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Adsorption of Polycyclic Aromatic Hydrocarbons (PAH) on *Sphagnum* Moss Peat

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Department of Civil and Environmental Engineering
Division of Water Environment Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
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Abstract

In this project *Sphagnum* peat moss adsorption of polycyclic aromatic hydrocarbons (PAH) to peat, has been studied for the potential use as filter material for treatment of contaminated waters and remediation of contaminated soils. The adsorption of PAH to peat, and the adsorption of PAH to peat when cadmium is present was investigated. This was done by determination of two sorption coefficients: the Freundlich coefficient, K_f , and the distribution coefficient normalized relative to the total organic carbon, K_{oc} , which were determined by constructing a Freundlich isotherms and a linear distribution isotherms respectively. Batch experiments were performed, and solid phase extraction (SPE) was used to pre-concentrate the samples prior to analysis with a gas chromatography/mass spectrometry (GC/MS) instrument. For the construction of the sorption isotherms, a constant initial concentration was used, and 1, 0.75, 0.5, 0.25 and 0.1 g of peat were used. The results show that *Sphagnum* peat moss has a good potential to be used as a filter material for waters contaminated with PAH, but the experimental procedure needs to be improved before reliable results for the sorption isotherms can be obtained. The sorption isotherm for indeno(1,2,3-cd)pyrene was the only sorption isotherm that could be adjusted to a Freundlich isotherm. None of the PAH could be adjusted to a linear isotherm. An initial concentration of 100/50 $\mu\text{g/l}$ was better to use than a lower concentration of 50/25 $\mu\text{g/l}$. For the SPE procedure, the heptane showed to be a better elution solvent than a mixture of MTBE:heptane (50:50 v/v). The results also indicate that a large amount of the PAH is evaporated and adsorbed to surfaces of the equipment and to the peat. Low recovery of naphthalene- d_8 for the SPE procedure indicates that the low molecular weight PAH is evaporated when drying of the SPE-disk during the extraction.

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Göteborg, september 2006

Åsa Mårdberg

“Allt som kan gå fel, går fel”

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1 Introduction

1.1 Description of the problem

The extent of contaminated sites in Sweden has been estimated by the Swedish EPA to a figure of 40 000 sites. The costs so far for the remediation by the government have been up to 1 milliards and, it will be necessary with an additional 45 milliards to remediate the most severe sites. This brings a need of cost-efficient ways to remediate. The most common way so far in Sweden to remediate is to treat the contaminated soil ex-situ or on-situ, even though in-situ methods many times is preferred as these methods lead to less disturbance of the soil. Sometimes a disturbance of the soil can lead to an increase in mobility of the pollutant. In-situ methods are also often preferred when dealing with natural soils, to prevent excessive disturbance of the soil profile, which is preferred to promote long-term sustainability of the soil quality.

Permeable reactive barriers (PRB) are a relatively new in-situ technology to remove pollutants from groundwater and have been tested in many pilot and full-scale projects with promising results (ITRC, 2005). They are installed across the flow path of a contaminant plume and consist of a trench back-filled with barrier material. As the groundwater passes the barrier, pollutants are removed from the water by chemical, physical or biological processes, hence, protecting the surrounding environment. Different design and construction techniques exist to ultimately capture the groundwater plume, such as the funnel-and-gate system. The PRB method offers a simple, cost-efficient way to reduce risk in the scope of contaminated sites. The main advantage of PRB is that its operation, for the most part, does not depend on any external labor or energy inputs (Gavaskar, 1999). The opportunity to construct a PRB and to continue exploitation of the property is another great advantage (Honkonen, 2005).

A wide range of reactive medium is used in PRB, and varied depending on the type of contaminants being treated. The most commonly used medium in field barrier is zero-valent granular iron (Gavaskar *et al.*, 2000; ITRC, 2005). Other barrier mediums tested include granular activated carbon, zeolite, limestone, dithionite, other zero-valent metals and magnesium dioxide (Honkonen, 2005; ITRC, 2005; Gavaskar, 1999; Gavaskar *et al.*, 2000). These medium are however rather expensive. Peat has been tested in the scope of research for its use in PRB and has shown to give good results to remediate different contaminants (Viraraghavan *et al.*, 1999; Kao *et al.*, 2000; Guerin *et al.*, 2002; Rasmussen *et al.*, 2002) but so far peat is not extensively used in field PRB. Peat could also be used to remediate pollutants in other situations. One interesting area is to use peat to clean leachate from landfills. Peat has also been investigated for its use in purifying wastewater at sewage treatment works. For treatment of highway runoff (stormwater) in USA, a peat filtration system has been evaluated for removal of heavy metals and PAH (Zhou *et al.*, 2003). In Sweden, several pilot-plant and even full-scale facilities with peat filters for treatment of contaminated leachates from landfills are in use. These filters have been constructed without basic knowledge from research, now being requested for further technology development.

Sweden has a good potential in using peat in PRB and for use as filter material for treatment of contaminated leachates from landfills and contaminated stormwater. With about 10 million hectares of peat of which 6.4 million hectares have a depth greater than 30 cm, Sweden is one of the countries that have the highest density of peat area. Currently, 0.1% is being used whereas most of this explored area, 7000 hectares, is used for energy production (Fredriksson *et al.*, 1993). Even though this large peat area in Sweden, it is not certain if further exploitation of peat for the usage in filters will be sustainable. This is because of the growth rate of peat, which varies between 0.2 - 4.0 mm/year depending on the character of the peat (Schilstra, 2004). In a human perspective this growth rate is considered small thus making the peat a non-renewable resource (Naturvårdsverket, 2003). Thus a life cycle assessment should be made before commercialising peat as a reactive filter medium.

1.2 Aims and limitations

Master theses have been carried out at Chalmers that found peat as a potential sorbent for heavy metals (Kalmykova, 2004) and organic contaminants (Potrebko, 2004). The idea of this thesis is to further investigate the potential of using peat as a reactive medium to be used in PRB for the purpose to remediate groundwater contaminated with polycyclic aromatic hydrocarbons (PAH) and heavy metals. This thesis can be regarded as a first step into the research for an appropriate method to examine the peat's potential to adsorb PAH. Batch experiments with artificial solutions will be performed to minimise interference from factors that might affect the sorption, and to increase the reproducibility of the experiments. The focus should be to investigate only the PAH and metal sorbed to the solid peat, as the dissolved parts of the peat is assumed to be leached out. Furthermore, low concentrations of the PAH is meant to be used to avoid interactions between the PAH molecules, and to be able to study mechanisms.

The aims of this thesis are:

- (i) investigate the use of the Solid Phase Extraction (SPE) method with C₁₈-disks for extraction of the 16 PAHs from a liquid solution containing organic matter, and
- (ii) determine sorption isotherm coefficients, K_F and K_{OC} , for the 16 PAH on peat, and
- (iii) investigate any interference between the PAH and heavy metals on the sorption to peat. Having the report from Kalmykova (2004) and adsorption isotherms for PAH on peat as a basis, conclusions may be made for this aim.

This work is limited by the time consuming experimental procedure, and therefore only a restricted number of experiments can be performed.

2 Background

2.1 Polycyclic Aromatic Hydrocarbons

PAH is a group of over five hundred different substances and exist naturally in the environment. They are organic, flat molecules that consist of two or more benzene rings fused together and consist of carbon and hydrogen. The PAHs are formed by incomplete combustion of hydrocarbons and the sources in our surroundings constitute of biological processes, derivation from petroleum and incomplete combustion of fuels, of which the largest contribution of PAHs is antropogenic (Perhans, 2003; Thorsen *et al.*, 2004). For soils, diffuse emissions from combustion processes and the usage of creosote and coal tar are the main sources of PAH (Nielsen *et al.*, 1997). Creosote has been frequently used as an impregnation substance for wood preservation and railway tracks, and can also be found on old gas refinery stations. Coal tar has been used for surface coatings, as building material and as binding substance in road material, among others.

Attention has drawn to the PAH because of their toxic, mutagenic, carcinogenic and persistent properties. In many cases, exposure of very low dose of some of the PAH could lead to irreversible damages such as damages on the reproduction systems or on the DNA (KEMI, 2006). The PAH can be biotransformed by mammals, birds and many fish species, due to an enzyme, P450, and therefore these animals do not bioaccumulate or biomagnificate the PAH (Perhans, 2003). PAHs are removed from the environment through volatilization, photooxidation, chemical oxidation, sorption, leaching and biodegradation. During the degradation processes, more water-soluble and highly toxic, secondary products such as oxy-PAH and decarboxylated transformation products could be formed (Lundstedt *et al.*, 2003; Meckenstock *et al.*, 2004).

In this review the focus has been on 16 PAHs (Figure 1) that the U.S. EPA has included in their priority list over hazardous substances in polluted soils. These 16 PAHs occur in highest concentrations and they have the largest risk of exposure. They are also regarded to be the most dangerous for the environment and health, and the damages they are causing are representative for the PAH (Perhans, 2003).

The Swedish EPA have established recommendations of concentrations of the PAH-16 that should not be exceeded in soil, which ranges between 0.3 – 7 mg/kg dry weight (dw) for the carcinogenic PAH (C-PAH) and 20 – 40 mg/kg dw for the non-carcinogenic PAH (IC-PAH), depending on the sensitivity of the environment at the contaminated site (Naturvårdsverket, 1997; Svensson, 2003). Further, recommendations of concentration in groundwater has been set to 0.2 µg/l for C-PAH and 10 µg/l for IC-PAH (Naturvårdsverket, 2002). When examining surface soil (0 – 0.2 m) that where expected to be clean in the region around Göteborg, the concentrations were between 0.01 – 120 mg/kg dw for the C-PAH and 0.13 – 44 mg/kg dw for the IC-PAH (Svensson, 2003). At one of the most contaminated sites in Sweden so far, the maximum measured PAH concentrations were 38 600 mg/kg dw for the IC-PAH, 2100 mg/kg dw for the C-PAH and in the groundwater 2 – 15 mg/l PAH-16 (Golder, 2000).

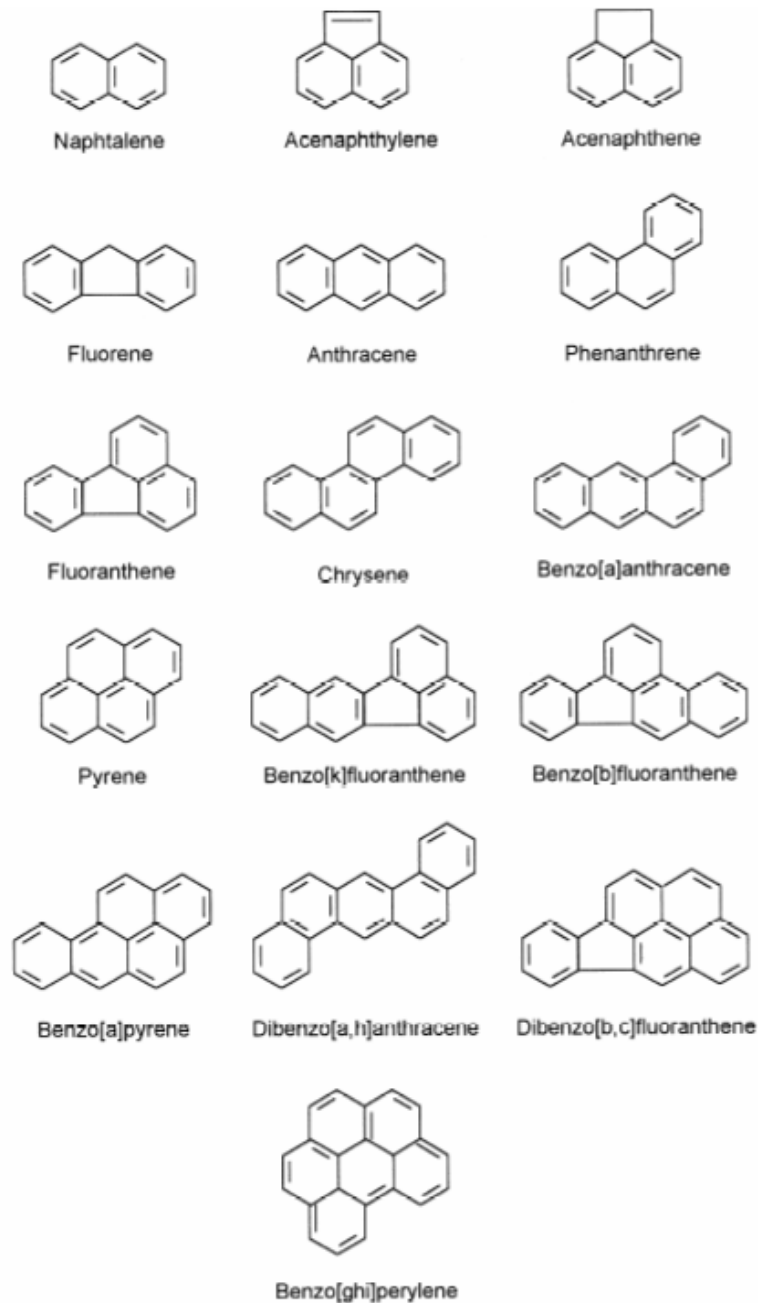


Figure 1. The molecular structure of the PAH-16 (Marcé *et al.*, 2000).

