Remediation of soils, sediments and sludges by extraction with organic solvents

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Stellingen

1. Het grote voordeel van het reinigen van extractie- en baggerslib door extractie met aceton ten opzichte van de reiniging met behulp van biologische methoden, is dat slibben met verouderde PAK-verontreiniging kunnen worden gereinigd tot aan de wettelijke streefwaarde voor de PAK-concentratie in schone grond (PAK = polycyclische aromatische koolwaterstof).
   Dit proefschrift

2. Tegen de verwachting in blijkt het bij een verouderde PAK-verontreiniging moeilijker te zijn om PAK's met relatief lage molecuulgewichten, zoals fenanthreen en anthraceen, geheel uit slib te extraheren met aceton dan PAK's met relatief hoge molecuulgewichten, zoals benzo[g,h,i]peryleen en indeno[1,2,3-c,d]pyreen.
   Dit proefschrift

3. Het WAU-acetonproces is een technisch, financieel en milieuhygiënisch haalbare reinigingstechniek voor gronden en slibben met hoge organische stof-, water- en kleigehalten die verontreinigd zijn met biologisch slecht beschikbare of moeilijk afbreekbare organische verbindingen.
   Dit proefschrift

4. Modellen, voor het beschrijven van de desorptiesnelheid van organische verontreinigingen uit grond, die uitgaan van twee of drie verschillende soorten grondbestanddelen, zoals amorfe organische stof en kristallijne organische stof, en waarbij verondersteld wordt dat ieder bestanddeel een verschillend effect heeft op de desorptiesnelheid (b.v. gepostuleerd door Xing en Pignatello) zijn pas wetenschappelijk van groot belang indien een verband kan worden gelegd tussen de desorptiesnelheid en *meetbare* fysisch/chemische eigenschappen van de grond(bestanddelen).
   B. Xing and J.J. Pignatello, Environ. Sci. Technol., vol. 31 (1997), 792-799.

5. Het verschil tussen een leider en een lijder zit in de mate van overwicht.

6. Vooral mensen die sterk bij hun werk betrokken zijn en dit werk zeer serieus nemen zijn gevoelig voor aandoeningen die te maken hebben met fysieke overbelasting zoals RSI (Repetitive Strain Injury).

7. In tegenstelling tot wat gesuggereerd wordt, geven analysemethoden voor het meten van de PAK-concentratie in grond, zoals NEN 5731, slechts een semi-kwantitatief beeld van de werkelijke PAK-verontreiniging.
Nederlands Normalisatie-instituut, NEN 5731, 2^{e} ontwerp, okt. 1994

8. De Mens zou zich als een beschaafder en menselijker ras ontwikkeld hebben als men zich wat meer had aangetrokken van het volgende gezegde:
'Wat ge niet wilt dat u geschiedt, doe dat ook een ander niet'.

9. Voor een experimenteel te bestuderen systeem is het kiezen van statistisch optimale waarden voor de stuurbare variabelen alleen mogelijk als het verband tussen de variabelen en het systeem globaal duidelijk is.
N.a.v. de case-studies: Optimaal ontwerpen van proeven bij enige AIO-projecten, D. Rasch en A. Vervuurt, Department of Mathematics, Wageningen Agricultural University, feb. 1994.

10. Hoewel het tempo van een muziekstuk goed gemeten en vastgesteld kan worden, is de beleving van het tempo zeer subjectief. Het hangt ondermeer af van de moeilijkheidsgraad van het muziekstuk voor de betreffende muzikant, van zijn/haar humeur, en van de mate waarin het ritme dat de muzikant speelt, past bij dat wat de andere muzikanten spelen.

11. Verontreiniging van de bodem door PAK's heeft veel minder effect op de Volksgezondheid dan luchtverontreiniging door roken.

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Remediation of soils, sediments and sludges by extraction with organic solvents

E.R. Noordkamp

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Abstract

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Remediation of contaminated soils, sediments and sludges by extraction with organic solvents is still in the initial stages of development. So far hardly any scientific research has been carried out into this approach. Therefore, the main objective of the present investigation was to study the effect of several process parameters on the efficiency of the extraction step of a solvent extraction process for soils, sediments and sludges (generally indicated as solids) contaminated with polycyclic aromatic hydrocarbons (PAHs). The process parameters of interest were: type of solvent, extraction time, extraction procedure, water content of the extraction solvent, type of solids, size of the solid particles, and water content of the solids.

In the development of a remediation method, a critical factor is the analysis of the PAH concentration in the solids. Therefore, several extraction methods were investigated to remove PAHs from an aged sandy soil, a harbour sediment and an extraction sludge. Extraction with N-methyl-2-pyrrolidinone in a microwave oven at 130°C for one hour was the most efficient method for the extraction of PAHs. The second best method was extraction with a mixture of 80 vol.% acetone and 20 vol.% water in a microwave oven at 100°C for one hour.

Acetone is suitable for use in a solvent extraction process, because it is less toxic than most other organic solvents, easily biodegradable, and socially acceptable in the Netherlands. In addition, it showed high removal efficiencies in the extraction of spiked pyrene and benzo[a]pyrene from sandy, silty and clayey soils, even when water was present in the soil or extraction agent. In the extraction of air-dried soil with mixtures of acetone and water, maximum efficiencies were reached with 10 to 20 vol.% water in the mixture.

To determine the extraction efficiency of a mixture of 80 vol.% acetone and 20 vol.% water, a procedure comprising seven extraction steps was carried out at 20°C using a rotary tumbler for mixing. In this way, an aged extraction sludge and an aged harbour sediment were remediated. After seven extractions, the Dutch target level established for clean soil was reached in the sludge and almost reached in the sediment. The PAH concentrations decreased from about 1,000 mg kg^{-1} in the sludge and about 650 mg kg^{-1} in the sediment to about 2 mg kg^{-1} in both the sludge and the sediment. Of the PAHs studied, those of low molecular weight (phenanthrene, anthracene and fluoranthene) were found to be most difficult to remove from the solids.

Another important aspect of the extraction process is the rate at which PAHs are removed. Experiments revealed that about 90% of the PAHs concerned were desorbed from the aged sludge within 10 minutes of extraction with a mixture of 80 vol.% acetone and 20 vol.% water. Within 40 minutes, at least 95% of the PAHs concerned were removed from the sludge and the extraction was then assumed to be complete. The experimental desorption curves were fitted by means of a radial diffusion model and a first-order reaction model. The diffusion model fitted the curves best for a situation in which it is assumed that the PAH contamination is accumulated in the core of the sludge particles.

Because of the high extraction efficiencies and high desorption rates attained, realisation of the solvent extraction process with acetone is probably worthwhile. This process is especially suitable for the remediation of sediments and sludges containing high amounts of water and clay and contaminated with barely (bio)available or biodegradable organic contaminants.

Contents

Chapter 1

General introduction

Abstract

A remediation process for the treatment of contaminated soil, sediment and sludge based on extraction with organic solvents may be a useful technique in addition to the conventional remediation techniques being applied in the Netherlands. A solvent extraction process comprises five subprocesses: 1. pretreatment of the contaminated solids, 2. extraction of the contaminants from the solids, 3. separation of the solids and extraction solvent, 4. removal of the extraction solvent from the solids, 5. recovery of the extraction solvent. The most important subprocess is the extraction step itself (subprocess 2), because during this step the highest possible extraction efficiency and the amount of solvent needed for decontamination are established.

