. Independent on what the source of error may be, USEPA (1999) and Yin et al (2002) drew the conclusion that K_d values based on batch experiments conducted with a solid:solution ratio significantly less than those that exist in the field would overestimate contaminant sorption and underestimate contaminant migration. They stated that higher soil:solution ratios more closely approach natural conditions. Delle Site (2001) agreed with the USEPA regarding the particle concentration effect. He also meant that if K_d is very low the use of batch equilibration is then problematic, and that immiscible displacement or equilibrium head space then should be used instead. Ludwig et al (1991) compared dried soil samples with moist samples and found that the dried samples resulted in solutions of higher concentration. The study performed by Yin et al (2002), also used a dried soil, but that clearly did not compensate for the lower ion concentrations.

The equilibration time allowed for the soil solution is typically 24 hours, it is questionable whether equilibration is reached during that time in every case. Because

treatment of the slurry differs from different laboratories, i.e., the slurry is shaken in different apparatus or treated in ultrasonic trays, the solution probably varies.

Serne and Releya (1981) conducted an interlaboratory evaluation on K_d measurements on radionuclides by batch equilibration. They gave general guidelines on groundwater composition, radionuclides and procedural details to nine different laboratories. The contaminants investigated were strontium, cesium and plutonium. As much as three orders of magnitude difference was determined for two of three compounds; for example, cesium ranged from 1.3 ± 0.4 to 880 ± 160 ml/g. A comment to the results of Serne and Releya (1981) is that radionuclides are very strongly sorbing compounds, which show high K_d-values. Since Delle Site (2001) meant that batch equilibration is problematic, this brings us to the conclusion that batch equilibration can not be used neither when K_d is very low or high. This is not surprising because K_d is in general hard to determine under these conditions (Baes and Sharp 1983). A small deviance in the smaller of the two variables leads to drastic changes on K_d, which basically concern all methods.

Another problem described by the USEPA (1999) is the difficulty of extracting all of the supernatant from the centrifuge tube without disturbing the soil surface. Close to the surface, there is a thin layer of colloids suspended in the solution, which can make it harder to distinguish the soil from the solution. Great care is needed to extract the right portion. Often, filtration is used to treat the liquid for analysis.

Even though the drawbacks of batch equilibration are obvious, there are advantages in choosing this method as the standard method. It is cheap; there is often no need for extra equipment in the lab. No chemicals are involved that are not already in the soil. The preparations can typically be done in one or two days, so it is a quite fast method as well. Last but not least, it is widespread, which makes it easy to compare with results from other studies. Batch equilibration can, due to these arguments, be a solution to this thesis. But since other methods seem to agree better with nature it has been given low priority.

3.2.2 ESS-method (Equilibrium Soil Solution)

As described in the previous chapter, it is widely assumed that the concentration of individual ions is a function of the added amount of water (Ullrich and Khanna 1972). Matschonat and Vogt (1996) developed an iterative method that compensates for this assumed source of error. They concluded: "Because complete extraction is impossible, a suitable method should instead reproduce the ion concentrations of interest".

The ESS method is poorly described. The principles are based on the fact that concentrations in a water extract are a function of the soil:solution ratio employed. By

analysing a series of different soil:solution ratios, it is possible to estimate the correct concentrations of a compound at field moist state. At first, a simple water extraction is conducted. Thereafter an experimental solution is used with the aim to imitate the natural soil solution with respect to cation concentrations. The solution is shaken together with the soil. This step is repeated until no further exchange could be detected between the soil and the solution. Matchonat and Vogt (1996) found that four steps were normally enough to achieve equilibrium.

Matchonat and Vogt (1997) tested the method using a multi-step water extraction, with 1:2 and 1:1 water extractions as references. They found that the ESS-method “provided a sound estimate of the soil solution composition in the field at the time of the sampling for base cations, pH and the electrical conductivity”. The concentrations retained by the ESS method were generally higher, in accordance to the theory. The experiments were performed on three different German forest soils. In 2003, Matchonat et al tested the ESS-method on agricultural soils with respect to the same parameters as the previous experiment. They found that “the ESS method can be applied to agricultural soils with satisfying results”.

3.2.2.1 Pros and cons of the ESS-method

The strength of this method is the fact that it seems to solve the solid:solution effect, which is a serious problem. There are some obvious weaknesses of this method. The inventors of the method, which may affect the objectiveness of the studies, have only tested it. When searching in the Web of Science database, there are no works that are based on or using this study. Another heavy argument against the method is that it is not tested on organic contaminants.

This method has been given some consideration although it is most probably too slow and complicated to be used as a standard method. But if it can compensate for the solid:solution rate it would result in a solution that resembles the true soil solution. Then it would still be interesting to use, but then as a reference. It is though too complicated and poorly tested to be the solution to the problem of this thesis.

3.2.3 Column leaching/equilibrium

Another widely used method is the use of columns to characterise chemicals in soils (Delle Site 2001, Dahlgren 1993, MacDonald et al 2004(a), MacDonald et al 2004(b),

U.S. EPA 1999). Similar to the batch method, column leaching can be used both to simulate compounds in the environment and to extract a natural soil solution. The experimental setup is made up of a column, usually glass, in which the soil is placed. An example is depicted in Figure 9, where water flow in this specific setup is directed upward. It is also common to let water percolate through the soil in the opposite, downward direction. MacDonald et al (2004a-b) suggest a setup where syringes are used as columns, and a vacuum is applied, to increase extraction speed. Dahlgren (1993) used a similar device, packing 45g of soil in a 60 ml syringe. A vacuum was applied to this setup as well.

Tests can be performed in different ways, depending on the desired outcome. If chemical testing is performed, a soil is packed into the column and a fluid containing the chemical of interest is poured on top of the column (OECD 2002). The leachate is then collected either in one single batch or in several batches characterising the breakthrough of the chemical. When trying to measure the leaching characteristics of a natural soil, the leachate is extracted in one of the ways described above, and then either pumped back into the column to recirculate or collected in a vessel (MacDonald et al 2004a-b).