2.2 Heavy metals

At contaminated sites often a mixture of pollutants is present. Therefore, in order to remediate contaminated groundwater, leachates from landfills and urban stormwater through a reactive filter, a need of a more complete understanding of how different pollutants interact with each other is necessary. The group of heavy metals consists of cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn). Arsenic (As) is a half-metal, but is considered to be a member of the toxic heavy metals. The spreading of these metals is associated to the spreading of products that contain heavy metals and with ore- and metal industry, whereas PAH and heavy metals are associated with each other at industries such as oil industry, gas refinery stations and saw mills. Together they consists of about 55 % of the most common contaminants at the regional councils lists of prioritised sites in Sweden, where the heavy metals stands for about 45 % of the most common contaminants at the regional councils lists of prioritized sites in Sweden (Färnkvist *et al.*, 2005).

2.3 Peat as an adsorbent

The sorption capacity of peat for different substances depends on the composition of peat. There is however not much literature about the influence of the composition of peat on the sorption capacity. Therefore, a brief description of peat as a material will be given here.

Peat is the definition of organic soils that is formed at places with excessive moisture, where plant growth exceeds the rate of residue decomposition. This leads to an accumulation of organic matter as the decomposition is limited by the lack of oxygen. The term “peat” is used when classifying organic matter, and is used if the residues are sufficiently intact to permit the plant fibres to be identified. If most of the material has decomposed sufficiently so that little fibre remains, the term muck or sapric is used. Peat is found in different areas with different definitions and is found in peat lands, mires, histosols and in aquatic areas. Peat land is mainly a geological definition, while mire is more a botanic definition of an area covered with peat. Further, mire also requires living vegetation. Histosols is the soil scientific term of an organic soil, where the organic matter can be either peat or muck (Brady *et al.*, 2002).

Peat deposits are found most extensively in the cool climates and in areas that have been glaciated. Cool climates and acidic conditions favour slow decomposition, whereas warm and alkaline conditions favour rapid plant production. Enrichment of nutrients may increase the rate of organic production more than it does the rate of decomposition, leading to very high net accumulation rates (Brady *et al.*, 2002). Different effects of nutrient content in litter on decomposition has also been found (Berg, 2000).

The main constituents of peat are partially decomposed organic matter, mineral particles and chemical salts (Sylvia *et al.*, 1998). The detailed composition of peat, and thereby also its qualities, is not constant but varies with several factors. The original biota is an important factor for the organic matter, and four kinds of peat are recognized based on the nature of the remains of the parent materials (Brady *et al.*, 2002):

1. Moss peat, the remains of mosses such as *Sphagnum*.
2. Herbaceous peat, residues of *Herbaceous* plants such as sedges, reeds, and cattails.
3. Woody peat, from the remains of woody plants, including trees and shrubs.
4. Sedimentary peat, remains of aquatic plants and of faecal material of aquatic animals.

Organic deposits generally contain two or more of these kinds of peat, where woody peat often dominates in the surface layer. In Sweden peat is mostly found in bog and fen mires, of which poor fens are the most common type (Kellner, 2003). Fens receive more calcium-rich mineral matter from the surrounding landscape, and are therefore more alkaline and contain more available nutrients than the acidic bogs. Fens are also usually more decomposed than bogs (Sylvia *et al.*, 1998).

Peat differs from fresh organic matter as the decomposition stabilises and accumulates chemical compounds that are more resistant to degradation. Additionally, the decomposition alters some chemical substances. A precise identification of all constituents in peat is hardly possible, as peat is a very heterogeneous material. Therefore different ways to classify the constituents are made, where classification often is based upon how they dissolve in different solutions. The chemical composition of peat has been analysed (Bergner, 1995) and is presented in Figure 2.

A large part of peat consists of Klasonlignin, which is a group of phenolic substances, including lignin-like elements, humic acids and fulvic acids. Other constituents are bitumen, that consists of waxes, fats and resins, among others, and uronacids, that are sugars that have oxidized to their corresponding acid.

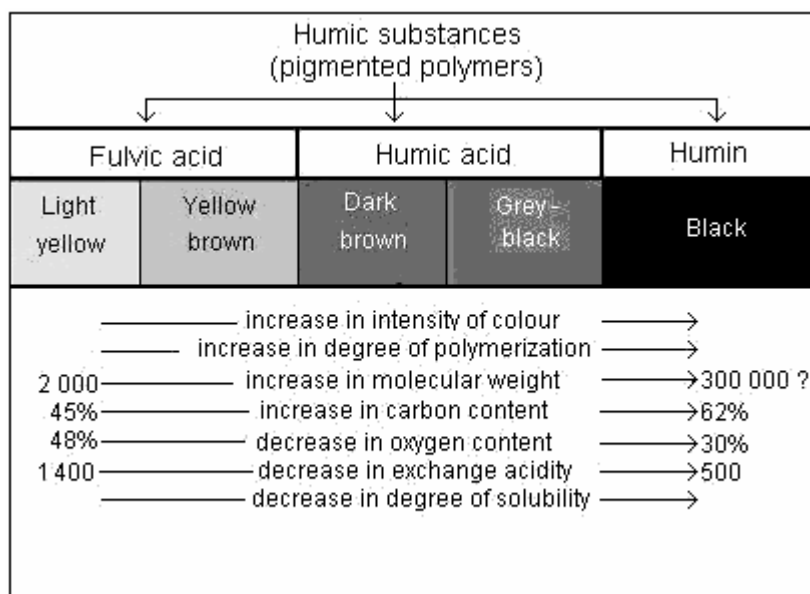


Figure 3. Properties of humic substances. Exchange acidity in mole_c/kg , and molecular weight in g/moles. Modified from Stevenson (1982) (Weber *et al.*, 1997) .

and seems to be richer in ketonic C=O content, whereas the quinone C=O content of humic acids is universally higher than for fulvic acids (Laboratory 3076, 2006).

When using peat in a PRB or other types of filters, it is important to consider the factors that affect the mobility of the HS. As mentioned before, the pH is an important factor. This is because of that the HS has a very large specific area and has a large number of functional groups, that give the HS a large capacity of ion exchange (both cation (CEC) and anion (AEC) exchange capacity) and ion binding (Mcbride, 1994). The capacity of ion exchange and ion binding is highly dependent on the pH, as the charge of the functional groups varies with pH. The main responsible groups for the pH dependent charges are the carboxyl-, phenolic- and amine-groups (Mcbride, 1994; SLU, 2002). As the pH increases, the more deprotonised become the functional groups, thus giving more negatively charged sites available for cation exchange and fewer positive sites available for anion exchange (Sylvia *et al.*, 1998). Thus, with a higher pH, humic substances are more dispersed, and contribute more to the pool of dissolved organic matter (DOM), whereas a low pH gives more flocculated forms (Mcbride, 1994). This phenomenon is however not always occurring. Soils with a high content of Al^{3+} and Fe^{3+} are giving the reverse process. These cations form complexes with the organic matter and are dissociated at lower pH, thus giving an increase of DOM at lower pH (SLU, 2002).

Peat has a pH at point of zero charge (pHpzc) that lies in the pH interval 3.0 - 3.5 (EMBL, 1995), meaning that below this pH the net charge of the surface in peat is positive and above negative. When the pH lies at pHpzc the peat molecules tend to aggregate, as the molecules do not repulse each other. The pH of groundwater varies depending on the flow path and retention times of the water particles, and deep groundwater has relatively high pH (pH 6 or higher), whereas shallow groundwater has a lower pH (pH 5) (Grip *et al.*, 2003). This is important when using peat in PRB or other types of filters were the peat is supposed to have a direct contact with the groundwater or leachates for a longer period.

The mobility of the HS may also depend on other factors. For example has calcium saturated conditions and clay stabilizing effect on organic matter (Kördel *et al.*, 1997). Calcium has however been observed to reduce the peat's potential to adsorb metals.

2.4 Solid Phase Extraction

Solid phase extraction (SPE) is a common method for the extraction of solutes from a liquid matrix (Edell, 1997; Manoli *et al.*, 1999), where the main principle is a liquid sample passing through a sorbent. It can be used to clean a sample or to concentrate the analytes (Marcé *et al.*, 2000). An advantage of this method is the wide variety of extraction conditions, which may be used to achieve the desired clean up or pre-concentration. The SPE method has been recommended for extraction of PAH from water solutions (USEPA, 1995), whereas the solution is passed through an adsorbent onto which the PAH are adsorbed. Thereafter the PAH is recovered from the sorbent by rinsing with an elution solvent, usually an organic solvent.

Several kinds of sorbents in either cartridges or disks may be used for SPE. Disks have some advantages over cartridges (Mayer *et al.*, 1994; Marcé *et al.*, 2000). Cartridges are more commonly used because only a few sorbents are commercially available in disks. The disks are composed of a matrix and an adsorbent, where the polytetrafluoroethylene (PTFE) matrix disks have been mostly used (Marcé *et al.*, 2000). The choice of adsorbent is often dictated by the chromatographic method used for PAH separation and identification (Marcé *et al.*, 2000), where the most used adsorbent for the extraction of PAH is octadecyl bonded silica (C₁₈), which has been used with good results (Mayer *et al.*, 1994; Marcé *et al.*, 2000; Brown, 2003). Other adsorbents used for PAHs are C₈, cyano, phenyl, immunosorbents (Marcé *et al.*, 2000) and polystyrene-divinylbenzene (Bernal *et al.*, 1997; Utvik *et al.*, 1999).

When applying the elution solvent, recovery of the low molecular weight PAHs are higher with non-volatile solvents, but recoveries for the most of the PAHs with 4-6 aromatic rings are higher when a non-polar solvent is used (Marcé *et al.*, 2000). To ensure higher recoveries of all the PAHs, two elution solvents are usually recommended (3M, ; Marcé *et al.*, 2000). Several elution solvents has been used when extracting organic solutes during SPE procedure and when using disks, for example hexane (Potrebko *et al.*, 2004), methanol (Edell, 1997), acetonitril:water (Cuyper, 2002) and Mayer *et al.* (1994) has compared different elution solvents for the recovery of semi-volatile compounds. When extracting PAH from a C₁₈-disk, different elution solvents has been used, for example methylene chloride (USEPA, 1995), methanol (Dachs *et al.*, 1997) and acetone:methylene chloride (Brown *et al.*, 2003).

Another critical step in the methodology is the addition of an organic solvent or a surfactant to increase the solubility of the PAH in a liquid sample. The concentration of the organic solvent is an important parameter because if low it may not be enough to solubilise the high molecular weight PAHs, whereas if high the breakthrough volume will be low for the low molecular weight PAHs (Marcé *et al.*, 2000). Common organic solvents that has been used in sorption experiments with PAH are methanol (Edell, 1997; Karapanagioti *et al.*, 1999; Kohl *et al.*, 1999; Rasmussen *et al.*, 2002; Ju *et al.*, 2004; Trembley *et al.*, 2005), 2-propanol or acetonitril (Marcé *et al.*, 2000).

Furthermore, when using the SPE method, several researchers have found that dissolved organic matter has lowered the recovery of the analytes (Ridal *et al.*, 1997; Sturm *et al.*, 1998).

3 Theory

3.1 Sorption isotherms

Sorption occurs when free energy of the interaction between an environmental solid sorbent and contaminant sorbate is negative. The sorption process can be either enthalpy or entropy driven, where entropy-related forces include van der Waals interaction, electrostatic interaction, hydrogen bonding, charge transfer, ligand exchange, direct and induced dipole-dipole interactions, and chemisorption. Hydrophobic bonding or partitioning is considered as the primary entropy driven force (Suthersan, 2002).

To describe to which content a substance distributes itself between a solid and the aqueous phase at equilibrium, sorption coefficients are used. They are generally determined from a sorption isotherm, a diagram that depicts this distribution in equilibrium over a range of concentrations at constant temperature. These isotherms can be linear or nonlinear, where nonlinear sorption are often characteristic of site-specific interactions between the sorbate and sorbent (Kohl *et al.*, 1999).