Extraction with organic solvents as studied in the USA is directed to application in practice, and so far hardly any studies have been conducted to gain more scientific and theoretical insight into the process itself. Therefore, the main objective of the present investigation was to study the effect of several process parameters on the efficiency of the extraction step of the solvent extraction process in order to develop an optimal process for the remediation of soils, sediments and sludges contaminated with polycyclic aromatic hydrocarbons (PAHs). PAHs frequently occur in soils, sediments and sludges in the Netherlands and are barely bioavailable. The process parameters investigated were: type of solvent, extraction time, extraction procedure, water content of the extraction solvent, type of solids, size of the solid particles, and water content of the solids.

1.1 Soil and sediment remediation in the Netherlands

Contamination of soil is a serious environmental problem in the Netherlands. Since the 1980s, many contaminated areas have been discovered and these cause serious social and economic problems. So far about 100,000 more or less highly contaminated sites have been detected in the Netherlands involving a total of 200 million tonnes of contaminated soil. The estimated costs for remediating these sites exceed 50 billion Dutch guilders [1]. The sites pose a risk to public health and the environment and most of them therefore need to be remediated. Another serious environmental problem concerns sediments dredged from waterways and harbours. Yearly, about 30 million cubic metres of sediment are dredged, about 30% of which are more or less heavily contaminated. At present, dredged clean sediment is returned to surface waters or spread on land, whereas dredged contaminated sediment is disposed of in special sediment depots. Because the latter has become a serious problem due to shortage of disposal capacity, the Dutch government has decided to expand both the disposal and treatment capacity. From an environmental viewpoint, treatment and reuse of contaminated sediments is preferable over their disposal. By the year 2000, about 20% of the dredged contaminated sediments should be treated and reused, and this percentage should further increase [2]. The development of a new technique for the remediation of contaminated soil and sediment may contribute to the solution of the environmental problems involved.

Nowadays, excavated soils and dredged sediments can be remediated by employing one of the following types of method [3]:

1. soil washing (extraction/wet classification),
2. thermal treatment,
3. biological treatment.

Soil washing consists of intensive mixing of contaminated solids and an extracting agent (comprising water-containing additives), followed by separation of the cleaned solid particles and contaminated extracting agent, and recovery of the latter. Thermal decontamination of soil or sediment generally consists of heating contaminated solids in order to evaporate the contaminants, which then move into the gas phase and are destroyed. Complete removal of the contaminants from the gas phase is carried out in a separate gas treatment system. Biological treatment consists of creating optimal conditions for the microbiological degradation of contaminants by influencing such factors as oxygen concentration, temperature, soil water content, pH and the availability of the contaminants to micro-organisms [3].

The current remediation methods cannot be applied efficiently to every soil, sediment and type of contamination. Soil washing is primarily suitable for the treatment of sandy soils with clay content values and humic content values below 10 to 15 wt%. By means of soil washing, both organic contaminants and heavy metals can be separated from the solids. However, these contaminants and clay particles accumulate in the residual sludge, which therefore has to be considered hazardous waste. Solvent extraction of this kind of residual sludge is studied in this dissertation together with contaminated sediments and soils. The term "sludge" or "extraction sludge" always refers to the residual sludge of a soil washing plant, whereas the term "solids" always refers to a combination of soil, sediment and sludge in this dissertation.

Thermal treatment is suitable for the removal of all types of organic contamination and can be applied to all types of solid. Such treatment may also reduce the leachability of heavy metals if high temperatures are applied. However, it is expensive if the solids contain high quantities of water and organic matter, because these are also evaporated during the treatment. Additionally, the removal of chlorinated organic compounds from solids is also expensive because of the high temperatures required and the fact that the process should be carefully controlled to prevent dioxin emission.

Biological treatment is suitable for all types of solid and most organic contaminants. However, barely bioavailable or barely biodegradable contaminants require a long remediation time, and biological treatment of contaminants usually results in relatively high residual concentrations in the solids [4].

A new technique for the remediation of soils, sediments and sludges is extraction with an organic solvent. This technique is being developed in, for instance, the USA for the remediation of contaminated sites [5]. In the Netherlands, extraction with organic solvents is thought to be especially suited for the treatment of excavated soils, dredged sediments and residual sludges of soil washing plants containing high amounts of clay, water and/or organic matter, which are contaminated with such barely bioavailable organic compounds as polychlorinated biphenyls and polycyclic aromatic hydrocarbons (PAHs). For these types of solid, the conventional remediation methods are not or less suitable.

The present investigation focusses on extraction with organic solvents for the removal of PAHs from soil, sludge and sediment as PAHs frequently occur in soils, sludge and sediments and are rather persistent to biological degradation. The properties of PAHs are explained in the next section.

1.2 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons are organic molecules consisting of two or more fused benzene rings. The Environmental Protection Agency (USA) selected 16 PAHs as being priority pollutants. Their chemical structure is shown in Figure 1.1; these PAHs are hereafter referred to as the (16) EPA-PAHs. The simplest PAH is naphthalene, which consists of two fused benzene rings, whereas the largest EPA-PAHs have six fused benzene rings (e.g. benzo[ghi]perylene).