The latter procedure is performed when the aim is to investigate whether a soil or waste will leach contaminants for a long time, due to the fact that the diffusive forces on the soil particle will continue. If you provide the column with new water of low concentration this will extract more contaminants just as in nature where new rain will extract more contaminants (Essington 2002).

3.2.3.1 Pros and cons of column leaching/equilibration

Columns offer a possibility to examine the leakage properties of the soil. This is desirable for example when the properties of a waste are to be examined. The assumption is that ions sorbed on the waste particles will desorb as the concentration decreases in the soil solution. This is also of interest when characterising a contaminated soil, where possible contaminants already are sorbed onto the soil particles.

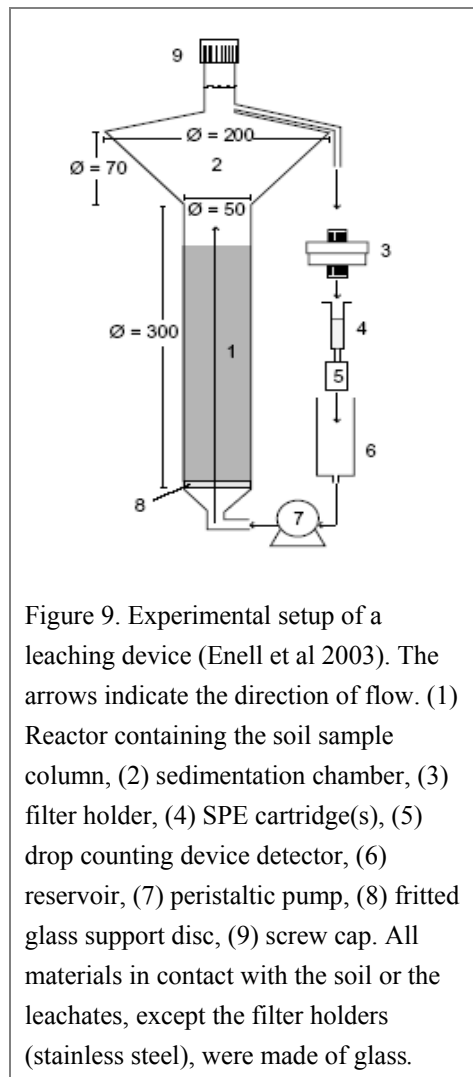


Figure 9. Experimental setup of a leaching device (Enell et al 2003). The arrows indicate the direction of flow. (1) Reactor containing the soil sample column, (2) sedimentation chamber, (3) filter holder, (4) SPE cartridge(s), (5) drop counting device detector, (6) reservoir, (7) peristaltic pump, (8) fritted glass support disc, (9) screw cap. All materials in contact with the soil or the leachates, except the filter holders (stainless steel), were made of glass.

The obvious drawback of this method is time. In order to get high quality data the column must equilibrate with a flow sometimes for weeks. Another negative aspect is as stated in chapter 2.1.2, that fingering occurs depending on the water saturation degree. For example, in an unsorted soil at a given L:S ratio, the flow regime will use only part of the range of pore sizes. Large pores are more important with oversaturation, whereas smaller pores are more important with undersaturation. This means that several columns at different saturation levels must be used to develop a complete picture of the contaminant situation in the soil.

Columns are most probably the best method for sequential leaching extracts. These describe a situation where rainwater of low concentration flows by a particle surrounded by a diffuse double layer. This will exert a diffusive force on the particle that drains the particle until equilibrium between particle and solution is reached. This is of great use when contaminants are solid and expected to leach into the soil or when contaminated soils are expected to leach low concentrations but large amounts of contaminant over a long time period due to sequential leaching. The question however remains whether they are the best true soil solution extractors. Column leaching describes a situation where desorption is the prevailing regime, i.e., in the back of the contaminant plume where contaminant concentrations in the soil solution is decreasing. Because of the hysteresis between sorption and desorption, this means that columns poorly describes a situation where sorption is prevailing.

3.2.4 Centrifugal extraction

The equipment for centrifugal extraction consists of a vial separated in two chambers where the moist soil is kept in the upper one. The lower chamber is in the Elkhatib (1987) method connected to the upper chamber through a 0.5-mm hole in the septum. After centrifugation of the vial, the soil water will be in the lower chamber, but the soil still in the upper one. Another method by Thibault and Sheppard (1992) uses a common syringe as the upper chamber, which is inserted in a conical centrifuge tube. A fibreglass sliver (8µm) is used as septum in the bottom of the syringe.

3.2.4.1 Pros and cons of centrifugal extraction

Comparisons of extraction methods tend to show that centrifugal extractions render higher concentrations of cations than other methods (Sheppard et al 1992, Dahlgren 1993, Giesler et al 1996, Ludwig et al 1999, Ranger et al 2001). The authors all come to different conclusions. Ludwig (1999) meant that centrifugation should be used sparingly since it differed in ion concentrations from the others. Dahlgren et al (1993) found that centrifugation solutions were higher in pH than the other methods, and that sodium and potassium concentrations were significantly higher. When studying pH-sensitive solutions this method may produce a laboratory artefact. Sheppard et al (1992)

recommended the use of the centrifugation method for unsaturated soil pore water removal prior to chemical analysis for pore water composition or K_d-value determination, although they suggested that special attention should be paid on centrifuge speed when anions are of interest. Ranger et al (2001) demonstrated that the three different methods, lysimeters, centrifuges and vacuum lysimeters, have different ideal applications: 1) lysimeters are suitable for ecosystem input-output budgets. 2) Centrifuges are useful when equilibrium between the solution and the solid phase is considered, as well as plant nutrition. 3) Vacuum lysimeters are potentially most useful for plant nutrition.