There are different distribution coefficients to depict the distribution. One is the partitioning or distribution coefficient, K_d , which describes a linear sorption isotherm between the soil matrix and the soil solution. The isotherm can be describes with the equation:

$$K_d = \frac{q}{C}$$

, where q is the concentration of the sorbed substance ($\mu\text{g/g}$) and C is the liquid phase concentration ($\mu\text{g/mL}$) (Mcbride, 1994). This approach expresses entropy driven processes, such as partitioning processes (Kohl *et al.*, 1999; SLU, 2005) and is the most commonly method for expressing the distribution of organic compounds (Suthersan, 2002).

To describe non-linear sorption there are two models that is frequently used: the Langmuir model and the Freundlich model. The non-linear models express enthalpy driven processes, such as Van der Waals attraction, electrostatic attraction, charge transfer and chemisorption. The Langmuir model is usually indicative of chemisorption and a mono-layer of adsorbates. The Freundlich isotherm equation is not based on theory, but has instead an isotherm that has empirically been established. The isotherm can be described with the equation:

$$K_f = \frac{q}{C^n}$$

, where K_f is the Freundlich sorption coefficient and n represent the energy distribution of the sorption process (Trembley *et al.*, 2005). The values of the constants are determined by plotting the logarithms of the q and C in a diagram, where the intercept is the K_f , which gives an indication of sorption capacity, and n is the slope, indicating the sorption intensity. The n value is also an indication of non-linearity, whereas an n value of unity would imply a linear sorption process (Kohl *et al.*, 1999; SLU, 2005).

Several researchers have found that if the distribution is correlated to the total organic carbon (TOC) content of the soil, much of the variation in observed K_d values between different soils is eliminated. Thus, a distribution coefficient normalized relative to the total organic carbon (TOC), K_{oc} , is frequently used. This coefficient is correlated to K_d by the f_{oc} , which is the fraction of organic carbon in a sample (mg organic carbon/mg soil dry weight). This equation is described as :

$$K_{oc} = \frac{K_d}{f_{oc}}$$

Table 1. Conducted experimental conditions to reach equilibrium between sorption and desorption.

Authors	Conc. PAH	solvent	Mixing time	Relevant information
Berset <i>et al.</i> , 2001	0.04-4.98 g/ml	Toluene	30 minutes	Batch experiment on extraction of PAH from peat.
Potrebko <i>et al.</i> , 2004	-	Isopropanol/ ether and methanol	48 hours	Batch experiments on sorption of diesel oil/C ₁₂ , C ₁₆ and C ₂₀ on peat.
Zytner <i>et al.</i> , 1994	-	De-ionized water	92 h	Batch experiments on sorption of BTEX on peat
Ju <i>et al.</i> , 2004	-	Methanol	N/A	Batch experiment on competitive sorption of 1,2 dichlorobenzene in a binary system on peat.
Kohl <i>et al.</i> , 1999	-		7 days	Flourene- and phenanthrene adsorption on soil organic matter.
Loffredo <i>et al.</i> , 1999	-	7.5% ethanol in H ₂ O	20 h	Batch experiments on adsorption of chlordane on humic acids.

N/A= not apparent

Many factors can affect the sorption coefficient, where the most important are temperature, pH, ionic strength, dissolved or colloidal matter, cosolvents, organic matter type and origin, kinetics (equilibrium time) and ionisability (Suthersan, 2002). The factors affect the sorption coefficient differently. For instance, for the PAH, the equilibrium time of sorption decreases in most cases with increasing temperature, whereas temperature has been seen to have no or very little effect on the sorption process of the PAH. Further, a decline in temperature has been seen to decrease the desorption for the PAH (Enell, 2005). In addition, there are many other factors that indirectly affect the sorption coefficient such as contact time, solubility of the compound or laboratory procedure.

3.2 Equilibrium time

Under natural conditions sorption kinetics is important to consider, especially under short contact situations. True sorption equilibrium under natural conditions may require weeks to months to achieve depending on the chemical and environmental solid of interest. However sorption generally is regarded as a rapid process and in laboratory experiments, equilibrium is often observed within several minutes or hours. For convenience, an equilibrium time of 24 hours is often used. Two processes govern sorption: transport of the substance to the sorption sites and the sorption process itself. In many instances, an early period of rapid and extensive sorption, followed by a long slow period, is observed and generally adsorption processes tend to be rapid and nearly instantaneous, whereas non-surface sorption tends to be slower (Suthersan, 2002).

When performing laboratory sorption experiments with PAH, the equilibrium time should carefully be chosen because it can yield diverse results (Hwang *et al.*, 2002). Researcher used different equilibrium times and it is not apparent which equilibrium time that is consistent for the sorption of PAH to organic material, see Table 1. The more hydrophobic and the more high molecular weight the PAH is, the longer it takes to reach equilibrium (Mcbride, 1994; Suthersan, 2002).

Additional experiments on the equilibrium time have been performed. Trembley *et al.* (2005) found that an apparent equilibrium time was obtained after 7 days and the sorption observed at 49 days was not statically different. Kohl *et al.* (1999) found that while naphthalene is in apparent sorption equilibrium

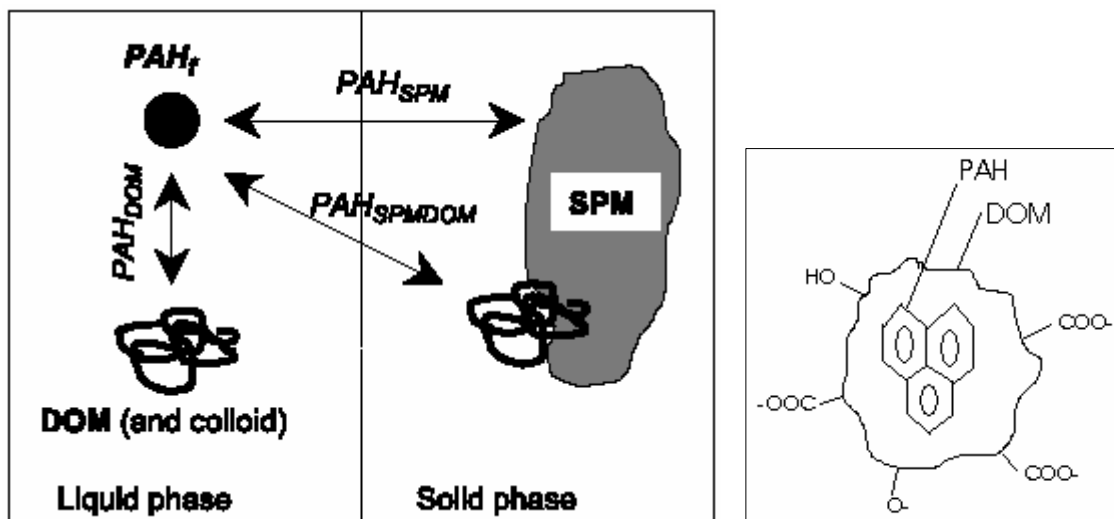


Figure 4. a) The distribution of the PAH in a soil (Trembley, 2005) b) the transportation of PAH bound to DOM.

after 1 day of incubation, flourene and phenanthrene require more than 1 day to reach equilibrium. Cornelissen *et al.* (2004) found that an equilibrium time of 20 - 25 days was found to be sufficient for d10-phenanthrene in both natural and combusted sediments.

3.3 Behaviour of PAH in soil

When PAH are present in the soil, they are distributed between the free phase (PAH_f) and sorbed phase. As a free phase they may occur as a non-aqueous phase liquid (NAPL) and to some extent, as a dissolved molecule in the soil solution. The PAH can be sorbed to soil particle matter (SPM) or bound to DOM and colloids or sorbed to DOM coated on SPM, as shown in Figure 4a (Trembley *et al.*, 2005). The spreading of PAH is mainly contributed by the sorption to DOM and other colloids (Raber *et al.*, 1998; Perhans, 2003), of which DOM represent the most important colloidal material in soil solution (Raber *et al.*, 1998). A colloid is a particle that keeps floating and does not sedimentates in a solution. These particles size is 1 nm - 10 µm, and consist of larger molecules to smaller particles of both inorganic and organic substances. Colloids can also be either hydrophobic or hydrophilic of which PAH binds to the hydrophobic colloids (Perhans, 2003). The fraction of DOM becomes larger at higher pH. This is because of the larger extent of deprotonisation of soil organic matter (SOM) at higher pH. (Perhans, 2003) The DOM consists of a heterogeneous mixture of soluble organic substances that passes through a 0.45 µm silver or glass fiber filter, and about 80 % of the dissolved organic carbon (DOC) (which is analogous to DOM) consists of humic and fulvic acids (Kördel *et al.*, 1997). The DOM has been discussed elsewhere (Stevenson, 1994; Leenheer, 2004), and it is not clear to which part of the DOM the PAH has the highest affinity. One way to illustrate this transportation is shown in Figure 4b, where the PAH is capped into a micelle of DOM (SLU, 2005). The knowledge of the exact chemical speciation of the PAH when entering the peat would facilitate a fully understanding of the adsorption of the PAH to peat.

Different molecules have affinity for different phases in the soil. For the PAH, soil organic material is the most important factor for sorption, and it is generally accepted that the humic substances play a major role in the sorption. Thus, peat has a good potential to sorb PAH. To which part of the humic substances the PAH have most affinity for is still unclear. McBride (1994) claim that the PAH have most affinity for the hydrophobic phases in humic acids, whereas other researchers have found that humin may play an important role in the sorption of PAH (Kohl *et al.*, 1998; Kohl *et al.*, 1999; Nam *et al.*, 2002; Pan *et al.*, 2006). The sorption of PAH also increase with increasing carbon content, especially aromatic carbon, of the organic matter (Gauthier *et al.*, 1987; McCarty *et al.*, 1989). Further, other compounds in the soil may compete with the PAH for the sorptive sites. Kohl *et al.* (1999) showed that lipids naturally occurring in the soil strongly compete with the PAH for hydrophobic sorption sites in the SOM. The contact time between PAH and the SOM is also relevant. The sorption

Table 2. Chemical properties of PAH-16. (Perhans, 2003)

	MW ^a g/mole	HLC ^b atm- m ³ /mole	Saq ^c mg/l	Log Kow ^d	Log Koc ^e	Toxicity ^f
Naphtalene	128.2	4.83E-04	31	3.36	2.74	Environmental hazardous, Long-term effects
Acenaphthylene	152.2	n.i.f. ^g	3.9	3.74	n.i.f. ^g	n.i.f. ^g
Acenaphthene	154.2	1.55E-04	4.24	3.92	n.i.f.	n.i.f. ^g
Fluorene	166.2	6.36E-05	2.0	4.21	3.7	n.i.f. ^g
Phenanthrene	178.2	n.i.f. ^g	1.3	4.46	3.72	n.i.f. ^g
Antracene	178.2	6.50E-05	4.34E-02	4.55	4.65*	PBT / vPvB ⁱ
Fluoranthene	202.3	1.61E-05	0.21	5.12	4.62	n.i.f. ^g
Pyrene	202.3	1.10E-05	0.14	5.11	4.66	n.i.f. ^g
Benz(a)anthracene	228.3	3.35E-06	0.0094	5.7	6.14	CMR ^h , Environmental hazardous, Long-term effects
Chrysene	228.3	9.46E-05	1.6E-03	5.7	5.39	CMR ^h , Environmental hazardous, Long-term effects; Mutagenic
Benzo(b)fluoranthene	252.3	1.11E-04	1.5E-03	5.2	5.74	CMR ^h , Environmental hazardous, Long-term effects
Benzo(k)fluoranthene	252.3	8.29E-07	8.0E-04	5.2	6.64	CMR ^h , Environmental hazardous, Long-term effects
Benzo(a)pyrene	252.3	1.62E-03	1.6E-03	6.11	6.27*	CMR ^j , Environmental hazardous, Long-term effects
Indeno(1,2,3-cd)pyrene	276.3	2,00E-07	2.6E-04	7.23	7.29	n.i.f. ^g
Benzo(g,h,i)perylene	276.3	1.47E-08	2.5E-03	6.7	6.89	n.i.f. ^g
Dibenz(a,h)anthracene	278.35	1.60E-06	2.2E-05	6.65	6.22	CMR ^h , Environmental hazardous, Long-term effects

a) Molecular Weight (Perhans 2004)

b) Henry Law's Constant (Perhans 2004)

c) Solubility in aqueous liquid (Perhans 2004)

d) Octane-Water coefficient (Perhans 2004)

e) Soil sorption coefficient normalized for total

organic carbon content. (Suthersan 2002; *Nielsen et al., 1997)

f) KEMI, 2006

g) no information found

h) Persistent, Bioaccumulating, Toxic/
very persistent, very Bioaccumulating

i) Carcinogenic

j) Carcinogenic, Mutagenic, Reproductiontoxic

of PAH to SOM increases with increasing contact time till equilibrium is achieved, and the sorption becomes also more irreversible (e.g. sequestration) with increasing contact time (Nam *et al.*, 2002). Sequestration is another sort of sorption mechanism as the PAH nestle itself into micropores current in the soil matrix.