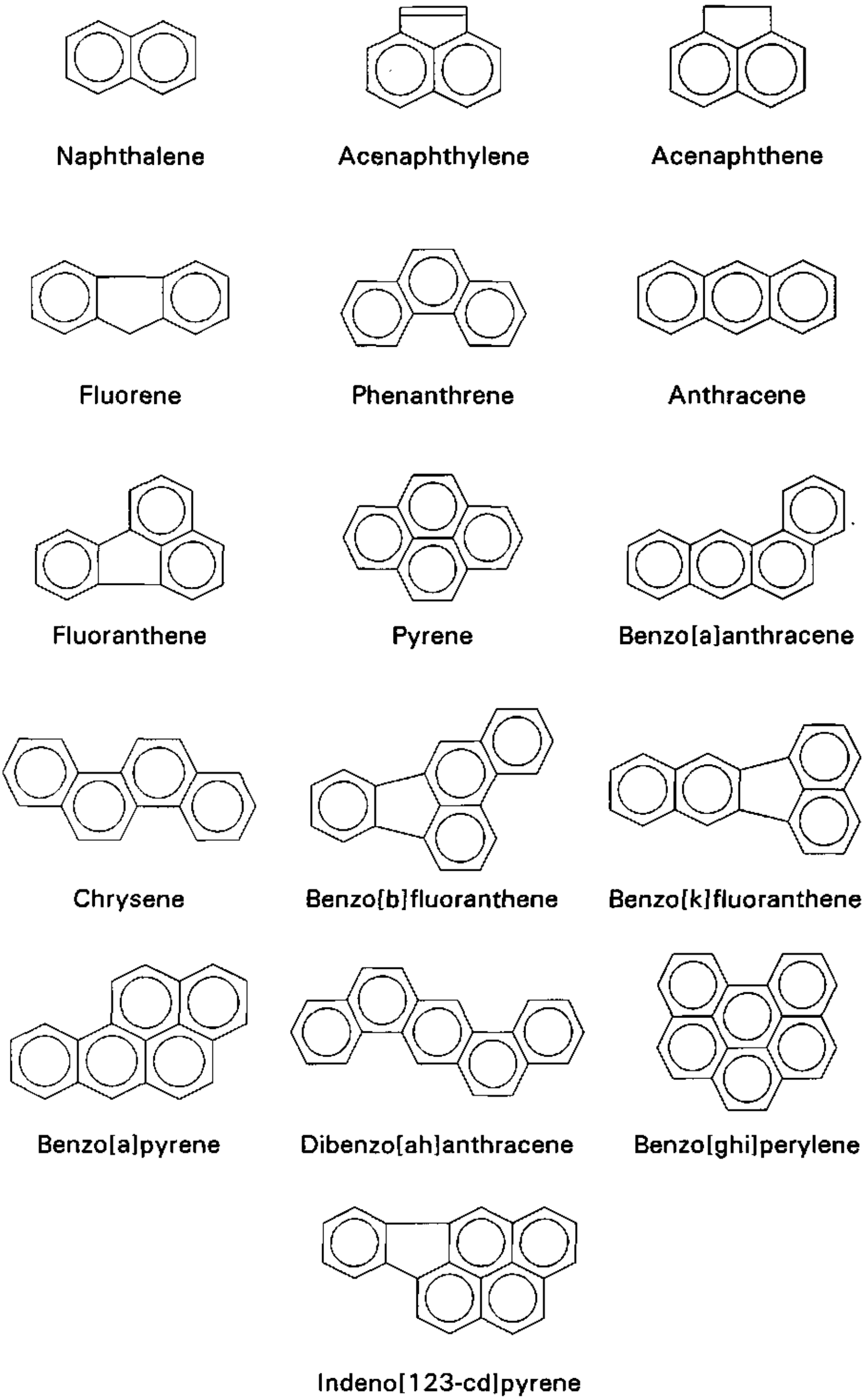
PAHs are hydrophobic compounds; their hydrophobicity generally increases with an increasing number of aromatic rings. Their hydrophobicity is related to their aqueous solubility and octanol/water partition coefficient. These properties, the chemical composition and molecular weight of the 16 EPA-PAHs are shown in Table 1.1.

Table 1.1 Chemical and physical properties of the 16 EPA-PAHs [6]

PAH	Chemical composition	Molecular weight	Aqueous solubility at 30°C ($\mu g\ l^{-1}$)	Log octanol/water partition coefficient (-)
Naphthalene*	$C_{10}H_8$	128	$31.7 \cdot 10^3$	3.37
Acenaphthylene	$C_{12}H_8$	152	$3.93 \cdot 10^3$	4.07
Acenaphthene	$C_{12}H_{10}$	154	$3.47 \cdot 10^3$	4.33
Fluorene	$C_{13}H_{10}$	166	$1.98 \cdot 10^3$	4.18
Phenanthrene*	$C_{14}H_{10}$	178	$1.29 \cdot 10^3$	4.46
Anthracene*	$C_{14}H_{10}$	178	73	4.45
Fluoranthene*	$C_{16}H_{10}$	202	260	5.33
Pyrene	$C_{16}H_{10}$	202	135	5.32
Benzo[a]anthracene*	$C_{18}H_{12}$	228	40	5.61
Chrysene*	$C_{18}H_{12}$	228	2.0	5.61
Benzo[b]fluoranthene	$C_{20}H_{12}$	252	0.55	6.84
Benzo[k]fluoranthene*	$C_{20}H_{12}$	252	1.2	6.57
Benzo[a]pyrene*	$C_{20}H_{12}$	252	4.0	6.04
Dibenzo[ah]anthracene	$C_{22}H_{14}$	276	0.50	5.97
Benzo[ghi]perylene*	$C_{22}H_{14}$	276	0.26	7.23
Indeno[123-cd]pyrene*	$C_{22}H_{14}$	276	62	7.66

* VROM-PAHs: reference PAHs selected by the Dutch government

PAHs are formed during incomplete combustion of organic materials and during carbonization processes. Such processes can have a natural cause, such as volcanic activity or bush fires, or originate from human activities. Anthropogenic sources of PAHs in the environment are, for instance, the incomplete combustion of fossil fuels, oil spillage, the dumping of coal tar on gas production sites, and the use of such PAH-containing products as asphalt, coatings for ships, wood-preserving creosote and anthracene oil [7].



Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo[a]anthracene
Chrysene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[a]pyrene
Dibenzo[ah]anthracene
Benzo[ghi]perylene
Indeno[123-cd]pyrene

Figure 1.1 Chemical structure of the 16 EPA-PAHs

Contamination of the environment by PAHs is a serious threat to public health and ecosystems, because more than 30 PAH compounds and several hundred derivatives of PAHs are reported to be carcinogenic. This makes PAHs the largest single class of chemical carcinogens known so far [8]. In view of this, the Dutch government has established standards for the highest acceptable concentrations of PAHs in soils and sediments, which are based on ecotoxicological research [9]. If the PAH concentration in a soil or sediment is below the so-called target level, the solids concerned are considered clean and may be used without restrictions. Solids containing PAH concentrations above the so-called intervention level are regarded as too highly polluted for further use and should be treated. If the PAH concentration level of a contaminated site is between the target level and intervention level, other factors (e.g. function of the site) are considered to decide whether or not the site should be remediated [10].

The target level and intervention level in soil or sediment are based on the concentration of the 10 VROM-PAHs given in Table 1.1. These PAHs were selected by the Dutch government, because they frequently occur in the environment, are part of other internationally used PAH series and can be reliably measured [11]. The target level of the VROM-PAHs is 1 mg per kg of dry matter for a soil or sediment with 10 wt% organic matter. For a soil or sediment containing less than 30% of organic matter the target level for the sum of VROM-PAHs is calculated as follows [10]:

target level (mg PAHs per kg of dry matter) = 0.1 · wt% of organic matter.

The intervention level for a soil or sediment with an organic matter content between 0 to 10 wt% is 40 mg VROM-PAHS per kg of dry matter, whereas for soils and sediments with an organic matter content between 10 to 30 wt% this level is calculated by the following equation [10]:

intervention level (mg PAHs per kg of dry matter) = 4.0 · wt% of organic matter.

Containing more than 30 wt% of organic matter the intervention level for a soil or sediment is 120 mg VROM-PAHs per kg of dry matter.

Soil, sediment and sludge can also be used as a building material. For building materials the maximal allowed concentration of the sum of VROM-PAHs in the solids is calculated equally to the intervention level for soil and sediment and therefore, this value depends on the organic matter content in the building material [10].

The behaviour of PAHs in soil depends on their hydrophobic character. Because of their low aqueous solubility, PAHs in soil will be mostly associated with organic matter. As a result, they are barely available to micro-organisms in soil. Their distribution coefficient between soil and the water phase often shows a strong correlation with the octanol-water partition coefficient and/or their aqueous solubility (Table 1.1) [12]. Because organic solvents have a higher affinity for such hydrophobic organic compounds as PAHs than water, PAHs are more easily soluble in organic solvents. Consequently, a remediation process based on extraction with organic solvents will probably provide high removal rates and removal efficiencies for solids contaminated with PAHs. The main features of such an extraction process are detailed in the next section.