In line with Ranger et al's conclusion was a study by Tiensing et al (2001), who compared centrifugation with a rhizon sampler. They found that cadmium and zinc concentrations were higher in the centrifugal extracts. An earlier study by Bufflap and Allen (1995), however, contradicts these studies when comparing four different extraction methods for an artificial sediment; centrifugation, dialysis, vacuum filtration and squeezing. The authors suggested that centrifugation was the best of those four, although it results in significantly lower concentrations of cadmium which the sediments were spiked with. The experiment was performed in artificial kaolinite clay, with a batch method as reference. The method of the centrifugation is very poorly described, and no sample yields are reported.

Grieve (1996) offered an explanation to the phenomenon of raised pH noted by Dahlgren et al (1993). He studied the effect of the centrifugal drainage method on DOC concentration in the extract. Grieve noted a significant increase in sodium concentrations when using glass wool. Since this was not observed in the other cases (GF/C glass fibre filter disc, no filter and membrane) he assumed that this was an effect of the glass wool and suggested that the interaction with base cations was the reason to the difference in pH.

Centrifugation time (Grieve 1996, Gollany et al 1996), but also speed (in extent gravitational forces) is crucial to the results of extraction (Grieve 1996, Ross and Bartlett 1990, Zabowski 1989). An experiment using 1000 rev/min showed that 80% of the soil water was extracted after 30 minutes and over 90% after 1 h (Grieve 1996). The TOC-concentration decreased with time, from concentrations of 28 mg/l in the first 10 minutes to 15 mg/l after 50 minutes. The results from the experiment using different speeds are in line with the previous experiment. TOC concentrations decreased with increasing speed. There was a difference between the GF/C filter and the glass wool filter, where there were significantly higher TOC concentrations at 500 rev/min. This was probably an effect of the glass wool being too porous when the pressure was low. Centrifugation speeds over 3000g (approx. 4000 rev/min) lead to an artificial increase in DOC concentration due to the rupture of biota (Ross and Bartlett 1990, Zabowski 1989) Grieve (1996) concluded that when base cations or pH sensitive species are to be

measured, the membrane filter is the best, but for measurements of TOC the GF/C filter is preferable. Further, Grieve came to the conclusion that 1 h centrifugation is appropriate for routine use and if you want to resemble the conditions of vacuum lysimeters, a speed of 1000 rev/min should be for their equipment.

Raber et al (1998) studied PAH partitioning with respect to DOC and found that DOC concentrations were higher in centrifugal extracts than in lysimeters and vacuum lysimeters. The reason was that centrifugation also extracts water from mesopores, where DOC concentrations are higher. Raber et al (1998) came to the conclusion that “centrifugation of soil material at natural moisture was the most suitable method for obtaining large volumes of soils solution similar to field condition”. The compared methods were pressure filtration (similar to method 3.2.8) and column extraction (chapter 3.2.3).

Positive aspects of centrifugation are; it's low cost, it is a very rapid process that is easy to use and requires no special skills, it is non-destructive and no additional chemicals are needed. In addition to this, it reflects the ion composition of natural soil water well. On the negative side special equipment is needed, totally dry soils impose a problem, and the equipment may differ between polar and non-polar substances.

It is assumed that centrifugation extract water more strongly retained by the soil than other methods. This will explain the fact that the cation concentration is higher in centrifugation solutions, since it also is assumed that the solution chemistry differs between pores of different sizes. In natural conditions, the dominating flow regime is a function of the water content, which is why comparison between for example zero pressure lysimetry and centrifugation is difficult.

Sample yield is an important question when soils are dry. Since centrifugation relies on a naturally moist soil it can not be performed on a totally dry soil. A common method is then to wet the soil before centrifuging. In this case you risk losing the advantage of the method, where the soil water has been able to equilibrate with its environment. Then it will be like any other extraction but with a rapid final stage of extraction. According to Giesler R. (personal communication), the three main difficulties of centrifugation are: too small sample yield, soil texture (i.e., soils that either retain soil water too hard or soils that do not retain the water at all) and soils that are too dry. These difficulties seldom appear in a typical Swedish forest moraine, but might occur for different contaminated soils.

The diffusive force that is applied by sequential leaching on the soil particles may be able to be replaced by centrifugal forces. Then it is possible to replace column leaching with centrifugation, although sequential leaching is a process closer to natural processes.

3.2.5 In situ batch method/soil core sampler

A method that aims to solve the mixing problem is the in situ batch method (U.S. EPA 1999). The mixing problem arises when a soil sample is taken and stirred around, because of transference between mediums, which generates new surfaces to sorb to. This affects the total concentration of the compounds of interest. The basic idea is to keep the soil and soil water untouched.

A soil core that contains soil water is removed from the aquifer, with the device in Figure 10, and the aqueous phase is removed by centrifugation of the whole core. Concentrations in the solid phase and the solution are then analysed. This approach is a variation of the centrifugation method, but it is described separately to avoid complications when discussing the two procedures.

1.2.1.1 Pros and cons of in situ batch method/soil core sampler

The in situ batch method is tempting. If no interactions occur between the soil core sampler and the contaminants, the sample would reflect a natural soil, which is desirable. The use of the method is not well described, nor extensively used. Two applications of this method are U.S. EPA (1999) investigation of radionuclides and a Scandinavian study of podzolization, although this latter study uses a different name for the study (Ilvesniemi et al 2000).