The sorption of PAH is dependent on the composition of the peat as discussed above, but also on the qualities of the PAH, as shown in Table 1. PAHs are highly insoluble in water due to their high activity coefficient in an aqueous solution, where the magnitude of the activity coefficient is highly indicated by the hydrofobicity (Suthersan, 2002). Generally, their solubility decreases with increasing non-polarity, molecular weight and molecular size. The most soluble of the studied PAHs is naphthalene and the least soluble is indeno(1,2,3,-cd)pyrene (Perhans, 2003).

The volatilisation of a compound is determined largely by its vapour pressure, although this is tempered by its sorption to the soil matrix and its Henry's Law constant between the soil solution and the air (Suthersan, 2002). The PAHs have low vapour pressures and are therefore barely volatilised, whereas naphthalene is the most volatile PAH with a vapour pressure of 0.0109 kPa (Perhans, 2003).

Table 3. Common dissolved forms of Cd, Cr, Cu, Ni, Pb and Zn (SLU, 2005).

Cd	Cr	Cu	Ni	Pb	Zn
Cd ²⁺	Cr ³⁺	Cu ²⁺	Ni ²⁺	Pb ²⁺	Zn ²⁺
CdCl ⁺	H ₂ CrO ₄ -CrO ₄ ²⁻	Cu-N-DOM	Ni-O-DOM	PbCl ⁺	Zn-S/O-DOM
Cd-S/O-DOM				Pb-S/O-DOM	

Hydrofobicity is also an important characteristic of the PAHs and is usually described by the octanol-water partitioning coefficient K_{ow} . All the PAHs are hydrophobic and they have a log K_{ow} between 2 and 6.5 (Perhans, 2003). The hydrofobicity of the PAHs increases with an increasing molecular weight (Perhans, 2003), but also with an increasing angularity of the ring linkage (Kanaly *et al.*, 2000).

The forces involved in the sorption of PAH to soil organic matter is hydrophobic attraction or partitioning, but also van der Waals attraction. Hydrophobic attraction occurs when the non-polar organic compound has less affinity for the water in the soil solution than the water has for itself and is thus driven from the soil solution onto the weakly hydrated organic material. As the compounds adsorb to the organic matter, they displace a number of hydrated water into the solution. This results in an increase in disorder, which is proportional to the size of the sorbate molecule (e.g. PAH). Thus the larger the molecule, the larger is the hydrophobic attraction. The van der Waals attraction is a weak physical attraction caused by an imbalance in electron distribution, which produces instantaneous dipoles. This attraction becomes more significant in large molecules (Mcbride, 1994). The magnitude of the partitioning coefficient of PAH to soil organic matter is suggested to increase with increasing hydrofobicity (Voice *et al.*, 1983; Nielsen *et al.*, 1997).

3.4 Behaviour of metals in soil

Heavy metals are spread to the ground in divers ways, such as spillage or corrosion of products that contains heavy metals. The heavy metals that are spread to the ground by airborne particles are mainly remaining in the ground where they are deposited (Naturvårdsverket, 2006). This is due to that heavy metals have strong affinity for the soil matrix.

In the ground the heavy metals are distributed as soluble in the soil solution, sorbed to the soil matrix or precipitated as solids. In the soil solution the heavy metals can exist as a free ion, as soluble complexes with different organic and inorganic ligands or associated with organic and inorganic colloids. Common inorganic ligands in the soil are SO_4^{2-} , Cl^- , OH^- , PO_4^{3-} , NO_3^- and CO_3^{2-} , and common organic ligands are low molecular weight aliphatic, aromatic amino acids and soluble constituents of fulvic acids. Adsorption is referred to when a metal adsorb to the components in the soil matrix, which are for the metals mainly organic matter, clay, oxides and allophane, and absorption is referred to when the heavy metal is incorporated into the components in the soil matrix. Precipitation occurs when the metals form complexes with different inorganic ligands to form solid precipitates such as $Cu(OH)_2$.

The heavy metals are transported with the groundwater when they are soluble in the soil solution. Common dissolved forms can be seen in Table 3. The fate of the soluble metals when they enter the peat material depends on different factors, and surface complexation is thought to be the most efficient way to remove metals from the groundwater (SLU, 2003). The capacity of a heavy metal to form complex with peat components and to which part of the peat heavy metals have most affinity for, are still under revision, and have been discussed elsewhere (Kalmykova, 2006). The factors that affect the complexation of metals to natural organic matter (NOM) are thought to be pH, ionic strength, NOM source characteristics and competing ligands (Kördel *et al.*, 1997).

4 Experimental section

4.1 Introduction

To determine the adsorption of PAH on peat, batch experiments were performed, using beakers containing peat and a PAH solution, that were mixed for 48 hours to reach equilibrium. The samples were thereafter filtrated through silanised glasswool, to remove peat particles, and then extracted by SPE method and finally analyzed with a gas chromatography/mass spectrometry (GC/MS) for the PAH. The beakers containing the samples were covered with aluminium foil for UV protection, except for during the extraction and analysis. The 16 PAHs were obtained diluted in methylene chloride from the supplier (Restek), and had a purity of 98 – 99 % and concentrations of 500 – 1000 µg/ml (Appendix 1). The SPE was performed by using a 47 mm Empore C₁₈-disk, and an Empore Filter Aid 400, both manufactured by 3M. The SPE procedure followed the manual brought by the disk and the filter aid (see Appendix 2). The Filter Aid 400 was used to prevent clogging by organic matter of the disk and thereby facilitate the percolation of the sample through the SPE-disk. The flow rate was calculated to approximately 1 ml/min. The analysis of the PAH-16 was conducted using a Varian CP-3800 gas chromatography and a Saturn 2200 mass spectrometry.

The experiments performed during this work were:

1. Pre-test.
2. Testing the extraction method.
3. Sorption isotherm experiment.
4. Sorption of PAH and heavy metals.

4.2 Preparation

4.2.1 Cleaning of the equipment

The glass equipment used were washed with detergent, and then readily rinsed with hot tap water. Thereafter the equipment was rinsed with a mixture of heptane/acetone and left to dry in the cupboard draught. The filter aid was further dried at 400°C. The stirring metal paddles were cleaned with de-ionized water and acetone.

4.2.2 Initial solution

A buffer solution with CH₃COONa, CH₃COOH and de-ionised water, was prepared to a final concentration of 20 mM and a pH of 5.6. The buffer solutions could be stored for a longer period (about one month) without being altered, but the pH was controlled just before being used. One ml of the obtained PAH diluted in methylene chloride was further diluted with 25 ml of methanol to a PAH mixture with the concentration of 40/20 µg/ml. The buffer solution and the PAH solution were used to prepare initial solutions.

4.2.3 Internal standards

Internal standards (IS) were prepared in adequate concentrations. Biphenyl-d₁₀ and pyrene-d₁₀ were dissolved in heptane and, had a concentration of 1000 mg/l, and were further diluted in methanol to a final concentration of 50 mg/l. The naphthalene-d₈ and chrysene-d₁₂ were dissolved in methanol to a final concentration of 50 mg/l.

4.2.4 Pre-treatment of the peat

The peat used was a leftover from previous and related experiments (Kalmykova, 2004; Holmberg, 2006). It was classified as a *Sphagnum* peat moss and was ground and sieved to a size range of 0.5 – 0.125 mm. Minimum amounts of peat should be prepared because the prepared peat can not be preserved for a longer period (> 2 days). The amount peat used in this thesis was chosen to allow comparison with previous experiments (Kalmykova, 2006). Prior to usage, the peat was soaked and washed with 0.25 M buffer solution (CH₃COONa, CH₃COOH) over a coarser filter paper (Munktells) until the elute was clear. This procedure was done to wash out dissolved components from the peat,

thus preventing the adsorption of the PAH to the dissolved organic carbon. The washing was also done to keep the pH relatively stable during the experiments (Kalmykova, 2000). The washed peat was stored in a refrigerator till being used if not immediately used. The water factor (f_{TS}) was calculated by drying a 1 g peat sample in 105°C for 1h, and the lost of ignition was determined by further heating the sample in 500°C for three hours. Physical and chemical properties of the peat used have previously been characterised (Kalmykova, 2004): pH = 4.02 in nanopure water, humification degree H3, water content 83.6 %, fiber content 77.5 %, bulk density 0.095 g/cm³, saturated hydraulic conductivity 0.034 cm/min and a cation exchange capacity of 30.85 meq/100g. The humic substance composition was 78 % humic acid and 22 % fulvic acid.

4.3 Pre-test

The laboratory procedure was conducted once before performing the experiments to assure the correctness of the experimental techniques and to decide a reasonable concentration of the PAH in the initial solution (C_0). The amount of peat for each beaker was 1 g dry weight (dw), which correspond to 8.80 g wet peat according to the f_{TS} . The prepared concentrations of the PAH were 100/50 µg/l and 50/25 µg/l, and 500 ml of the initial solution was used for each beaker. One sample of 500 ml of the initial solution was taken out for the determination of the C_0 . Naphthalene-d₈ and chrysene-d₁₂ were used as IS. A mixture of heptane:methanol was used as elution solvent.

4.4 Testing the extraction method

Two samples of 500 ml initial solution with same amounts IS added and without peat were extracted using the SPE method. This was done to investigate the recovery of the IS when using heptane in comparison to a mixture of heptane:MTBE as elution solvents. The C_0 used were 50/100 µg/l, and the IS used were naphthalene-d₈, chrysene-d₁₂, biphenyl-d₁₀ and pyrene-d₁₀. In addition, naphthalene-d₈ and chrysene-d₁₂ were added to heptane for analysis in the GC/MS instrument. This was done to be able to evaluate the recoveries of the naphthalene-d₈ and the chrysene-d₁₂, for the extraction procedure.

4.5 Sorption isotherm experiment

Five samples were used to determine sorption isotherms. During the laboratory performance the concentration of the PAH was kept constant while the amount of peat was varied. The amounts of peat used were 1, 0.75, 0.5, 0.25, 0.1 gram and the C_0 was 100/50 µg/l, which was prepared by adding 7.5 ml of the PAH mixture to 3 l of the 20 mM buffer solution. One sample of the initial solution was taken to determine the C_0 . The organic solvent content in the initial solution was 0.25 % v/v. Naphthalene, which has the highest solubility of the PAH-16, had a concentration of 0.3 % of its solubility in water, but indeno(1,2,3-cd)pyrene, which has the lowest solubility of the PAH-16 had a concentration of 20000 % of its solubility in water.

Prior to SPE, 2000 µl naphthalene-d₈, 100 µl chrysene-d₁₂, 2000 µl biphenyl-d₁₀ and 100 µl pyrene-d₁₀ were added to each sample. The concentrations of the IS in the samples were 200 µg/l, 10 µg/l, 200 µg/l and 10 µg/l respectively. The total concentration of organic solvent in each sample was 1.09 % v/v.

4.6 Sorption of PAH and heavy metals

The same experimental set up as for the sorption isotherms was made, but now with an addition of cadmium. The concentration of cadmium used was the same as the concentration used in a previous experiment (Kalmykova, 2004), and was set to 100 ppb by adding 300 µl to 3 l of initial solution. Depending on a laborious failure these samples could not be analysed for the cadmium content by ICP-MS.

4.7 GC/MS analysis

The solvent extracts were analysed on a Varian CP-3800 gas chromatograph, equipped with a VF-5ms (0.25µm) fused silica open tubular (30m x 0.25mm i.d.) column, and a Varian Saturn 2200 mass spectrometer as detector. The extracts, 1 µl, were injected by a Varian auto-sampler 8400 with the split off for 60s, and thereafter with a split ratio of 20. The injector temperature was 290°C, and the constant column flow 1.0 ml / min. The compounds were separated during increase of the column temperature, + 5.0 °C / min, from 50°C to 290°C. The electron-impact mass spectrometer analysed ions, 1 scan sec⁻¹, within the mass scan 40 – 400 m / z; giving a total ion chromatogram. The interface temperature was set to 280°C. The specific 16 PAH and the internal standards used (naphthalene-d₈, chrysene-d₁₂, biphenyl-d₁₀ and pyrene-d₁₀) were identified in all chromatograms, and verified by a comparison of the given mass spectrum with mass spectra from a computer library (Wiley and NIST), and by comparisons of retention times. The areas of one of the most abundant ions, the quantification ions, was used for the quantification of the specific compounds in all chromatograms. For PAH one of the most abundant ion in the mass spectrum is the molecular weight ions, e i the ions with the same masses as the PAH molecules. The retention times and the mass values of the most abundant specific ions for each PAH used in this study can be seen in Appendix 3.