1.3 The solvent extraction process

1.3.1 General description

The solvent extraction process comprises five basic treatment steps:

1. pretreatment of the solids,
2. extraction of the contaminants from the solids,
3. separation of the solids and extraction solvent,
4. removal of the extraction solvent from the solids,
5. recovery of the extraction solvent.

The solvent extraction process is shown in Figure 1.2.

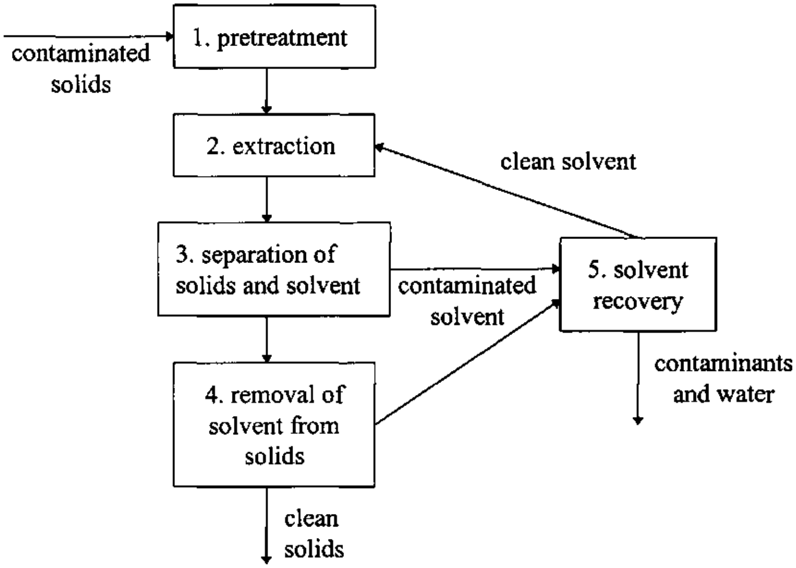


Figure 1.2 General diagram for solvent extraction of contaminated solids

During the solvent extraction process, the untreated contaminated soil, sediment or sludge is first pretreated. This step consists, for instance, of sieving the solids to remove large solid pieces that may damage the installation. It may include the removal of certain (almost) clean size fractions (e.g. the sand fraction), which can be reused thereafter. During the second treatment step, the contaminated solids are thoroughly mixed with the extraction solvent, and the contaminants are dissolved in the extraction solvent. The third step comprises the separation of the extraction solvent from the solids. After this step, a small amount of solvent remains in the solids and it is removed from the solids during the fourth treatment step. Finally, the extraction solvent is recovered and reused for extraction of contaminated solids. The residual waste of the process consists of a mixture of concentrated contaminants and water originating from the untreated solids, which may be combusted.

For a solvent extraction process to be technically feasible, it should have a high extraction efficiency. In order to use the remediated soil/sediment without restrictions, the soil or sediment should be cleaned to the Dutch target level established for clean soil. As mentioned in the previous section, this value depends on the type of contamination, the organic matter content and clay content of the solids. Another requirement for the process is that the amount of residual waste of the process should be as small as possible. This means that entrapment of small solid particles in the solvent during steps 3 and 4 should be avoided. For the environmental feasibility of the process, it is also important that the cleaned solids can be reused and that the energy consumption of the process is low. This last requirement means that the amount of contaminated solvent that needs to be recovered should be as small as possible. It is therefore efficient to operate the extraction in counter current flow of solids and solvent. This also promotes very low residual contaminant concentrations in the treated solids. Furthermore, the safety of the process for people and the environment should be guaranteed, and finally the costs should be reasonable compared to those of other remediation processes and the deposition of solid wastes [13].

1.3.2 Choice of solvent

For the development of a solvent extraction process, the choice of solvent is essential. The physicochemical properties of the selected solvent determine the design of the treatment steps of the solvent extraction process, except for the pretreatment of solids (step 1). For the extraction process to be economically and technically feasible, the solvent should meet the following requirements [14]:

- high capacity: the concentration of the contaminants in the extraction solvent should be high compared to that of the contaminants in the solids;
- high selectivity: only the contaminants should be removed from the solids, not the other soil substances such as organic matter;
- efficient separation of solvent from contaminants;
- chemically stable under the circumstances used;

- preferably not explosive, inflammable or extremely corrosive;
- low price.

Another property of the solvent important for the extraction efficiency is the miscibility of the solvent with water. Soil, sediment and sludge always contain water, which may be present either as a pure water phase or as a water layer around the solid particles. If the solvent is miscible with water, the water layer around the solid particles will dissolve and not act as a barrier to the transport of contaminants. In the extraction of wet soils, solvents miscible with water show in practice a higher extraction efficiency than solvents that are not miscible with water [15].

From an environmental and social point of view, the solvent should be biodegradable, as little toxic as possible and acceptable to the society. This means that such substances as toluene, benzene and dichloromethane are unsuitable. Suitable solvents are, for instance, ketones (e.g. acetone), alcohols (e.g. methanol, ethanol, propanol and butanol), triethylamine, and isopar-L [14].

1.3.3 Detailed description of the relevant treatment steps

The design of the treatment steps of the solvent extraction process depends very much on the physicochemical properties of the solvent to be used. Two principles can be applied to realise the step of the extraction of solids. The first is based on the mixing of solvent and solids as a suspension in, for instance, a tank or scrubber. A continuous version of this principle is extraction of solids in a vertical upflow column, vertical-plate column or screw extractor. The second extraction principle is percolation of the solvent through a fixed bed of solid particles. This can be carried out as a continuous process in, for instance, a Bollman vertical extractor or a belt extractor. For all apparatuses and systems, the most efficient flow of solvent and solids to limit the required amount of solvent is countercurrent [16].

Separation of the solvent and solids can be carried out in the same apparatus as where extraction occurs, for instance, by sedimentation, thickening and decanting of the solvent. If the solvent is percolated through a fixed bed of solid particles, the extraction solvent is separated from the solids immediately after extraction. Other apparatuses suitable for the separation of solids and solvent are centrifuges, hydrocyclones, filters and sieves.

The residual solvent can be removed from the extracted solids by biological degradation after the addition of water, evaporation of the solvent by heating, stripping with steam, or extraction of the solvent with another solvent. In the case of biological degradation, the solvent must, of course, be biodegradable. Two disadvantages of this method are the loss of solvent and the large reactors required for the degradation of rather large amounts of solvents. In case of evaporation of the solvent, the solvent needs to have a low boiling point. This method consumes much energy for heating the solids and evaporating the solvent. Additionally, special safety measurements need to be taken to control the vapour of the organic solvent. The removal of the solvent by steam stripping also consumes much energy and makes it necessary to take safety measures. The solvent needs to be highly volatile for efficient removal. In the case of extraction of the solvent with another solvent, the two solvents need to be miscible and have to be separated afterwards. The most promising methods for removing the solvent from the solids are stripping with steam, extraction of the solvent with water, and biological degradation of the solvent. This last method can be efficiently applied only if most of the solvent is mechanically removed from the solids before degradation, e.g. by centrifuging [14].