A soil corer would be ideal in a soil with a low gravel content. With gravels there is a mixing problem and a problem with taking a sample as well. This method can be difficult to use in Swedish moraines because they contain varying material and often large fractions. However, Ilvesniemi et al (2000) were able to use it in the Fennoscandian project. If it can be used in northern Sweden where stony moraines are very common, it should not be a serious problem elsewhere. Other sampling difficulties may be soil from industrial areas, which can include bricks, rocks or even building-site wastes. This will in fact complicate sampling, but it is questionable whether it is relevant to estimate K_d in these cases since the rate of contaminant migration is probably under greater influence from macropores (cavities surrounding wires, tubings etc.) in this very heterogenic material. A high K_d in the soil does not mean that the contaminant is retarded. The only place where a K_d -value

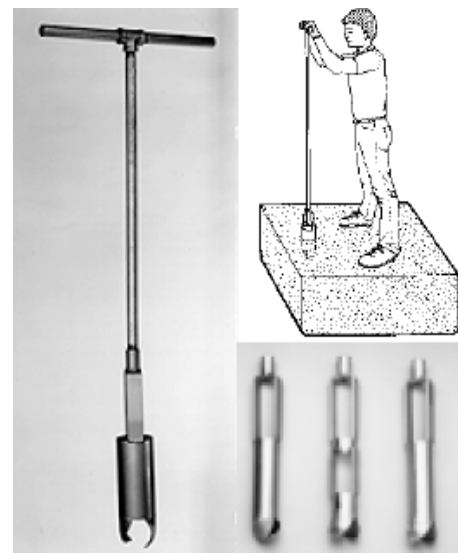


Figure 10. Soil core sampler (Soil Moisture Corp., 2004)

is of interest is where the soil itself constitutes the retardant. This makes intact soil core sampling interesting.

3.2.6 K_d analysis for organic compounds

There are a number of methods that are only applicable on organic substances (Della Site 2001). Table 5 very briefly describes those methods. Since the aim of this study is to present one method for all types of contaminants no more attention will be paid to these methods.

Table 5. Different methods for determination of K_d for organic substances (methods after Della Site 2001).

Method	Description
Equilibrium head space	A method for determination of sorption coefficients for vapours on oven-dry or moist sorbents in the absence of an aqueous phase.
Diffusion	The method is based on the relationship between the diffusion coefficient and K _d . Diffusion is measured through a slow experimental procedure.
Gas purge	Gas purge yields the kinetic constants for the sorption and desorption for hydrophobic substances.
Fluorescence quenching	A method developed to determine equilibrium constants for PAH:s with dissolved organic matter (DOM). It is based upon the observation that PAH:s fluorescence in aqueous solutions, but not when associated with DOM. The fluorescence is assumed proportional to the amount of free PAH.
Equilibrium dialysis	Through a dialysis experiment the amount of bound compound is measured as a function of the free compound concentration. It is used to measure organic substance association with DOM.
Reversed-phase separation	Another method examining the relation between DOM and organic compounds. DOM spiked with ¹⁴ C is allowed to equilibrate with an organic substance. The sorption is determined through HPLC.
Solubility enhancement	By measuring enhanced solubility due to the presence of various amounts of cosolutes, the K _{dom} values for chemicals on humic acids are being calculated.
Adsorption on the glass	PCB:s association constant with humic material is determined with this method. It is based on the measurement of the fraction of compounds that is adsorbed on the wall of a glass vessel. PCB:s not sorbed by humic material is assumed adsorbed on the glass.
Humic acid titration	Since carboxyl groups are responsible for the sorption of atrazine and its hydroxylated form, titration of carboxyl groups gives both sorption constants and reaction rates for atrazine.

3.2.7 Immiscible displacement

Immiscible is another word for non mixable. In this case, a fluid that is not mixable with water is introduced in abundance to the soil and thereby pushing the water out of the soil (Sheppard et al 1992, Dahlgren 1993, Della Site 2001, Essington 2004). Since the fluid does not mix with water, the soil water and the immiscible fluid form separate phases and can therefore be recovered one by one. Immiscible displacement can be used together with column leaching, batch experiments, but mostly in combination with centrifugation. Examples of substances that can be used are 1,1,2-trichloro-1,2,2-trifluoroethane, TFE (Dahlgren 1993) or ethyl benzoylacetate, EBA (Sheppard et al 1992).

3.2.7.1 Pros and cons of immiscible displacement

According to Sheppard et al (1992), the separation of the fluids with immiscible displacement is rather difficult. This method will however not be seriously considered in this thesis, since the chemical substances that are used are often carcinogenic. This would create unnecessary hazardous waste and exposure of laboratory staff to dangerous chemicals. The advantages of the method do not seem to overcome these disadvantages.

3.2.8 Desorption method

A form of immiscible displacement is the displacement of soil water with gas. There are several variations on this theme. One is the device presented by Blattner et al (2000), which is shown in Figure 11. The procedure is simple. Soil is put in a pressure chamber and pressure is applied (in this case 170 kPa pressure). From 30 ml of field moist soil, a volume of 1.5 ml soil water can be collected, depending on the actual water potential of the soil. The sampling time is dependent on the soil type; for example, up to 24 h are required for clays.

This principle of evacuating soil water with an applied gas is commonly used for determining the water retention curve of a soil.

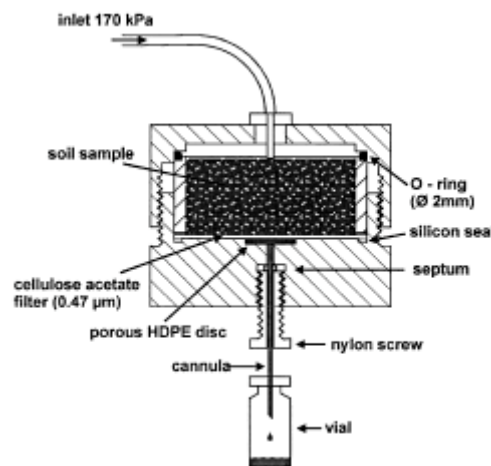


Figure 11. Pressure chamber to obtain the desorption solution (Blattner et al, 2000). A pressure of 1.7 bars, i.e., pF 3.2 and a 0.45 µm filter was used.

Soilmoisture Equipment Corp. offers several setups, with pressures up to 10 000 kPa, which corresponds to pF ~5. The apparatus are constructed similar to the device in Figure 11, as a low and wide cylinder. In the bottom of the chamber there is a ceramic plate.