4.8 Calculation procedure

The calculation of the remaining amounts of PAH in the samples after the experimental procedure is based on a method that is independent from the volume of the samples. The method requires the calculation of a calibration factor, which is calculated for each PAH from the sample with the initial concentration:

$$K = \frac{(AC/AIS)}{(mC/mIS)}$$

, where AC is the area of the compound, AIS is the area of the internal standard, mC is the mass of the compound and mIS is the mass of the internal standard. This calibration factor is further used to calculate the amounts of each PAH in the other samples:

$$mC = \frac{(AC/AIS) * mIS}{K}$$

The calculated amount of the PAH is adjusted with the IS and the amounts can therefore be regarded as equal to the amounts left in the samples after evaporation or adsorption to the peat or to surfaces of the equipment. Further can the adsorption of the PAH to the peat be evaluated by comparing with the sample where no peat was used.

The Freundlich isotherms were adjusted to the logarithm of the Freundlich equation:

$$\text{Log}(q) = \text{log}(Kf) + n\text{log}(C)$$

The q was further calculated with the equation (x):

$$q = \frac{(C(0)-C) * V}{m_p}$$

, where m_p is the weight of the peat (g), C is the liquid phase concentration (µg/ml) in the sample, C(0) is the liquid phase concentration (µg/ml) in the sample with the initial concentration, q is the amount of the sorbed substance per unit peat (µg/g) and V is the volume (ml) of the sample.

5 Results

5.1 Introduction

The experiments are relatively time consuming, why the experiments were run with only one sample for each parameter. Therefore the obtained results cannot be used for statically methods to evaluate the significance of these results. The reproducibility has neither been evaluated in this work. Thus, any conclusions for the sorption of the PAH to peat cannot be made here. The results will only be showing trends and indications of results. The percentages reported are the amounts that have vanished, probably both by evaporation and adsorption to surfaces of the equipment and to the peat. Throughout the experiments the areas obtained from the GC/MS were small and near the limit of detection (0.1-10 µg/l).

The content of carbon in the peat was calculated to 77 %, and a value of foc was calculated to 0.79. The f_{ts} was determined to 0.1136. The Freundlich isotherm was calculated on a weight basis, whereas the figures presented in the tables below is based on moles. The q is meant to be a value related to the adsorption on the peat, but here it is also including the evaporation and the adsorption to the equipment. This means that it is difficult to evaluate the q , but it can serve as a comparison for approaching experiments. For the calculation of the PAH, the initial concentration has theoretically been decided. The calculation procedure do not affects the relative adsorption/evaporation of the PAH, and the results that are calculated in percentages can therefore be regarded as more correct then results calculated in concentrations.

5.2 Pre-test

Results from the pre-test are presented in Table 4. The values from dibenz(a,h)-anthracene are not realistic and has not been taken into account. The results indicate that the adsorption/evaporation of the PAH is not considerably different between the lower and the higher concentrations.

Table 4. Percentage of the amount of PAH in moles and the amount of the PAH in moles per gram peat, that is adsorbed/evaporated from the samples.

	No peat PAH 100/50 µg/l	1 g peat No PAH	1 g peat PAH 100/50 µg/l	1 g peat PAH 50/25 µg/l	No peat PAH100/50 µg/l	1 g peat No PAH	1 g peat PAH 100/50 µg/l	1 g peat PAH 50/25 µg/l
	ads./eva. (10^{-7} mole)		q (10^{-7} mole/g)		%			
Naphthalene	3,84	nd	3,68	3,75	99	nd	99	99
Acenaphthylene	3,17	nd	2,75	2,76	97	nd	89	87
Acenaphthene	3,23	nd	2,81	2,75	100	nd	92	88
Fluorene	2,73	nd	2,50	2,56	91	nd	88	88
Phenanthrene	1,17	nd	1,19	1,25	83	nd	90	92
Anthracene	2,74	nd	2,59	2,71	98	nd	97	99
Fluoranthene	1,02	nd	1,02	1,15	82	nd	88	96
Pyrene	1,04	nd	0,99	1,14	84	nd	85	95
Benzo(a)anthracene*	0,73	nd	0,91	1,05	66	nd	88	98
Chrysene*	0,79	nd	0,92	1,03	72	nd	89	97
Benzo(b)flouranthene*	0,80	nd	0,88	0,95	81	nd	94	99
Benzo(k)flouranthene*	0,63	nd	0,81	0,93	64	nd	86	97
Benzo(a)pyrene*	0,71	nd	0,82	0,94	71	nd	88	98
Indeno(1,2,3-cd)pyrene*	0,69	nd	0,79	0,87	77	nd	92	99
Benzo(g,h,i)perylene	0,67	nd	0,65	0,83	74	nd	76	95
Dibenz(a,h)-anthracene*	0,90	nd	-3,07	0,29	100	nd	-337	35
PAH total	24,85	-	20,25	24,96	89	-	91	94
PAH* total	5,25	-	2,07	6,06	78	-	87	99

nd = Not detected

* = Carcinogenic PAH

The areas of the PAH-16 in the chromatogram were larger for the higher concentration, and therefore this concentration was used in the proceeding experiments. The results from the sample without any peat indicate that a large part of the PAH is lost due to adsorption to surfaces of the equipment and through evaporation. The same sample also slightly indicates that the lighter PAH is lost to a larger extent when peat is absent. Further, an indication can be seen that the heavier PAH are lost to a greater extent to adsorption/evaporation in the samples with peat compared with the sample without peat, which further indicates that the peat adsorb the heavier PAH to larger extent than the lighter PAH. The results for the q is difficult to evaluate as the loss of the PAH is not only due to adsorption to the peat.

5.3 Testing the extraction method

This experiment implies that heptane alone is a better elution solvent than a mixture of heptane and MTBE. This could be seen as the ratio between the area of the PAH and the area of the IS was slightly greater for the heptane than for the mixture of heptane and MTBE. Further it was concluded that it is easier to handle one elution solvent than two elution solvents that are not mixable, and that heptane is preferred to use due to its less toxic character. The results also imply that the naphthalene- d_8 has a low recovery of about 1 %.

5.4 Sorption isotherm experiment

The results from this experiment showed that only the sorption isotherm for indeno(1,2,3-cd)pyrene could be adjusted to a Freundlich isotherm ($r^2 = 0.90$), with a Freundlich coefficient of 0.31. The isotherm for phenanthrene ($r^2 = 0.53$) and benzo(b)fluoranthene* ($r^2 = 0.62$) had rather high, but not enough, probability to be able to be adjusted to a Freundlich isotherm. The Koc could not be calculated as none of the PAH could be fitted to a linear isotherm. Results in terms of adsorption/evaporation of the PAH are presented in Table 5. The values of the benzo(g,h,i)perylene are not realistic, and have not been taken into any concern. These results indicate that the adsorption/evaporation is great for all the PAH. Further, no apparent trend in adsorption can be seen in between the PAH and between the different samples. The sorption q is decreasing with increasing amount of peat. This is an indication that the maximum sorption capacity of peat is not achieved.

Table 5. The percentage of the amount of PAH in moles and the amount of the PAH in moles per gram peat that, is adsorbed/evaporated from the samples with 1, 0.75, 0.5, 0.25 and 0.1 gram of peat.

	1	0.75	0.5	0.25	0.1	1	0.75	0.5	0.25	0.1
	q (10 ⁻⁷ mole/g)					%				
Naphthalene	3.69	4.69	7.37	14.97	27.86	98	91	96	98	97
Acenaphthylene	3.12	4.02	5.98	12.49	30.27	98	93	93	97	95
Acenaphthene	2.94	3.33	4.91	12.06	31.52	94	78	78	95	100
Fluorene	2.85	3.37	3.68	8.59	26.48	98	85	63	74	91
Phenanthrene	1.24	1.64	2.00	4.04	10.47	92	88	73	74	77
Anthracene	2.70	3.68	5.42	10.95	26.76	100	99	98	100	98
Fluoranthene	1.14	1.62	2.34	4.72	11.55	96	99	96	98	96
Pyrene	1.14	1.62	2.34	4.72	11.59	96	99	96	98	97
Benzo(a)anthracene*	0.93	1.23	1.85	3.33	9.35	88	85	86	78	88
Chrysene*	0.85	1.10	1.55	2.79	8.82	81	76	72	66	83
Benzo(b)fluoranthene*	0.92	1.20	1.75	3.56	9.11	96	92	90	92	95
Benzo(k)fluoranthene*	0.82	1.01	1.44	2.87	8.07	85	78	74	75	84
Benzo(a)pyrene*	0.86	1.08	1.57	3.16	8.59	90	83	81	82	90
Indeno(1,2,3-cd)pyrene*	0.55	0.34	0.53	2.72	5.63	64	29	31	78	65
Benzo(g,h,i)perylene	-5.34	-9.52	-2.44	-18.97	-20.43	-587	-788	-133	-522	-223
Dibenz(a,h)-anthracene*	0.59	1.10	0.47	2.94	2.01	69	93	28	84	25
PAH total	19.02	21.51	40.75	74.93	207.64	41	56	31	41	24
PAH* total	5.53	7.06	9.16	21.37	51.57	18	24	34	21	24

* = Carcinogenic PAH

Table 6. The percentage of the amount of PAH in moles and the amount of the PAH in moles per gram peat that, is adsorbed/evaporated from the samples with 1, 0.75, 0.5, 0.25 and 0.1 gram of peat.

	1	0.75	0.5	0.25	0.1	1	0.75	0.5	0.25	0.1
	q (10 ⁻⁷ mole/g)					%				
Naphthalene	3.59	4.89	7.58	10.34	38.00	99	98	99	70	99
Acenaphthylene	2.80	3.78	5.89	4.87	30.38	92	90	92	41	94
Acenaphthene	2.62	3.38	5.85	5.60	31.51	87	82	92	47	99
Fluorene	2.36	3.23	4.78	5.69	21.20	85	84	82	51	72
Phenanthrene	1.31	1.80	2.73	5.32	13.56	100	100	100	99	99
Anthracene	2.60	3.56	5.41	10.22	26.02	99	99	99	95	95
Fluoranthene	1.13	1.50	2.30	3.86	10.04	98	94	95	82	83
Pyrene	1.13	1.49	2.29	3.83	10.12	98	94	95	82	84
Benzo(a)anthracene*	0.98	1.27	2.01	2.94	-2.59	97	91	94	71	-22
Chrysene*	0.97	1.24	1.97	2.09	-5.64	95	89	92	52	-49
Benzo(b)fluoranthene*	0.91	1.19	1.81	2.46	5.43	98	94	93	66	57
Benzo(k)fluoranthene*	0.89	1.16	1.83	2.46	-1.63	96	92	94	66	-14
Benzo(a)pyrene*	0.90	1.20	1.85	2.50	-0.29	98	94	96	67	-1
Indeno(1,2,3-cd)pyrene*	0.83	1.13	1.72	2.78	2.95	99	97	97	81	35
Benzo(g,h,i)perylene	0.80	0.93	1.56	1.73	-0.35	95	81	89	52	-2
Dibenz(a,h)-anthracene*	0.81	1.11	1.58	0.31	-17.15	97	96	90	13	-189
PAH total	24.63	32.85	51.14	67.00	161.54	96	91	97	63	60
PAH* total	6.30	8.30	12.75	15.54	-18.92	96	90	98	40	-25

* = Carcinogenic PAH

5.5 Sorption of PAH and heavy metals

The results from this experiment are presented in Table 6. Due to an experimental error, the sorption of cadmium could not be evaluated. Also, an average value of the internal standards for the samples with 1 gram of peat and initial concentration, were used for the samples with 0.75, 0.5, 0.25 and 0.1 gram of peat. The sample with 0.1 gram of peat shows unrealistic values for the heavier PAH, and should not be taken into any concern. As the previous experiment, these results indicate that the adsorption/evaporation is great for all the PAH. Further, no apparent trend in adsorption can be seen in between the PAH and between the different samples. Notably is that the isotherm for phenanthrene ($r^2 = 0.86$), anthracene ($r^2 = 0.87$), fluoranthene ($r^2 = 0.74$), pyrene ($r^2 = 0.71$), benzo(b)fluoranthene* ($r^2 = 0.83$) and indeno(g,h,i)pyrene* ($r^2 = 0.86$) had a rather high, but not enough probability to be adjusted to a Freundlich isotherm. As the previous experiment, the sorption q is decreasing with increasing amount of peat. This is an indication that the maximum sorption capacity of peat is not achieved.