For recovery of the contaminated solvent, distillation and extraction with a hydrophobic solvent seem to be the most successful methods. Distillation requires a solvent with a volatility different from that of the contaminants, and this method may consume much energy. For extraction with a hydrophobic solvent, the two solvents need to be miscible. In this case, the removal of the contaminants from the binary solvent mixture and the separation of the two solvents may be complicated [14].

The most critical step of the solvent extraction process is the extraction step itself. The highest possible extraction efficiency is determined during this step and also the amount of solvent needed for decontamination is determined.

1.3.4 Current solvent extraction processes

For the design of a solvent extraction process optimum in technical, economical and environmental respects, it may be of interest to study the current solvent extraction processes. Processes based on extraction with organic solvents have been developed especially in the USA and Canada for the remediation of contaminated soils, sediments and sludges. Two of the most promising extraction processes are the BEST process and the Carver-Greenfield process [14].

In the BEST process, triethylamine is used as an extraction solvent. This solvent is completely miscible with water below 10°C, whereas at temperatures above 55°C it is immiscible with water [17]. The extraction steps are carried out in two vessels. In a premix tank, contaminated solids are mixed with triethylamine below 10°C for dewatering and the extraction of solids. After water removal, the solvent and solids are mixed again several times at temperatures ranging from 36°C to 77°C. After each extraction step, the solids are allowed to settle and the solvent is decanted from the vessel. The residual triethylamine is removed from the solids by stripping with steam. The contaminated solvent is recovered by evaporation and phase separation of water and triethylamine at temperatures above 55°C [17].

In the Carver-Greenfield process, contaminated solids are extracted with a mixture of saturated hydrocarbons that are harmless and not toxic. The mixture has a boiling point of about

200°C. An example of such a mixture is the commercially available liquid isopar-L. The contaminated solids are extracted repeatedly with the solvent at 90°C. Afterwards, the solids and solvent are separated by centrifuging, and the residual solvent is removed from the solids by steam stripping. The contaminated solvent is recovered by distillation and reused for extraction [13].

Both processes have been developed practically to a commercial scale [5], which proves the technical feasibility of the solvent extraction process. In general, these processes are being developed for application in practice and optimised in an empirical way. This may result in relatively high treatment costs. So far hardly any studies aimed at gaining more scientific and theoretical insight into the solvent extraction process have been carried out. Little is therefore known about the extraction of aged soils, sediments and sludges with organic solvents. This is partly due to the fact that most scientific research is being carried out with spiked soils and systems of water and soil containing no organic solvent. It is known that the behaviour of aged contaminants can greatly differ from that of spiked contaminants. Furthermore, in only a few investigations the effect of adding an organic solvent to a system of spiked soil and water was studied [e.g. 18,19]. Therefore, the present investigation focusses on the development of theoretical and scientific insight into the most critical step of the solvent extraction process, i.e. the extraction step itself. Improvement of this step should increase the efficiency of the entire solvent extraction process.

1.4 Scope and outline

The main objective of the present investigation was to study the effect of several process parameters on the efficiency of the extraction step of the solvent extraction process in order to develop an optimum process for the removal of PAHs from soil, sediment and sludge with organic solvents. The process parameters of interest are: type of solvent, extraction time, extraction procedure, water content of the extraction solvent, type of solids, size of the solid particles, and water content of the solids.

To investigate the remediation efficiency of the solvent extraction process, the PAH concentration in contaminated soils, sediments and sludges need to be accurately determined. Therefore, experiments were carried out to select the most efficient method for the analysis of the PAH concentration in an aged industrial sandy soil, an aged sediment from the Petroleum Harbour in Amsterdam, and an aged residual sludge from a soil washing plant. The Dutch draft NEN method was chosen as a starting point, because this method is expected to become a standard method for the analysis of PAH concentrations in soil and sediment. This investigation is described in Chapter 2.

In Chapter 3, an appropriate solvent for application of the solvent extraction process in practice is chosen based on experiments carried out with six different solvents and clearly defined (model) soils. These soils were typical sandy, silty and clayey soils spiked with a known amount of pyrene and benzo[a]pyrene. Furthermore, the effects of several process parameters on the extraction efficiency were determined. These process parameters were: water content of the extraction solvent and soil, extraction time, aging of spiked pyrene, and solubility of the PAHs in the extraction solvent.

An important requirement for the solvent extraction process is that it should be capable of cleaning contaminated solids up to the Dutch target level of PAHs established for clean soil, and that little solvent should be needed to achieve this level. The extraction efficiency of multiple subsequent batch extractions with mixtures of acetone and water was therefore investigated, as detailed in Chapter 4. The experiments were carried out with an aged residual sludge from a soil washing plant and an aged sediment from the Petroleum Harbour in Amsterdam, both of which were also used to study the analysis of PAHs (Chapter 2). Additionally, different size fractions of the sludge were subjected to multiple subsequent batch extractions to determine whether separate treatment of fractions may raise the total extraction efficiency. Based on the PAH concentration measured in the solids after each extraction step, desorption isotherms were calculated, which can be used for process design purposes.

For the solvent extraction process, it is also important to determine the time needed for removal of PAHs from the solids. The extraction time required determines the residence time of the solids in the extractor and therefore the extractor size. Experiments were carried out to determine the desorption rate of PAHs during the extraction of an aged residual sludge (which was also used during the investigations presented in Chapters 2 and 4) with a mixture of 80 vol.% acetone and 20 vol.% water. The sludge was separated in several size fractions by sieving; next, two of these size fractions were separated in an upflow column on the basis of density and size. The reason for this separation was to study the effect of the size and density of particles on the desorption behaviour in order to determine whether separate treatment of size fractions may be advantageous. This investigation is detailed in Chapter 5.

Chapter 6 describes a simulation of desorption rates by two transport models. In this, the data reported in Chapter 5 were used. The transport models served to determine which PAH transport processes are important during the extraction of the aged sludge. Furthermore, the two models were use to study the distribution of PAHs in the sludge particles.

Finally, based on the results given in Chapters 2 to 6 a general discussion regarding the design and feasibility of the solvent extraction process is presented in Chapter 7.

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Chapter 2

Selection of an efficient extraction method for the analysis of PAHs in contaminated soil, sediment and sludge

Abstract

Extraction with N-methyl-2-pyrrolidinone (NMP) in a microwave oven at 130°C for one hour was significantly the most efficient method for the extraction of PAHs from extraction sludge and wet harbour sediment. It was also one of the most efficient methods for extraction of PAHs from air-dried industrial soil. During the first step of a two-step extraction, at least 99.8% of the PAHs were extracted with NMP. Extraction with NMP in a microwave oven was compared to methods based on extraction with acetone, methanol, ethanol, a methanol/toluene mixture and on hydrolysis with KOH and tetra methyl ammonium hydroxide. The used extraction equipment was an ultrasonic bath, a rotary tumbler, a Soxhlet extractor and a microwave oven. The second best method was extraction with a mixture of 80 vol.% acetone and 20 vol.% water in a microwave oven at 100°C for one hour. Regarding the composition of the individual PAHs as percentages of the total PAH concentration no difference was found between three of the most important extraction methods.