3.2.8.1 Pros and cons of the desorption method

Blattner et al (2000) thought this method “opens a wide range of possible applications for soil science...”. An obvious weakness is that they did not test it against other methods. The solution chemistry can be assumed to be similar to that of centrifugation at an equivalent driving force. It is possible that air will open new canals in the soil and thereby alter solution chemistry, but there are no definite statements. Another question to be answered is whether it works for unsorted soils, where pores retain pore water at different pressures. When the largest pores are emptied, the gas will most probably choose this low-resistance route through the soil. The form of the chamber means that the soil sample must be rearranged to fit the chamber. Another question is whether it is possible to replace the ceramic plate in the bottom of the large scale chambers. The chamber used by Blattner et al (2000) is too small for the use for site specific determinations of K_d. A small chamber means that the convenience of the method disappears.

Even though there are several aspects of the method that have not examined, this is an interesting approach. It is quick and it may extract water at large water holding capacities. Just like centrifugation it takes special equipment that is not common, and a way minimising the handling of the samples must be developed. It would be desirable to construct a closable sampler that can be inserted into the chamber, preferably a longer cylinder that would simplify the sampling of undisturbed soils.

3.3 Existing guidelines – benchmarking

A desirable property of the method for determining K_d is the possibility to compare results transectionally. Even though a certain method is not ideal from a natural science or an economic point of view, it can still be the best to use for K_d-determination. If it is widespread among other countries or scientists the sum of experience on this method can compensate to some extent for economical and scientific contradictions. Reference data for different soils and chemicals can then be compared with each others.

The international testing of K_d is mostly limited to testing of chemicals, where the test is performed with a known amount of substance in a well-characterised soil. This differs from the estimation of a site specific K_d where both parameters are unknown. This

benchmarking is most probably not a complete coverage. There may be guidelines in other countries that are not presented in this chapter.

3.3.1 OECD test guideline 312 – leaching column

This is a test to characterise the behaviour of chemicals in soils developed by the member countries of Organisation for Economic Co-operation and Development, OECD (OECD 2002). Columns are packed with soil and saturated with an “artificial rain”. The chemical of interest is then applied on the surface of the column. Artificial rain is added and the leachate collected and analysed. The K_d of the chemical is determined by how much of the added chemical that is collected in the leachate, while the rest is assumed sorbed. This system simulates both sorption and desorption. For relevant values of the partition coefficient, sorption equilibrium has to be established.

Five soils are pointed out to represent the soils of the OECD-countries, with the exception for cooler countries where OECD advises use of complementary soils. It is advised that three to four soils with varying pH, organic carbon and texture be used.

3.3.2 OECD test guideline 106 – batch equilibration

Similar to the previous method, this is used to estimate the adsorption/desorption behaviour of a substance on soils (OECD 2001). A known volume of a test substance, solved in 0,01M CaCl₂, is mixed with the soil. The mixture is agitated for more than 24 h and then separated by centrifugation and, if it is desirable, filtrated. K_d is determined in the same way as in test guideline 312. Seven reference soils are used, which are supposed to represent the OECD-countries. The European Chemicals Bureau has adopted this method for chemical testing (Annex V to Directive 67/548/EEC, C 18).

3.3.3 OECD test guideline 121 – K_{oc} determination by HPLC

The adsorption coefficient normalised to the organic carbon content of the soil K_{oc} is a useful indicator of the binding capacity of a chemical on organic matter in soils. This test is also performed in order to characterise a chemical substance (OECD 2001). According to the ECB (Annex V to Directive 67/548/EEC, C19), this method is more reliable than QSAR calculations and it is of use in addition to, but can not replace, test guideline 106.

The principle behind HPLC (High Pressure Liquid Chromatography) is that a substance is pumped through a column at high pressure. While passing the through column, substances will interact to a different extent with the column. This will retard the substance similar to soil sorption and interactions. The column is based on a silica matrix, which is slightly polar. The retention time is therefore related to the adsorption

coefficient on organic matter. The European Chemicals Bureau has adopted this method for chemical testing (Annex V to Directive 67/548/EEC, C19).

3.3.4 ICP Forests submanual on soil solution collection and analysis

A program implemented by the United Nations Economic Commission for Europe (UNECE) is the ICP Forests (the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests). The main objectives of ICP Forests include the monitoring of forest condition on a representative, systematic grid net throughout Europe and the intensive monitoring on a number of selected permanent plots. To achieve this goal, standardised methods for sampling and analysis have been created. Since the measurements are being made in 36 different countries standards must be followed in order to be able to compare results.

This is the only guideline that has been found where concentrations of chemicals in natural soil solution are the object (UNECE 2002). Four different methods are recommended; zero-tension lysimetry, lysimetry, centrifugation and saturation extraction. Since it is a monitoring program, it seems fair that lysimetry is a recommended method. Installation will not be a problem when using the same sampling site numerous times. The centrifugation procedure is recommended to be performed in 30 minutes at 10 000 g in a polyethylene or poly-oxymethylene cup. The saturation extraction method is very sparingly described but seems to be a batch method and it is recommended when centrifugation is impossible, because of too stony or heavy clay soils. ICP Forests' recommendation for choosing sampling method is depending on how often samples will be taken. For repeated sampling at short sampling intervals, lysimeters are recommended and when monitoring with large time intervals centrifugation is also possible.

4 Discussion of methods and guidelines

The experimental aim of this study is to find a successful combination of the parameters quality, time and cost for a soil-water extraction method. In this case quality is the most important parameter. It is important to ensure that no inaccurate conclusions are drawn that would lead to leakage of contaminants to the environment after remediation. The second most important parameter is time. It is not always important, but at for example construction sites where this analysis would mean a delay, it is. Price is a priority, but since the costs for analysis are small in comparison to the benefits of an accurate estimation of remediation needs, the analysis costs are not the most important.

The definitions of these three parameters in this case are: Quality means high reproducibility and accordance with natural conditions. Cost is depending on the need

of material and chemicals and working time. Time is dependent on simplicity of handling and the time used for extraction. These six factors can be said to be the keys to success. The following comparison will be done in respect to those factors.