5.6 Relative composition of PAH-16

The relative composition of the PAH-16 left in the sample solutions for the isotherm experiment and for the experiment with PAH and cadmium was calculated (see Appendix 4 and 5). This was done to investigate any trend between the PAH that were not adsorbed/evaporated.

5.7 Internal standards

The areas from the chromatography of the IS used in the experiments are presented in Appendix 6. By comparing the areas for naphthalene-d₈ and chrysene-d₁₂, when they are supposed to have 100 % recovery during the test of the extraction method (see section 4.4), with the areas of naphthalene-d₈ and chrysene-d₁₂ during the other experiments, the recovery of these two IS, can be calculated.

6 Discussion

The results indicate that a large amount of the PAH is adsorbed and evaporated, thus giving low concentrations close to the limit of detection of the GC/MS instrument. The results also indicate that the PAH, except for indeno(g,h,i)perylene, could not be fitted to a Freundlich isotherm, and this could be due to the low concentrations of the PAH in the GC/MS instrument for these experiments. Any conclusions on the possible interference between the PAH and the cadmium is not possible due to these low concentrations and due to the experimental error (see section 5.5). Due to the low concentrations in the GC/MS instrument, the focus for this thesis has become to be on the methodology and on an improvement of the experimental part.

The low recoveries of the PAH from the experiments can have different explanations. As noted in the pre-test (see section 5.2), the great loss of the PAH when peat is absent indicates that the PAH is lost to adsorption to the equipment and to evaporation. This may not be valid for the samples with peat as the PAH may have larger affection for the peat than for the surfaces of the equipment and for being evaporated. For example did Sturm *et al.* (1998) find that the adsorption of the PAH on walls of glass vessels is less abundant when humic substances is present than when they are not. An explanation for the low recoveries is losses during the SPE procedure. This indication was observed due to the low recovery of the naphthalene-d8 when testing the extraction method (see section 5.3). The low recovery is probably due to evaporation of the naphthalene-d8, but multiple experiments on this needs to be performed to be able to confirm this indication. One explanation for the losses during the SPE procedure is that the PAH may have been evaporated during the drying of the SPE-disk before applying the elution solvent. This explanation could be confirmed for example that Mayer *et al.* (1994) observed lower recovery of semi-volatile compounds when longer drying times were applied before the elution step. The evaporation should thus be seen in the results as a trend towards larger losses for the lighter PAH. This trend may also appear due to the greater difficulties to extract low-log Kow (4-6) compounds owing to their higher aqueous solubility (Ridal *et al.*, 1997) This trend can only be seen for the sample without peat in the pre-test (see section 5.2).

Another explanation for the low recoveries could be that the SPE-disk was not appropriate. The DOM may have been adsorbed in the disk, thus competing with the PAH for the adsorption sites (Ridal *et al.*, 1997). The adsorption of peat particles to the SPE-disk was apparent during the experiments as the disk obtained a brownish color on spots where the filter aid had displaced itself, and that were directly exposed to the sample solution during the extraction. Also, the PAH that were associated with the mobile peat fraction (e.g. organic colloids and humic substances) passed probably through the SPE-disk (Sturm *et al.*, 1998; Brown *et al.*, 2003), thus giving a underestimation of the mobile PAH. Thus another disk or a combination of disks may improve the method.

The losses during the SPE procedure may also been due to the initial solution. The prepared initial solution for the experiments formed a precipitation that evidently consisted of the PAH. This was not surprising due to the low solubility of the PAH. These particles could have been removed from the samples during the experimental procedure, such as clogged on the filter aid, but perhaps also clogged on the silene wool during the filtration. Other explanation could be that the PAH was readably oxidized in contact with the sunlight during the SPE procedure, but this process is believed to be relatively slow.

To improve the experimental procedure, the PAH should be directly added to each beaker. This would prevent an uneven distribution of the PAH between the beakers, that most likely occurred due to the precipitations. The initial concentration should be assumed to the amount that is added, as the real initial concentration is difficult to determine, due to adsorption to the surfaces of the beakers and due to the precipitations. Further, the initial concentration could be raised to a higher concentration, even though the concentration exceeds the solubility of the PAH in water. This is because of that the equilibrium state of the PAH is suggested to shift from an adsorption to the surfaces of the beakers and from the precipitations towards an adsorption to the peat, when peat is present.

The concentrations of the PAH that were analysed in the GC/MS instrument were close to the limit of detection and therefore the values of the areas for each PAH were integrated manually. The values of the areas of the PAH showed frequently a great difference between the manual and the automatic integration, and the values for the manual integration was used here. In addition, the analysis with GC/MS instrument has a marginal of errors of 20 %, which has to be taken into account.

No apparent trend of the relative composition of the PAH that is left in the sample solutions in the isotherm experiment (se section 5.4), can be seen (se Appendix 4). In the experiment with PAH and cadmium (se section 5.5), the relative composition of the PAH, that is left in the sample solutions, indicates a shift from the high and middle molecular weight PAH to the low molecular weight PAH as more peat is added (see Appendix 5). Also a shift towards the carcinogenic PAH can be seen as more peat is added in the sorption isotherm experiment, whereas the opposite is occurring at the experiment with PAH and cadmium.

The efficiency of the elution solvent should also be questioned. Heptane may not be the best elution solvent for PAH and further investigation of this should be made. Finally the equilibrium time could be extended to one week to ensure that equilibrium is achieved. This would facilitate the construction of a sorption isotherm, as the sorption isotherm depicts the distribution of a substance in equilibrium. A contact time of one week between the PAH and peat in a field filter may, however, not be realistic.

7 Conclusions

The results from this project show that *Sphagnum* peat moss has a good potential to be used as a filter material for waters contaminated with PAH, but the experimental procedure needs to be improved before reliable results for the sorption isotherms can be obtained:

- Heptane was a better elution solvent than a mixture of heptane and MTBE for the SPE procedure
- The higher concentration as initial concentration of 100/50 µg/l was better to use than the lower concentration of 50/25 µg/l.
- Low recovery of naphthalene-d8 was seen for the SPE procedure.
- The Freundlich coefficient could only be determined for indeno(1,2,3-cd)-pyrene.
- The SPE extraction methodology needs to be improved to ensure a higher recovery of the specific PAH, but especially for the most volatile PAH, in waters such as leachates from peat containing humic substances.
- The accuracy of the quantification of PAH in low concentrations needs to be determined, and the quantification method further improved.
- The beaker tests should be done with higher concentrations of the specific PAH, to ensure more accurate quantification and to give better results as basis for construction of isotherms. The PAH should also be added directly into each test beaker to avoid problems with precipitation in the initial solution. If possible these experiment should be carried out in closed vessels.

8 References

- 3M. Instructions for use-Extraction disks for environmental analysis.
- Berg, B. (2000). "Litter decomposition and organic matter turnover in northern forest soils." Forest Ecology and Management **133**(1-2): 13-22.
- Bergner, K. (1995). Vad innehåller torv? – En sammanställning av botaniska, fysikaliska och kemiska data. Umeå. SLU Reprocentralen Umeå Sweden.
- Bernal, J.L., Nolzal, M.J., Toribio, L., Serna, M.L., Borrell, F., Marcé, R.M., Pocurull, E. (1997). "Determination of polycyclic aromatic hydrocarbons in waters by use of supercritical fluid chromatography coupled on-line to solid phase extraction with disks." Journal of Chromatography **778**(1-2):321-328.
- Berset, J.D., Kuehne, P., Shoty, W. (2001). "Concentration and distribution of some polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in an ombrotrophic peat bog profile of Switzerland." The Science of The Total Environment **267**(1-3): 67-85.
- Brady, N.C., Weil, R.R. (2002). The Nature and Properties of Soils. Prentice Hall.
- Brown, J.N., Peake, B.M. (2003). "Determination of colloiddally-associated polycyclic aromatic hydrocarbons (PAHs) in fresh water using C18 solid phase extraction disks." Analytica chimica acta **486**(2): 159-169.
- Cuypers, C., Pancras, T., Grotenhuis, T., Rulkens, W. (2002). "The estimation of PAH bioavailability in contaminated sediments using hydroxypropyl- β -cyclodextrin and Triton X-100 extraction techniques." Chemosphere **46**(8): 1235-1245.
- Dachs, J., Bayona, J.M. (1997). "Large volume preconcentration of dissolved hydrocarbons and polychlorinated biphenyls from seawater. Intercomparison between C18 disks and XAD-2 column." Chemosphere **35**(8): 1669-1678.
- Edell, Å. (1997). Effects of natural organic matter on herbicide adsorption to activated carbon. Sanitary engineering. Gothenburg. Chalmers University of Technology.
- EMBL (1995). Gateway to Isoelectric Point Service. Available on the internet at www.embl-heidelberg.de/cgi/pi-wrapper.pl.
- Fredriksson, D., Tammela, P.-T., Larsson, L.-E. (1993). Torvmarker och jämförande arealer. Torvfakta. Storvreta. Stiftelsen Svensk Torvforskning (SST). **1**.
- Färnkvist, K., Österlund, Y. (2005). Contaminated soils: ICCP presentation. Naturvårdsverket. Paris.
- Gauthier, T.D., Seitz, W.R., Grant, C.L. (1987). "Effects of structural and compositional variations of dissolved humic materials on pyrene Koc values." Environ. Sci. Technol. **21**(3): 243-248.
- Gavaskar, A.R. (1999). "Design and construction techniques for permeable reactive barriers." Journal of Hazardous Materials **68**(1-2): 41-71.
- Gavaskar, A.R., Gupta, N., Sass, B., Janosy, R., Hicks, J. (2000). Design Guidance for Application of Permeable Reactive Barriers for Groundwater Remediation. Battelle Memorial Institute.
- Golder (2000). Fördjupad miljö- och hälsoriskbedömning inom och invid kv Lyftkranen. Stockholm. Golder Grundteknik KB.
- Grip, H., Rodhe, A. (2003). Vattnets väg från regn till bäck. Uppsala. Hallgren & Fallgren Studieförlag AB.
- Guerin, T.F., Horner, S., McGovern, T., Davey, B. (2002). "An application of permeable reactive barrier technology to petroleum hydrocarbon contaminated groundwater." Water Research **36**(1): 15-24.
- Honkonen, K. (2005). Markfilter. Available on the internet at www.marksaneringsinfo.net/markfilter.htm.
- Hwang, S., Cutright, T.J. (2002). "The impact on contact time on pyrene sorptive behavior by a sandy-loam soil." Environmental Pollution **117**(3): 371-378.
- Ju, D., Young, T.M. (2004). "Effects of competitor and natural organic matter characteristics on the equilibrium sorption of 1,2-dichlorobenzene in soil and shale." Environ. Sci. Technol. **38**(22): 5863-5870.
- ITRC, Interstate Technology and Regulatory Council (2005). Permeable Reactive Barriers: Lessons Learned/New Directions. PRB-4. Washington. D.C. Available on the internet at www.itrcweb.org.