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2.1 Introduction

Organic solvents often used for the extraction of PAHs from soils and sediments are acetone, methanol, dichloromethane, benzene, toluene, hexane and mixtures thereof [1-7]. The draft version of the official Dutch standard (NEN) detailing how to determine the concentration of PAHs in soils [8] and sediments [9] prescribes extraction with acetone and petroleum ether. Earlier experiments carried out at our department [10] with soils to which pyrene and benzo[a]pyrene were added showed that methanol, ethanol and acetone are suitable extraction solvents. Methanol and ethanol are also used in combination with bases (e.g. potassium hydroxide and ammonium hydroxide) to extract PAHs [11,12], herbicides [13] and pesticide residues [14] from soils and sediments for analytical purposes. Saponification with bases is applied to increase the availability of contaminants in soil by hydrolysis and solvation of organic matter. N-methyl-2-pyrrolidinone (NMP) is used in the fuel processing industry to extract coal [15-17]. NMP dissolves most of the organic matter in coal, depending on the extraction temperature and type of coal [15,16].

The extraction yield depends not only on the type of solvent used but also on the method employed to extract solids. The most common methods are ultrasonic treatment [3,4,12], shaking at room temperature [8,10,13,14], and boiling of the solvent used, in which the solvent is usually recycled, for example in a Soxhlet apparatus [1-7,11,15-17]. Another method is extraction in a microwave oven, which is for example used to extract PAHs [18] and PCBs [19] from soils and sediments.

It is not clear which of the extraction solvents and methods mentioned are most efficient, because to our knowledge no studies exists in which these methods are compared. The objective of this study is to select a solvent and method for efficient extraction of PAHs from soil, sediment or sludge, based on extraction yields.

2.2 Materials and Methods

2.2.1 Samples

Three samples were used: air-dried soil from an industrial site (= (industrial) soil) with a dry matter content of 93 wt%, sediment from the Petroleum Harbour of Amsterdam (= (harbour) sediment) with a dry matter content of about 35 wt%, and residual sludge from a Dutch extractive remediation plant (= (extraction) sludge). The extraction sludge was delivered after being dried using a sieve band press and had a dry matter content of 52 wt%. The content of mineral particles smaller than 2 mm in the soil, sediment and sludge samples was 11 wt%, 17 wt% and 28 wt% of the dry matter, respectively, and the content of particles smaller than 63 mm was 52 wt%, 59 wt% and 94 wt% of the dry matter, respectively (Tauw Milieu, Environmental Laboratory, Deventer, the Netherlands). The organic matter content was 6.8 wt%, 11 wt% and 26 wt% of the dry matter, respectively, determined after heating at 500°C.

2.2.2 Extraction experiments

The extraction experiments were carried out by using the Dutch draft NEN method, which was compared with extraction in a rotary tumbler, ultrasonic treatment, Soxhlet extraction, and extraction in a microwave oven. The most promising extraction methods were used to extract samples a second time. All experiments were carried out in triplicate.

Draft NEN methods. The soil (20 g of dry matter) was treated by using the Dutch draft NEN method for soil [8], and the sediment and sludge (20 g of dry matter) were treated by using the draft NEN method for sediment [9]. The soil was homogenized by mixing it manually with a shovel and sieving it at a diameter of 2 mm before sampling, instead of by carrying out the prescribed pretreatment by cryogenic grinding. As prescribed, the sediment and sludge were homogenized by mixing it manually in combination with an ultra turrax. All samples were extracted with acetone (50 ml for soil, 200 ml for sediment) on a shaker with a horizontal motion (200 strokes per minute, amplitude: 5 cm) for ten minutes, followed by the addition of petroleum ether of 40-60°C (50 ml for soil, 100 ml for sediment) and extraction for another ten minutes. The industrial soil was extracted once more in the same fashion with 50 ml of petroleum ether after removal of the extraction solvent. Afterwards, the acetone/petroleum ether extracts were purified by using the draft NEN method detailed below.

Rotary tumbling. Pure acetone, methanol and ethanol (50 ml) were used to extract soil (20 g) in a bottle (250 ml) with a screw cap in a rotary tumbler (25 rpm, rotating diameter: 50 cm) at 20°C for 40 minutes.

During a second experiment, soil (15 g), wet sediment (5 g) and wet sludge (3 g) were extracted with 51 ml, 27 ml and 23 ml, respectively, of a mixture of 80 vol.% acetone and 20 vol.% water in a rotary tumbler (25 rpm) at 20°C for one hour. The water content of the extraction solvent included the water already present in the samples.

During a third experiment with the rotary tumbler, the effect of saponification was examined with two types of bases: a. KOH (9M solution in water) and b. tetra methyl ammonium hydroxide (solution of 25 wt% in methanol). In a bottle with a screw cap (250 ml), 1.8 g of soil or 5 g of wet sediment, 1 ml of 9M KOH, 1 ml of surfactant Dehypon LS 104 (Henkel) and 21 ml of methanol were mixed. When tetra methyl ammonium hydroxide (TMAH) was used, 3.25 ml of TMAH solution, 1 ml of water, 1 ml of surfactant Dehypon and 17 ml of methanol were added to the soil and sediment. Furthermore, 3.5 ml of water was added to the soil samples in order to obtain a water content (2.6 g of water (g of dry matter)$^{-1}$) similar to that of the sediment. Surfactant Dehypon LS 104 (formula: $R\text{-}(C_2H_4O)_{10}\text{-}C_4H_9$, $R = C_{12}\text{-}C_{14}$) was added to increase the solubility of PAHs in solution. The mixtures were shaken intensively by hand and then kept at room temperature in the dark for about 16 hours. Next, the mixture was placed in the rotary tumbler (25 rpm) at 20°C for one hour.

Ultrasonic treatment. Acetone, methanol and ethanol (50 ml) were used to extract the soil (20 g) in a bottle (250 ml) with a screw cap in an ultrasonic bath (Branson 5200, 60 Watt) at 20°C for 40 minutes.

Soxhlet. Samples of soil (20 g) and wet sludge (20 g) were extracted with acetone (160 ml) in a Soxhlet apparatus at about 56°C for 7 hours.

Microwave oven. In a microwave oven (CEM, MDS-2100), the effect of saponification with KOH (9M solution in water) and TMAH (solution of 25 wt% in methanol) was investigated in order to compare it with the effect of saponification in the rotary tumbler. In a Teflon microwave vessel, samples of soil (1.8 g) and wet sediment (5 g) were mixed with the same quantities of hydroxide, surfactant and methanol used for saponification in the rotary tumbler. The mixtures were kept in the dark at room temperature for 16 hours and then heated in the microwave oven at 70°C for one hour.

During a second experiment with the microwave oven, the temperature was chosen as high as acceptable in view of the safety requirements applying to the microwave oven. Soil (6 g), wet sediment (4 g) and wet sludge (3 g) were extracted in the microwave oven with: a. 22 ml of NMP at 130°C for 1 hour; b. 22 ml of a mixture of 75 vol.% methanol and 25 vol.% toluene at 100°C for 1 hour; c. 22 ml of a mixture of 80 vol.% acetone and 20 vol.% water at 100°C for 1 hour. The water content given for experiment c again includes the quantity of water present in the samples.