4.1 Quality

The first aspect of quality, reproducibility, is not well examined for all of the methods. Reproducibility concerns the whole chain of treatment, from sampling to chemical analysis. In the discussion of batch extractions there is an example from a survey in USA where significant deviations were found (Serne and Releya 1981). This is most probably a result from the fact that it takes skill to perform the extraction. Accuracy is demanded because several steps where contaminants can be lost are involved. Sieving and transferring soils and liquids between different vessels are all possible artefacts that will lower reproducibility. It is probable that all methods will show these types of divergences.

Since no material on reproducibility on the described methods was found, this parameter will be judged from the following discussion. To assure high reproducibility as possible, the chosen method should allow very small discrepancies by influencing factors other than human. Another argument in favour of laboratory methods is that there exists a system for quality assurance in labs. It is easier to introduce a new standard into this existing system - than to create a new standard to be used by field-sampling personnel. It is also a great advantage if the method results in very simple field and laboratory sampling and handling. More steps increase the possibility for artefacts. For field methods, it is more difficult to control or measure different parameters that may influence the partition coefficient, which makes reproducibility difficult. Also, testing of different scenarios, e.g. at different pH values, is complicated.

The second aspect of quality is the agreement with nature. The extracted water must be similar to the soil water that would eventually leak out in nature, since it is the true mobile fraction of the soil water that is of interest. The nature and behaviour of natural soil-water (section 2.1) vary a great deal, dependent on soil structure, texture and water content. Extraction from all pore sizes is one important quality parameter that can be difficult to control in field methods. A saturated soil sample that is extracted by centrifugation or desorption method will yield pore water from nearly all sizes of pores, up to the retention forces of the applied pressure, which gives a picture of the total ion concentration of the soil. This makes desorption and centrifugation interesting.. Sequential leaching by column leaching will, on the other hand, reflect the risk of future leakage. This would be desirable if the concentrations are low, but the amount of leached contaminants over a long time period is expected to be large. There is, however, a problem incorporating amounts, rather than concentrations, into the Swedish model.

As a first approach, laboratory methods like centrifugation, desorption and column leaching are of interest, even though they reflect different sorbing regimes in the soil.

4.2 Time and cost

The amount of time that is consumed by the three methods of interest: column, centrifugation and desorption differ a lot. Column leaching is set up for at least a week, while the other two are in performed during shorter time intervals.

The running cost of material for the different methods is also quite equal. But because column tests take longer time they are more expensive. The big difference is the starting cost. Because the column method is so widespread, many labs have equipment and established procedures, although equipment for organic contaminants are more rare. The other two methods, centrifugation and desorption may require the purchase of new apparati. The desorption apparatus exists on the market, but in a form for determination of water retention characteristics, which is not suited for the purpose. These methods consequently not only mean a purchase cost, but also development of equipment.

The simplicity is perhaps the most subjective factor of the extraction procedure. Since there are several ways of performing each method it is hard to judge them on handling. In their most favourable way of execution, all of them should be quite easy. A part of handling that also can affect quality is the sample yield. If the sample yield is too small, the handling will undoubtedly be somewhat complicated since the procedure has to be repeated. This is a problem for the centrifugation and desorption methods.

Although centrifugation suffered from a loss with regard to the investment costs, the quality and time (if not several steps are needed to get enough test liquid) parameter clearly speaks for it, although more development is needed in order to improve the existing methods. This is why the aim of the laboratory work is to cope with the latter parameters.

4.3 Existing guidelines

Because the guidelines from OECD and EC concern the testing of chemicals they are not comparable to the aim of this study. Different requirements are to be met when conducting this research. It could be of interest to build a database from different soil types with some other key parameters regarding the soil. An extensive reference laboratory work will then have to be done, but that is not within the limitations of this study.

The guidelines of the UN are more relevant since these concern soil-water extractions. But these guidelines fall short on the description of the actual procedure. That is why these guidelines can not be used as a role model. The final outcome of this study will have to be something similar to OECD, which is very well described both in sampling and execution, rather than the UN guidelines.

5 Hypothesis of practical investigations

Referring to the discussion of chapter 4, centrifugation and desorption extractions are promising. A problem to be solved is the water saturation. It was stated that different saturations would result in different soil water concentrations and that sample yield must be assured for these methods to be an alternative. The thesis of the research is that these problems can be solved by saturating the soil in the lab. This is done through the capillary forces of the soil, by letting the sample stand in its container on a tray of water. Capillarity will fill pores, beginning with the smallest ones in the bottom of the sample, sequentially filling larger pores higher in the container. This handling will guarantee that the water content will be the same in soil samples of equivalent particle distribution and that sample yield is maximised. A probable scenario is that an artificial saturation of the soil will dilute the sample since the macropores probably already are being flushed by the contaminated water, but since water saturation is a probable scenario in nature, this is accepted.

When saturating the sample afterwards, there is a risk that desorption processes will start and that new equilibriums will be established. This is one of the questions to be investigated, starting with the laboratory research of this thesis. If the equilibrium rate is slower than the time for soil water saturation, or if equilibriums won't stabilise, the method have to be discarded. In addition to the ion concentrations, sample yield is also of great interest.

6 Materials and method during practical investigations

Authentic contaminated soil from the wood preservation factory of Sjösa in Södermanland, Sweden. The soil suffers from high contents of arsenic, cadmium and copper (CCA). Consultants from SWECO VIAK have surveyed the area and the soil sample was taken from an area that was found to contain high concentrations of contaminants. The soil consists of a sandy moraine with 4% silt and clay. Reminders from the wood impregnating could be found as small pieces of wood at about 0.5-mm size. Saturated soil was found at approximately 0.5-meter depth. The sample was taken from the layers above. Centrifuge cylinders were constructed in PVC-plastic. See figure

12 for description. The equipment was washed in acid solution prior to usage. A 0.45- μm GF/C-filter was placed in the bottom of the cylinder, on top of this a supportive net.