- Kalmykova, Y. (2004). Leachate treatment of heavy metals by natural and residual product materials. Water Environment Transport, Chalmers University of Technology, Gothenburg.
- Kalmykova, Y. (2006). Alternative Adsorption Materials for treatment of contaminated waters. Water Environment Transport, Chalmers University of Technology, Gothenburg.
- Kanally, R.A., Harayama, S. (2000). "Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons by bacteria." *Bacteriology* **182**(8): 2059-2067.
- Kao, C.M., Lei, S.E. (2000). "Using a peat biobarrier to remediate PCE/TCE contaminated aquifers." *Water Research* **34**(3): 835-845.
- Karapanagioti, H.K., Sabatini, D.A., Kleinedam, S., Grathwohl, P., Ligouis, B. (1999). "Phenanthrene sorption with heterogeneous organic matter in a landfill aquifer material." *Chemical Earth (B)* **24**(6): 535-541.
- Kellner, E. (2003). Wetlands - different types. their properties and functions. *Dept of Earth Science/Hydrology*. Uppsala. Uppsala University.
- KEMI (2006). Prioriteringsguiden PRIO; Polycykliska aromatiska kolväten. Available on the internet at www.kemi.se.
- Kohl, S.D., Rice, J.A. (1998). "The binding of contaminants to humin: a mass balance." *Chemosphere* **36**(2): 251-261.
- Kohl, S.D., Rice, J.A. (1999). "Contribution of lipids to the nonlinear sorption of polycyclic aromatic hydrocarbons to soil organic matter." *Organic Geochemistry* **30** (8): 929-936.
- Kördel, W., Dassenakis, M., Lintelmann, J., Padberg, S. (1997). "The importance of natural organic material for environmental processes in waters and soils." *Pure & Appl. Chemistry* **69**(7): 1571-1600.
- Laboratory 3076, I.o.P.a.A.C. (2006). "Humic substances." Available on the internet at www.fch.vutbr.cz/home/kucerik/frame1.htm
- Leenheer, J.A. (2004). "Comprehensive assessment of precursors. diagenesis and reactivity to water of dissolved and colloidal organic matter." *Water Science and Technology: Water Supply* **4**(4): 1-9.
- Loffredo, E., D'Orazio, V., Brunetti, G., Senesi, N. (1999). "Adsorption of chlordane onto humic acids from soils and pig slurry." *Organic Geochemistry* **30**(6): 443-451.
- Lovley, D.R., Coates, J.D., B.-H., E.L., Phillips, E.J.P., Woodward, J.C. (1996). "Humic substances as electron acceptors for microbial respiration." *Nature* **382**(6590): 445-448.
- Manoli, E., Samara, C. (1999). "Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis." *Trends in analytical chemistry* **18**(6): 417-428.
- Marcé, R.M., Borrull, F. (2000). "Solid-Phase extraction of polycyclic aromatic compounds." *Journal of Chromatography A* **885** (1-2): 273-290.
- Mayer, M.L., Poole, C.F. (1994). "Identification of the procedural steps that affect recovery of semi-volatile compounds by solid-phase extraction using cartridge and particle-loaded membrane (disk) devices." *Analytica chimica acta* **294**(2): 113-126.
- Mcbride, M.B. (1994). *Environmental chemistry of soils*. Oxford University Press. Inc.
- McCarty, J.F., Roberson, L.E., Burrus, L.W. (1989). "Association of benzo(a)pyrene with dissolved organic matter: prediction of K_{dom} from structural and chemical properties." *Chemosphere* **19**(12): 1911-1920.
- Nam, K., Kim, J.Y. (2002). "Role of loosely bound humic substances and humin in the bioavailability of phenanthrene in aged soil." *Environmental Pollution* **118**(3): 427-433.
- Naturvårdsverket (2006). Tungmetaller. Available on the internet at www.naturvardsverket.se
- Naturvårdsverket (2003). Torv. Available on the internet at www.naturvardsverket.se.
- Naturvårdsverket (2002). Metodik för inventering av förorenade områden - Rapport 4918.
- Naturvårdsverket (1997). Generella riktvärden för förorenad mark - Rapport 4638.
- Nielsen, T., Helweg, C., Siigur, K., Kirso, U. (1997). "Application of HPLC capacity coefficient to characterize the sorption of polycyclic aromatic compounds to humic acids." *Talanta* **44**(10): 1873-1881.
- Pan, B., Xing, B.S., Liu, W.X., Tao, S., Lin, X.M., Zhang, X.M., Zhang, Y.X., Xiao, Y., Dai, H.C., Yuan, H.S (2006). "Distribution of sorbed phenanthrene and pyrene in different humic fractions of soils and importance of humin." *Environmental Pollution* **143**(1):24-33.

- Perhans, A. (2003). Utlakning av polycykliska aromatiska kolväten (PAH) ur asfalt och förorenad mark. IVL Svenska Miljöinstitutet AB. B1532.
- Potrebko, I. (2004). Removal of organic contaminants from landfill leachate by natural and rest product adsorbents. Water Environment Transport. Gothenburg. Chalmers University of Technology.
- Raber, B., Kögel-Knaber, I., Stein, C., Klem, D. (1998). "Partitioning of Polycyclic aromatic hydrocarbons to dissolved organic matter from different soils." Chemosphere **36**(1): 79-97.
- Rasmussen, G., Fremmersvik, G., Olsen, R.A. (2002). "Treatment of creosote-contaminated groundwater in a peat/sand permeable barrier-a column study." Journal of Hazardous Materials **93**(3): 285-306.
- Ridal, J., Fox, M., Sullivan, C., Maguire, R., Mazumder, A., Lean, D. (1997). "Evaluation of Automated Extration of Organochlorine Contaminants from Freshwater." Journal of Analytical Chemistry **69**(4): 711-717.
- Schilstra, A.J. (2004). "Peat resource." Encyclopedia of Energy: 805-810.
- SLU (2002). Laborationskompendium i marklära. 2002:2. Sveriges Lantbruks Universitet, Institutionen för markvetenskap. Uppsala.
- SLU (2003). Undervisningsmaterial för kursen markkemi. Sveriges Lantbruks Universitet, Institutionen för Markvetenskap, Uppsala.
- SLU (2005). Undervisningsmaterial för kursen marksanering. Sveriges Lantbruks Universitet, Institutionen för skogsekologi. Umeå.
- Stevenson, F.J. (1994). Humus chemistry: genesis, composition, reactions. New York. John Wiley cop.
- Sturm, B., Knauth, H.-D., Theobald, N., Wünsch, G. (1998). "Hydrofobic organic micropollutants in samples of coastal water: efficiencies of solid-phase extraction in the presence of humic substances." Journal of Analytical Chemistry **361**(8): 803-810.
- Suthersan, S.S. (2002). Natural and enhanced remediation systems CRC Press LLC.
- Svensson, A. (2003). PAH-undersökning av ytjord inom Göteborg. Rapport R 2003:10. Göteborgs Stad. Miljöförvaltningen.
- Sylvia, D.M., Fuhrmann, J.J., Hartel, P.G., Zuberer, D.A. (1998). Principles and applications of soil microbiology. Prentice Hall Inc.
- Thorsen, W.A., Cope, G.W., Shea, D. (2004). "Bioavailability of PAHs; Effects of Soot Carbon and PAH source." Environ. Sci. Technol. **2004**(38): 2029-2037.
- Trembley, L., Kohl, S.D., Rice, J.A., Gagne, J.-P. (2005). "Effects of temperature, salinity, and dissolved humic substances on the sorption of polycyclic aromatic hydrocarbons to estuarine particles." Marine Chemistry **96**(1-2): 21-34.
- USEPA (1995). Method 525.2-Determination of organic compounds in drinking water by liquid-solid extraction and capillary column gas chromatography/mass spectrometry. N. e. r. l.-O. o. r. a. development.
- Utvik, T., Durell, G., Johnsen, S. (1999). "Determining Produced water originating Polycyclic Aromatic Hydrocarbons in North sea waters: Comparison of sampling techniques." Marin Pollution Bulletin **38**(11): 977-989.
- Weber, J., Michalczyk, A. (1997). "Soil humic substanses." Available on the internet at www.ar.wroc.pl/~weber/humic.htm
- Viraraghavan, T., Slough, K. (1999). "Sorption of pentachlorophenol on peat-bentonite mixtures." Chemosphere **39**(9): 1487-1496.
- Voice, T.C., Rice, C.P., Weber, W.J. (1983). "Effects of solids concentration on the sorptive partitioning of hydrophobic pollutants in aquatic systems." Environ. Sci. Technol. **17**(9): 513-518.
- Zytner, R.G. (1994). "Sorption of benzene, toluene, etylbenzene and xylenes to various media." Journal of Hazardous Materials **38**(1): 113-126.

9 Links

www.prb-net.org
www.rtdf.org/public/permbarr
www.marksaneringsinfo.net
www.renaremark.se

APPENDIX 1



CERTIFICATE OF ANALYSIS

FOR LABORATORY USE ONLY - READ MSDS PRIOR TO USE

110 Benner Circle
 Bellefonte, PA 16823-8812
 Tel: (800) 356-1688
 Fax: (814) 353-1309

Catalog No.: 31264 Lot No.: A034449
 Description: 610 PAH Calibration Mix A
 Expiration Date¹: September 2011 Storage: Refrigerate

Elution Order	Compound	CAS#	Percent Purity ²	Concentration ³	Percent Uncertainty ⁴
1	Naphthalene	91-20-3	99%	1000 ug/mL	+/- 0.1
2	Acenaphthylene	208-96-8	99%	1000 ug/mL	+/- 0.1
3	Acenaphthene	83-32-9	99%	1000 ug/mL	+/- 0.1
4	Fluorene	86-73-7	98%	1000 ug/mL	+/- 0.1
5	Phenanthrene	85-01-8	99%	500 ug/mL	+/- 0.1
6	Anthracene	120-12-7	99%	1000 ug/mL	+/- 0.1
7	Fluoranthene	206-44-0	98%	500 ug/mL	+/- 0.1
8	Pyrene	129-00-0	99%	500 ug/mL	+/- 0.1
9	Benz(a)anthracene	56-55-3	99%	500 ug/mL	+/- 0.1
10	Chrysene	218-01-9	98%	500 ug/mL	+/- 0.1
11	Benzo(b)fluoranthene	205-99-2	99%	500 ug/mL	+/- 0.1
12	Benzo(k)fluoranthene	207-08-9	99%	500 ug/mL	+/- 0.1
13	Benzo(a)pyrene	50-32-8	98%	500 ug/mL	+/- 0.1
14	Indeno(1,2,3-cd)pyrene	193-39-5	99%	500 ug/mL	+/- 0.1
15	Dibenz(a,h)anthracene	53-70-3	99%	500 ug/mL	+/- 0.1
16	Benzo(g,h,i)perylene	191-24-2	99%	500 ug/mL	+/- 0.1

Solvent: Methylene Chloride 75-09-2 99%

Column:
 30m x .25mm x .5um
 Rtx-5 (cat.#10238)

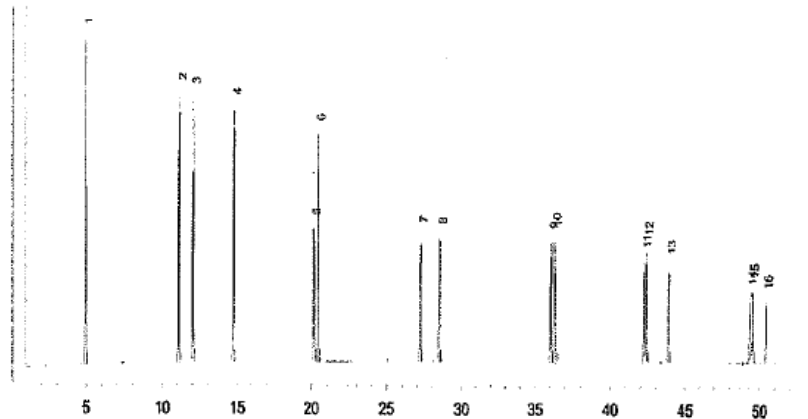
Carrier Gas:
 hydrogen @ 40 cm/sec.

Temp. Program:
 100°C to 330°C @ 4° C/min.

Inj. Temp:
 250°C

Det. Temp:
 330°C

Det. Type:
 FID



Manufactured By: FJT

John Lidgett
 John Lidgett - QA Analyst

1 Expiration date of the unopened ampul stored at recommended temperature.
 2 Purity was determined by one or more of the following techniques: GC/FID, HPLC, GC/ECD, GC/MS. Value rounded to the nearest LOWER whole percentage. In addition to detectors listed above, chemical identity and purity are confirmed using 1 or more of the following: MS, DSC, solid probe MS, GC/FPD, GC/NPD, GC/TC, FTIR, melting point, refractive index, and Karl Fisher. See data pack or contact Restek for further details.
 3 Based upon gravimetric preparation with balance calibration verified using NIST traceable weights (7 mass levels).
 4 Percent Uncertainty based upon balance AND ASTM Class A volumetric glassware accuracy.



APPENDIX 2

Solid Phase Extraction manual

Solid Phase Extraction procedure

1. Put high vacuum grease (silicon lubricant) on the shrewd part.
2. Pour beads uniformly on disc surface to about 1.0 cm depth.

Pre-wash

3. Add 20 ml heptane to the bed. **All solvent volumes should be sufficient to submerge the bead bed.**
4. Draw a small amount of solvent through the disk and release vacuum. Allow soaking for approximately one minute.
5. Turn on vacuum and draw remaining solvent through the disk and let vacuum continue to draw until disk has dried.

Condition

6. Add about 20 ml methanol to the reservoir
7. Draw a small amount through the disk with the vacuum. Release the vacuum and allow the disc and bead bed to soak for about one minute.
8. Draw the methanol down with vacuum to just above the level of the bed. **It is critical that a layer of methanol remain above the disk.** With bed in place, the level should be maintained just above the surface of the bead bed.
9. Add 20 ml milli-Q water to the reservoir. With vacuum on, draw level of water/methanol down, to just above the level of the bed. **A layer of fluid must remain on the surface of the disk.**
10. Turn off vacuum.

Extraction

11. Pour the sample into the reservoir and apply vacuum to draw through the disk. Flow rate is dependent on vacuum setting and solids content of the sample. However, recoveries are not affected by flow rate.
12. After sample extraction is complete, remove residual water from the disk by applying vacuum to dry the disk for approximately 5-20 minutes.