During a final experiment with the microwave oven, wet samples of the sludge (3 g) were extracted with 1 ml of KOH (9M solution in water) and 22 ml of methanol in the microwave oven at 100°C for 1 hour.

Second extractions. To verify the assumption that the residual concentrations of the PAHs in the samples after one extraction are negligible, second extractions were performed. Samples of extracted soil, sediment and sludge were treated for one hour in a way similar to the first extraction in the microwave oven with: a. NMP at 130°C; b. a mixture of 75 vol.% methanol and 25 vol.% toluene at 100°C; c. a mixture of 80 vol.% acetone and 20 vol.% water at 100°C. After the first extraction and after sedimentation of solids, as much extraction solvent as possible was removed and 10 ml of fresh extraction solvent was added to the extracted soil.

Samples of the sludge treated with KOH/methanol in the microwave at 100°C and samples treated with acetone/water in the rotary tumbler were extracted once more in the same way with 1 ml of 9M KOH/10 ml of methanol and 15 ml of a mixture of 80 vol.% acetone and 20 vol.% water.

The PAH concentrations in the sample extracts of extraction steps one and two were determined by HPLC. The PAH concentration in the dry matter obtained in step two was calculated, taking into account the quantity of PAHs present in the residual extraction solvent in the solids resulting from the first extraction.

2.2.3 Clean-up of sample extracts

By using the NEN method [8,9], the sample extracts consisting of acetone and petroleum ether were extracted twice with water (400 ml for soil, 800 ml for sediment) in a separation funnel in order to remove acetone. The separated and concentrated petroleum-ether extract (1 ml) was purified in a column (length: about 95 mm, diameter: 6 mm) with 1 cm of anhydrous sodium sulphate (Merck) and 2.0 g of aluminum oxide (J.T. Baker: neutral, Brockmann activity grade I, 11 wt% water). The PAHs in the eluate were transferred into acetonitrile by stripping the petroleum ether with nitrogen, and the acetonitrile solution was injected into the HPLC. Because this clean-up procedure did no affect the interference shown by the chromatograms of the samples, it was not applied to the other sample extracts.

Another clean-up method [20], consisting of liquid/liquid extraction with dimethyl sulphoxide (DMSO), caused even more interference in the chromatograms. Petroleum ether extracts (5 ml) obtained by using the draft NEN method were extracted three times with aliquots of DMSO. After dilution of the DMSO layers with two aliquots of water and after three extractions with aliquots of petroleum ether, the PAHs in the petroleum ether phase were transferred into acetonitrile by stripping the petroleum ether with nitrogen. The acetonitrile solution was injected into the HPLC.

Since the above clean-up procedures did not have a positive effect on the interference shown by the chromatograms, all sample extracts (except for the samples extracted by using the draft NEN method) were centrifuged at 10,000 rpm for three minutes and then directly injected into the HPLC. A guard column (Vydac, C 18 Rev. phase, length: 30 mm, diameter: 4.6 mm) in front of the HPLC column served as a clean-up medium. If tailing of peaks was observed this precolumn was replaced immediately.

2.2.4 Quantification with HPLC

The concentrations of the 16 PAHs selected by the Environmental Protection Agency of the United States (16 EPA-PAHs) were determined in the sample extracts by separation in an HPLC column (Vydac 5, C18 Rev. phase, length: 250 mm, diameter: 4.6 mm) followed by the use of a photo diode array detector (Waters, 1991). The mobile phase was a mixture of acetonitrile and degassed water (flow rate: 1.0 ml min^{-1}) with changing composition: a mixture of 50 vol.% acetonitrile and 50 vol.% water for 5 minutes, followed by a linear increase in the acetonitrile concentration to 99 vol.% for 15 minutes, after which the concentration was kept at 99 vol.% acetonitrile for 19 minutes.

The 16 EPA-PAHs were identified in the chromatograms by manual comparison of the spectra of peaks in the samples and in the standard of EPA-PAHs. In the extracts of the soil and sediment, 11 EPA-PAHs were identified: phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, and indeno[123-cd]-pyrene. The extracts of the sludge contained the same PAHs, except for anthracene, which could not be clearly identified in the sample extracts. The concentrations of the identified EPA-PAHs were derived from the chromatograms at 254 nm. The PAH concentrations in the dry matter were calculated based on the those in the extracts, assuming that all PAHs were extracted from the samples.

The correctness of the recovery resulting from the use of this analytical quantification method was checked by adding a known quantity of the standard of EPA-PAHs to extracts of the three samples obtained by extraction with NMP in the microwave oven. The average recoveries of the sum of the identified EPA-PAHs added to the samples were 99%, 97% and 102% for extracts of the soil, sediment and sludge, respectively.

2.2.5 Statistical analysis

From the triplicates, the average extraction yield and the sample standard deviation were calculated for the various extraction methods and the three samples. The sample standard deviation is defined as the square root of $\Sigma(Y_i-Y_a)^2/n$, where Y_i is the measured extraction yield, Y_a is the average yield of the three measurements, and n equals 3. The extraction methods applied to a certain sample were compared by analysis of variance. Extraction methods were regarded as significantly different, if the significance level was lower than 10%. If more than two extraction methods were compared, a multiple range test was performed by applying the Duncan criterion with a confidence level of 90% [21]. The multiple range test divided extraction methods into such groups that no significantly different yields existed between the extraction methods within one group, but significantly different yields existed between groups.

2.3 Results and discussion

As the Dutch draft NEN method is expected to become a standard method for the determination of PAHs in soils and sediments in the Netherlands, it was chosen as a starting point for comparison with other extraction methods. A comparison made with extraction using a mixture of 80 vol.% acetone and 20 vol.% water in a rotary tumbler (Table 2.1) showed that the extraction yields obtained for the soil and sludge using a mixture of acetone and water were significantly higher than those obtained by using the draft NEN method (significance levels < 10%). For the sediment however, the PAH concentrations resulting from the rotary tumbler were not significantly higher (significance level = 67%).

Table 2.1 **The average concentrations (mg (kg of dry matter)$^{-1}$) of EPA-PAHs, including sample standard deviations, in the three samples, determined by using the Dutch draft NEN method and by using a mixture of 80 vol.% acetone and 20 vol.% water in a rotary tumbler**

Extraction Method				**PAH concentration**[a] (mg (kg of dry matter)$^{-1}$)		
Solvent	Method			Industrial soil	Harbour sediment	Extraction sludge
- acetone and petroleum ether	- draft NEN: horiz. shaking	23°C	20 min.	78 ± 2	557 ± 38	489 ± 57
- acetone/water	- rotary tumbler	20°C	1 hr.	104 ± 16	590 ± 104	961 ± 4

[a] Significance level between extraction methods: 5.1% (soil), 67.1% (sediment), 0.0% (sludge).

The results of extraction experiments carried out using pure acetone, methanol and ethanol are shown in Table 2.2. From the multiple range test performed regarding the extraction yields, it was concluded that extraction using acetone in a rotary tumbler and in a Soxhlet apparatus results in yields significantly higher than those resulting from the other extraction methods given in Table 2.2. Furthermore, acetone turned out to be preferable over methanol and ethanol as an extraction solvent. This may be a result of the higher solubility of PAHs in acetone. For instance, the solubility of anthracene in acetone is about 17 times higher than that in methanol, and the solubility of fluoranthene and pyrene in acetone is about 14 and 10 times higher, respectively, than that in ethanol [22]. Furthermore, ultrasonic treatment (Table 2.2) was found to be significantly less effective than extraction in a rotary tumbler or Soxhlet apparatus using acetone or methanol.