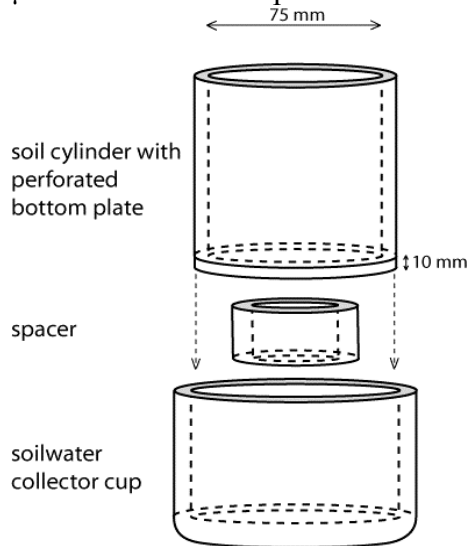


Figure 12. The centrifuge apparatus constructed for the laboratory work.

The soil was sieved at natural moist content through a 1-cm sieve and stirred around to ensure conformity. Approximately 300 ml of soil was transferred and packed by hand into the centrifuge cylinders, which were placed in a tray filled with artificial rain (CaCl_2 0.01 M). The soil cylinders absorbed the rainwater through holes in the bottom of the cylinders. The water table in the tray was gradually raised in four steps during the first four hours to level with the soil surface in the cylinders. Water level was adjusted when samples were removed from the tray. The temperature was kept at a level that resembles the natural conditions ($+4^\circ\text{C}$), as far as possible.

The samples were kept in cool storage until the moment of extraction. This means that the possible desorption increase will affect all samples in the same way.

Extraction was done after 4, 10, 24 and 72 hours from wetting. Triplets were taken after 10 hours to ensure accuracy.

Centrifugation was done at 4000 rev/min. The pressure in the vessel is calculated by Equation 6 (Grieve 1996, Giesler 1996):

$$p = \Delta\rho \left(\frac{2\pi n}{60} \right)^2 \frac{(r_2^2 - r_1^2)}{2} \quad \text{Equation 6}$$

where:

$\Delta\rho$ is the difference between the displacing medium (air) and water (g/cm^3)

n is the centrifuge speed (rev/min)

r_2 is the distance in centimetres from the centre of the rotor to the surface of the soil

r_1 is the distance in centimetres from the centre of the rotor to the bottom of the soil

This results in 4000 rev/min exerting the soil of $1.13 * 10^7$ Pa, which is slightly over pF 5.

7 Results and discussion

The method was easy to perform and did not demand constant supervising, which is positive for quality and cost aspects of the method. If the rewetting will be a standard, an apparatus that serves to raise the water level in the tray is desirable to develop. As expected, the unsorted soil varied in respect to both concentrations and sample yields. Table 6 shows the large differences among individual soil cylinders concerning soil-water sample yield. The difference in saturation was also visible, so when doing the extractions, cylinders containing moist topmost soil were chosen. The sample yield for each sample shows also, that for many analysis purposes, especially organic samples, larger samples or a number of parallel samples is needed.

Table 6. Sample yields from the soil water extractions.

Sample	Sample yield (ml)
4	42.5
10:1	56
10:2	52
10:3	48
24	47.5
48	32.5
72	36.5

There was also a difference in the amount of particles in the soil-water samples. This indicates that the soil was very heterogeneous regarding porosity or particle distribution. The water content after centrifugation was 1.47% by weight. A moisture gradient in the cylinders was noticed where the topmost soil was totally dry and the bottom soil slightly moist. The soil cylinders were not completely filled, so it is possible to increase the yield by approximately 10-20%. This means that for a poorly sorted moraine as a worst case scenario, which suffers from low porosity and therefore low water content, 200 ml can be extracted in one hour (four cylinders simultaneously).

Metal concentrations in the extracted soil water were expected to drop as the sample yield increased, because the largest pores of the undersaturated soil were expected to be emptied. These are furthermore likely to have the lowest ion concentrations, even after wetting, because these have been flushed by large amounts of soil water in nature. This effect was most probably reduced because the soil was rearranged through the sieving and packing into soil cylinders; however, a positive correlation can be seen between sample yield and concentrations of arsenic and chromium ($r =$ chromium and arsenic, respectively, at -0.784 and -0.866 at the 0.05 level, 2-tailed Pearson). Copper showed no correlation.

Table 7: Data from centrifugation experiments

Sample	Cr		Cu		As	
	$\mu\text{g/l}$	mg/kg TS	$\mu\text{g/l}$	mg/kgTS	$\mu\text{g/l}$	mg/kgTS
Soil		150		170		260
4 h	36		37		870	
10h:1	35		27		720	
10h:2	33		31		670	
10h:3	36		31		880	
48h	48		33		990	
72h	59		28		990	

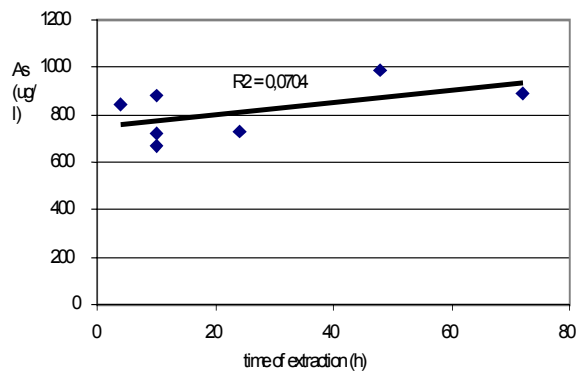


Figure 13 Concentration of arsenic in soil water extracted at different times after artificial wetting.

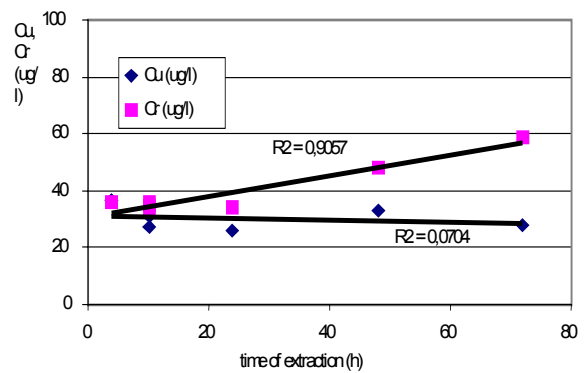


Figure 14 Concentration of copper and chromium in soil water extracted at different times after artificial wetting.