Elution

13. Place tip of filter base into the collection vessel.
14. Add 10 ml heptane to the sample container, carefully rinsing the sides. Transfer the methanol from the sample container to reservoir with a pipette, washing the walls of the reservoir in the process.
15. Apply vacuum and draw approximately 1 ml methanol through the disk. Vent the vacuum and allow the disk to soak for 30 seconds before reapplying vacuum to dry the disk
16. Repeat the elution process with 10 ml heptane

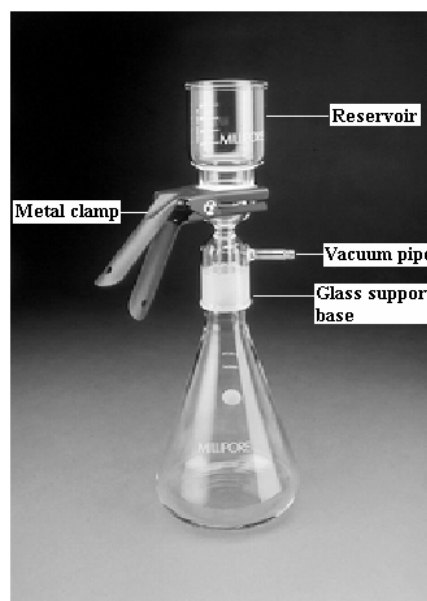


Figure 1. SPE equipment set-up. (Millipore)

APPENDIX 3

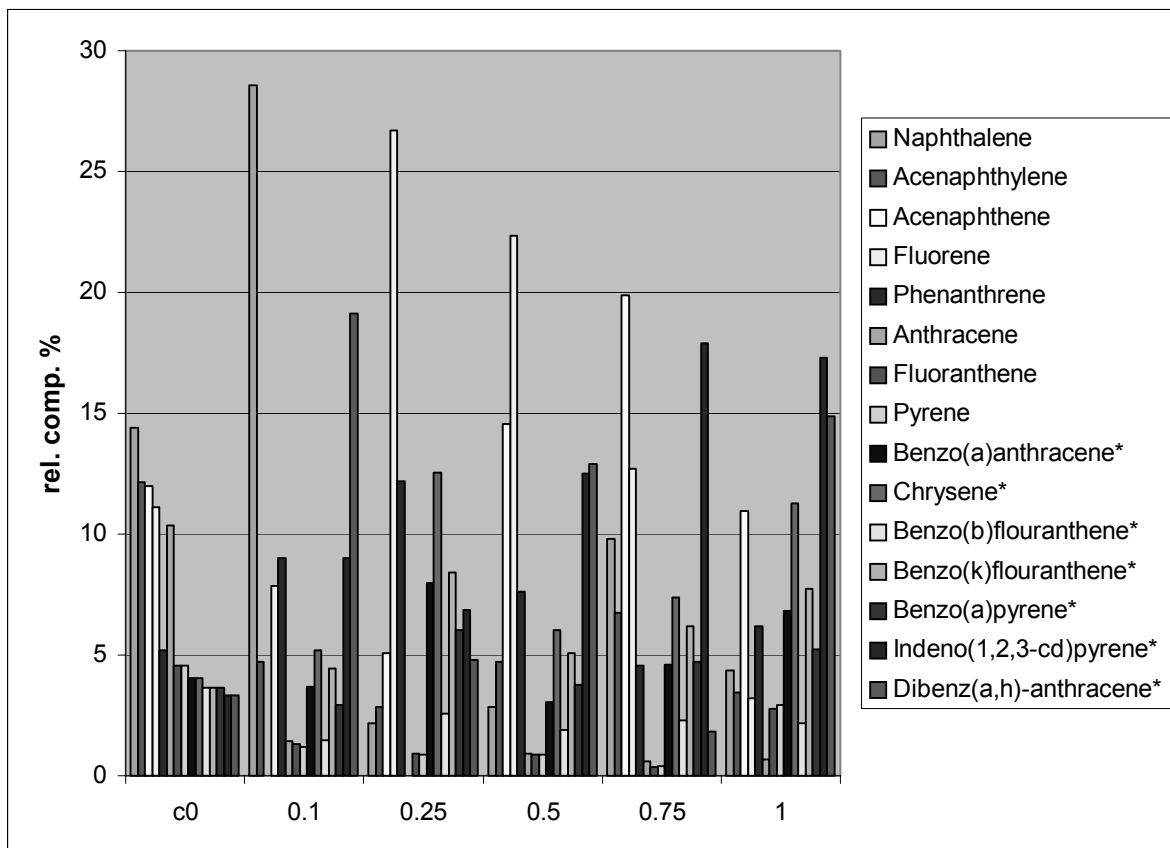
Retention times used for identification and quantification ions.

PAH compound	retention time	quantification ion
	t_s , min + / - 0.250 min	m / z
naphthalene	18.075	128.0
acenaphthylene	25.449	152.2
acenaphthene	26.288	153.2
fluorene	28.730	165.3
phenanthrene	33.179	178.2
anthracene	33.416	178.2
fluoranthene	38.740	202.2
pyrene	39.744	202.2
benzo(a)anthracene*	45.434	228.2
chrysene*	45.590	228.2
benzo(b)fluoranthene*	50.129	252.2
benzo(k)fluoranthene*	50.243	252.2
benzo(a)pyrene*	51.405	252.2
indeno(1,2,3-cd)pyrene*	55.963	276.3
benzo(g,h,i)perylene	57.208	276.3
dibenz(a,h)-anthracene*	56.178	278.4
naphthalene-d ₈	17.939	136.2
biphenyl-d ₁₀	23.491	164.2
pyrene-d ₁₀	39.663	212.3
chrysene-d ₁₂	45.385	240.3

APPENDIX 4

Relative composition, in percentages, of the PAH in moles, that is left in the solutions from the samples with 1, 0.75, 0.5, 0.25, 0.1 gram of peat and the initial solution (c0) for the isotherm experiment (see section 5.3). The values for benzo(g,h,i)perylene showed unrealistic values and has not be taken into account.

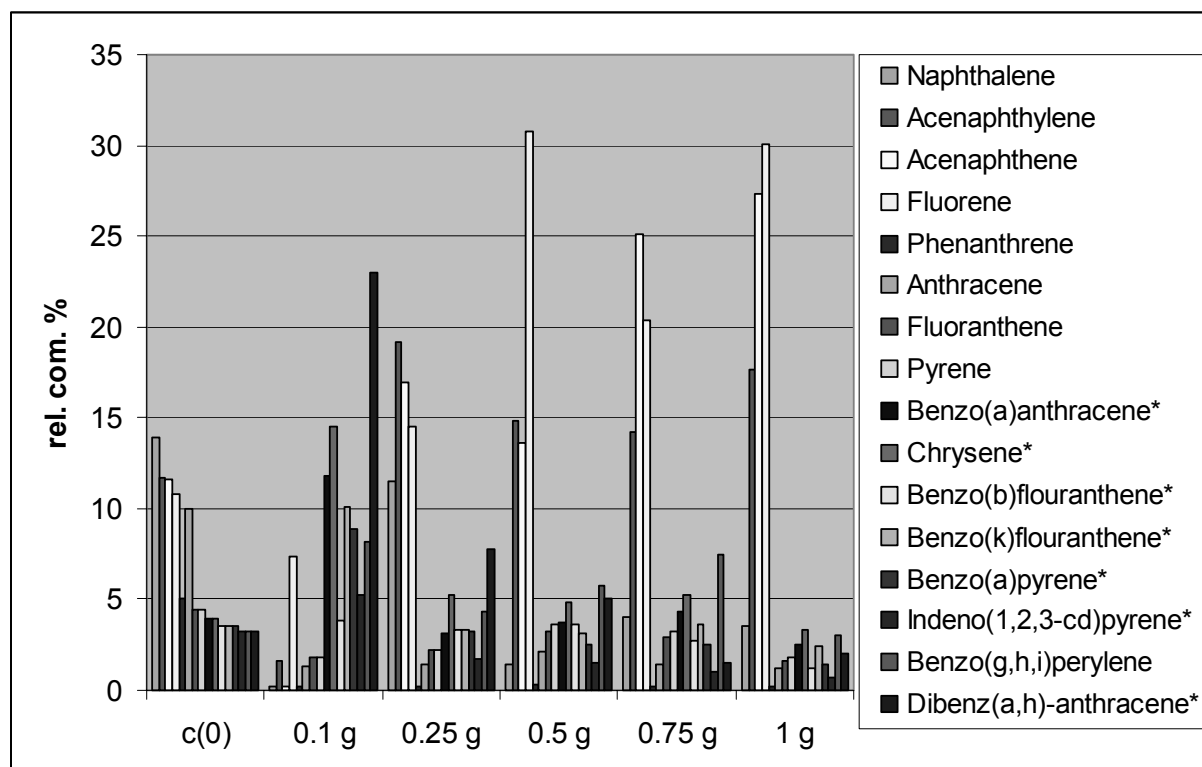
	c(0)	0.1	0.25	0.5	0.75	1
	rel. comp. %					
Naphthalene	14	29	2	3	10	4
Acenaphthylene	12	5	3	5	7	3
Acenaphthene	12	0	5	15	20	11
Fluorene	11	8	27	22	13	3
Phenanthrene	5	9	12	8	5	6
Anthracene	10	1	0	1	1	1
Fluoranthene	5	1	1	1	0	3
Pyrene	5	1	1	1	0	3
Benzo(a)anthracene*	4	4	8	3	5	7
Chrysene*	4	5	13	6	7	11
Benzo(b)flouranthene*	4	1	3	2	2	2
Benzo(k)flouranthene*	4	4	8	5	6	8
Benzo(a)pyrene*	4	3	6	4	5	5
Indeno(1,2,3-cd)pyrene*	3	9	7	13	18	17
Benzo(g,h,i)perylene	3	83	190	42	223	334
Dibenz(a,h)-anthracene*	3	19	5	13	2	15
PAH total	100	100	100	100	100	100
PAH* total	26	46	49	45	45	65



APPENDIX 5

Relative composition, in percentages, of the PAH in moles, that is left in the solutions from the samples with 1, 0.75, 0.5, 0.25, 0.1 gram of peat and the initial solution (c0) for the experiment with PAH and cadmium (see section 5.4). The values for the sample with 0.1 g peat show unrealistic values and should not be taken into account.

	c(0)	0.1	0.25	0.5	0.75	1
	rel. comp. %					
Naphthalene	14	0	11	1	4	4
Acenaphthylene	12	2	19	15	14	18
Acenaphthene	12	0	17	14	25	27
Fluorene	11	7	14	31	20	30
Phenanthrene	5	0	0	0	0	0
Anthracene	10	1	1	2	1	1
Fluoranthene	4	2	2	3	3	2
Pyrene	4	2	2	4	3	2
Benzo(a)anthracene*	4	12	3	4	4	2
Chrysene*	4	15	5	5	5	3
Benzo(b)fluoranthene*	4	4	3	4	3	1
Benzo(k)fluoranthene*	4	10	3	3	4	2
Benzo(a)pyrene*	4	9	3	2	2	1
Indeno(1,2,3-cd)pyrene*	3	5	2	2	1	1
Benzo(g,h,i)perylene	3	8	4	6	7	3
Dibenz(a,h)-anthracene*	3	23	8	5	2	2
PAH total	100	100	100	100	100	100
PAH* total	25	77	28	24	21	14



APPENDIX 6

Areas from the chromatogram of the internal standards used in the experiments. In the pre-test 5 µg of each internal standard (naphthalene-d₈ and chrysens-d₁₂) were added to each sample. For the testing of the extraction method, isotherm experiment, and for the experiment with PAH and cadmium, 100 µg of naphthalene-d₈, 100 µg of biphenyl-d₁₀, 5 µg pyrene-d₁₀ and 5 µg of chrysene-d₁₂ were added to each sample.

		Napthalene-d ₈	Biphenyl-d ₁₀	Pyrene-d ₁₀	Chrysens-d ₁₂
Pre-test	Co	275			26353
	No peat PAH 100/50 µg/l	239			21489
	1 g peat PAH 100/50 µg/l	337			19084
	1 g peat PAH 50/25 µg/l	177			16584
Testing the extraction method	Co Heptane	1280	723	234	2986
	Co Heptene+MTBE	1055	602	321	3637
	100 % recovery	24695			18567
Sorption isotherm experiment	Co	1508	872	591	1387
	1 g	2161	1374	910	452
	0,75 g	1599	873	4019	372
	0,5 g	1921	1345	2894	812
	0,25 g	1616	1042	2629	360
	0,1 g	1144	744	1468	751
Experiment with PAH and cadmium	Co	1413	771	574	876
	0,1 g	1742	946	1141	195