When plotting concentration against time of extraction it was expected to see no or only a slight increase of ion concentrations during the first extractions. This increase was not expected to be seen after 24 hours because this is the time used for equilibrating soil and solution in batch equilibrations. Chromium was expected to be hardest retained of the three species because it normally exists as Cr^{3+} on the particle surfaces or as insoluble $\text{Cr}(\text{OH})_3$ (aq) and is thus relatively immobile (Masscheleyn et al 1992, Kotaš and Stasicka 2000, Tokunaga et al 2001). Copper is more mobile than chrome but still expected to be retained effectively by soil particles (McBride 1994). Chromium takes place on the soil particle surfaces as inner-sphere complexes and copper is expected to be situated at the surfaces or in the second layer. The behaviour of arsenic was expected to somewhat different since it exists an anion in soils. This can be expected to be sorbed onto the first layer of cations.

Figures 13 and 14 show the concentrations of the contaminant species in individual soil cylinders extracted at different times after wetting. No significant differences could be seen for arsenic or copper. The only significant change was observed for concentrations of chromium, which increased in the 48 and 72 hour extractions. These samples yielded low sample volume and high concentrations for all species, which might be considered as outliers. These soil cylinders were the last to become moist at the topmost layer. This suggests that the soil in these cylinders differed from the others.

The reason for the increasing chromium concentrations is unclear. If the diffusive forces expropriated by the soil solution were the reason, i.e., that the chromium leached into the solution, then a greater effect should be expected for copper because of its lower affinity to soil particles. Chromium was not expected to be affected by the diffusive forces. This indicates some sort of chemical change in the sample, such as pH or redox conditions. Chromium can, under reducing conditions, be reduced (Kotaš and Stasicka 2000) to Cr²⁺ which could lead to a release of chromium from particle surfaces. This would in extent affect arsenic as well, because it is assumed that sorbed arsenic is attracted by chromium and other sorbed cations. A reducing environment would further reduce As(V) to As(III). But because pH and redox potential were not monitored, it is only possible to speculate on the actual process. This would explain the behaviour of chromium and to some extent arsenic, but not copper, because it would have affected copper as well. Another parameter that was not monitored was the organic content. Yin et al (2001) showed a positive correlation between the activity of Cu²⁺ and SOM, which means that the wooden remainders from the CCA-treatment could have influenced the concentrations in the extracted soil solution.

K_d-coefficients for the species were calculated by Equation 5: copper, 5.7 ±0.51; chromium, 3.9 ±0.56 and arsenic, 3.2 ±0.34. These results diverge from expectancy in the same way as the results above because the K_d value for chromium, which is expected to be most effectively retained, is only slightly higher than arsenic. The results show that K_d values for unsorted soils, if aimed to represent a large area, should be determined through multiple extracts.

8 Conclusions and suggestions for further research

8.1 Conclusions and suggestions from theoretical studies

- A soil water extract would avoid many of the assumptions made today when calculating contaminant levels in risk assessments, as literature values of the partition coefficient vary significantly.

- Attention must be paid to what kind of situation the extract reflects and what kind of situation is the aim of the investigation. An extract will represent a snap shot of the situation at the time of sampling. If risk assessments are to be valid for longer time periods, soils must be exposed to probable environmental changes, i.e., pH and redox potential changes.
- It is important to take into account if the soil/water equilibrium is established.
- Different compounds can influence the adsorption/desorption behavior of other compounds. Therefore testing methods with single compounds imply a certain risk of errors.
- Soil water from all pore sizes is of interest and it can be extracted by forces up to pF 5 without extracting inadequate soil water.
- A method for determination of the partition coefficient should avoid to change sample properties as far as possible, e.g. the soil texture through mixing, rupture of biota by high centrifugation forces etc.
- A standard filter of 1.1 µm size that lets colloids through should be used when filtering soil-water extracts, as colloids can be important for contaminant mobilisation and transport.
- Filter material should be chosen carefully to avoid interaction with the sample.
- Can the diffusive forces that sequential column leaching exerts be replaced by centrifugal forces or pressure? Comparing the methods would reveal what forces that correlates to leaching time and concentrations, if possible.
- Attention should be paid to the fact that SOM is not a stable solid phase and that contaminants bound to SOM eventually impose a leakage threat. Further research on site specific SOM deterioration rates and its impact on contaminant mobilisation would reveal if this is a factor to incorporate in risk assessments.
- Column methods have a main disadvantage as it regards the time for testing, but are interesting from other points of view. A possible research could address if it is possible to perform a short term column test with sufficient accuracy.

8.2 Conclusions and suggestions from practical experiments

- A sufficient sample amount is important for several reasons: Centrifuge extractions of unsorted soils render extracts that differ from each other. Depending on the

wanted resolution of the results, accumulated soil-water extracts can be used. This also increases the total yield.

- From the data in this project it is difficult to assess the influence of particle size, initial moisture content and organic content on soil solution concentrations. Ideally, the importance of each of these should be determined in standardised laboratory experiments where each parameter was in turn held constant. Furthermore, pH and redox potential should be monitored during the wetting and after extraction.
- If the centrifugation method is found to be attractive after testing with the above mentioned improvements, some areas are in need of further research:
 - 1) Suitability of the method for organic contaminant.
 - 2) Laboratory equipment design. For example, it might be necessary to use different filters when analysing for pH-sensitive species and non-sensitive species, in agreement with Grieve (1996).
 - 3) Sampling guidelines.
 - 4) The influence of temperature on sorption also has to be investigated. Does a temperature of 25°C overestimate the mobility of a substance at lower levels in soils where temperatures hardly ever reach 25°C?

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