During earlier experiments with soils to which pyrene and benzo[a]pyrene were added [10], we found that acetone is a suitable solvent for extraction, and that the highest extraction efficiency was reached with mixtures of 80 vol.% acetone and 20 vol.% water [10]. The latter was also found for the three samples used in this study (unpublished results). Therefore, during the remainder of this study mixtures of 80 vol.% acetone and 20 vol.% water were used instead of pure acetone.

Table 2.2 The average concentrations (mg (kg of dry matter)$^{-1}$) of the EPA-PAHs, including sample standard deviations, measured in the industrial soil

Extraction Method				**PAH concentration**	**MRT**[a]
Solvent	Method			(mg (kg of dry matter)$^{-1}$)	
acetone	rotary tumbler	20°C	40 min.	108 ± 8	1
acetone	ultrasonic	20°C	40 min.	65 ± 4	2
acetone	Soxhlet	50°C	7 hrs.	108 ± 15	1
methanol	rotary tumbler	20°C	40 min.	55 ± 1	2/3
methanol	ultrasonic	20°C	40 min.	38 ± 2	4
ethanol	rotary tumbler	20°C	40 min.	49 ± 6	3/4
ethanol	ultrasonic	20°C	40 min.	45 ± 6	3/4

[a] Multiple Range Test: number of the group(s) to which an extraction method belongs; significance level between extraction methods: 0.0%

The results of the saponification of the soil and sediment with potassium hydroxide (KOH) and tetra methyl ammonium hydroxide (TMAH) in the rotary tumbler and microwave oven are shown in Table 2.3. Analysis of variance did not reveal any statistically significant differences between the recoveries of the four extraction methods in Table 2.3. However, a comparison made between the extraction yields resulting from using the rotary tumbler and those resulting from using the microwave oven showed significantly higher yields for the microwave oven with a significance level of 8% for the soil and one of 7% for the sediment. In contrast, the extraction yields obtained using KOH were not significantly different from those obtained using TMAH.

As extraction in the microwave oven resulted in higher extraction yields than that in the rotary tumbler, subsequently most attention was paid to the microwave oven. Four solvents were used for two extraction steps with sludge in the microwave oven: NMP, a mixture of 75 vol.% methanol and 25 vol.% toluene, a mixture of 80 vol.% acetone and 20 vol.% water, and a mixture of methanol and 9 M KOH. During the treatments, the temperature was chosen as high as acceptable in view of the safety requirements applying to the microwave oven. Table 2.4 shows the results of the four treatments carried out in the microwave oven, as well as those of two extraction steps using a mixture of 80 vol.% acetone and 20 vol.% water in the rotary tumbler and using acetone in a Soxhlet apparatus.

Table 2.3 **The average concentrations (mg (kg of dry matter)$^{-1}$) of the EPA-PAHs, including sample standard deviations, in the industrial soil and harbour sediment as a result of saponification**

Extraction Method				**PAH concentration**[a] (mg (kg dry matter)$^{-1}$)	
Solvent	Method			Industrial soil	Harbour sediment
KOH/methanol/surf.	rotary tumbler	20°C	1 hr.	76 ± 14	493 ± 33
KOH/methanol/surf.	microwave	70°C	1 hr.	91 ± 27	537 ± 4
TMAH/methanol/surf.	rotary tumbler	20°C	1 hr.	70 ± 14	473 ± 61
TMAH/methanol/surf.	microwave	70°C	1 hr.	103 ± 19	525 ± 20

[a] Significance level between extraction methods: 34.4% (soil), 34.0% (sediment).

Extraction with NMP in the microwave oven at 130°C gave significantly higher recoveries than the other extraction methods given in Table 2.4. The treatments with methanol/toluene and acetone/water in the microwave oven at 100°C were equally effective, but less effective than NMP. The second extraction contributed 0.2%, 3.2% and 2.7% to the final extraction yields of the extraction with NMP, methanol/toluene and acetone/water in the microwave oven, respectively. The saponification with KOH/methanol in the microwave oven and the Soxhlet extraction with acetone gave significantly lower yields than the other extraction methods given in Table 2.4.

Table 2.4 **The average removal (% and mg (kg of dry matter)$^{-1}$) of the EPA-PAHs, including sample standard deviations, measured in extraction sludge after one and two extraction steps**

Extraction Method				**PAH removal**		**MRT**[a]
Solvent	Method			1st step[b] (%)	after 2 steps (mg (kg d.m.)$^{-1}$)	
NMP	microwave	130°C	1 hr.	99.8	1,123 ± 10	1
methanol/toluene	microwave	100°C	1 hr.	96.8	1,076 ± 18	2
acetone/water	microwave	100°C	1 hr.	97.3	1,068 ± 3	2
KOH/methanol	microwave	100°C	1 hr.	92.2	967 ± 7	4
acetone/water	rotary tumbler	20°C	1 hr.	94.8	1,014 ± 3	3
acetone	Soxhlet[c]	50°C	7 hrs.		962 ± 6	4

[a] Multiple Range Test: number of the group to which an extraction method belongs; significance level between extraction methods: 0.0%. [b] PAH concentration (%) after the first step as percentage of the total PAH concentration after two steps. [c] Extraction in a Soxhlet apparatus is regarded as a multiple step extraction.

The higher extraction yields obtained using the microwave oven compared to those obtained using the rotary tumbler (Table 2.3 and Table 2.4) may be caused by the higher temperature. A rise in temperature increases the solubility of PAHs in the extraction solvent and enhances the diffusion of PAHs in the solids. Lopez-Avila et al. [18] also found a higher recovery when 17 added PAHs were extracted from reference standard soils in a microwave oven at 80°C (70% recovery) compared to extraction at room temperature (52% recovery) for the same time with a mixture of hexane/acetone (ratio of 1:1).

The three methods resulting in the highest extraction yields for the sludge were also applied to the sediment and soil. For the sediment (Table 2.5), extraction with NMP in the microwave oven significantly showed the highest extraction yield, while extraction with acetone/water in the microwave oven was second best. The difference between the extraction yields resulting from using NMP and acetone/water was caused by chrysene, whose peak in the chromatograms of the acetone/water extracts was polluted with that of an unidentified compound. Therefore, the chrysene concentration could not be determined. This was an argument in favour of using NMP as an extraction solvent. No significantly different yields were found between extraction of the soil with NMP, methanol/toluene and acetone/water in the microwave oven (Table 2.6). Extraction of the sediment and soil with NMP resulted in an efficiency of 99.8% or more in the first extraction step, which is comparable to that of the first extraction step in which sludge was extracted with NMP.

Table 2.5 The average removal (% and mg (kg of dry matter)$^{-1}$) of the EPA-PAHs, including sample standard deviation, measured in the harbour sediment after one and two extraction steps

Extraction Method		**PAH removal**		**MRT**[a]
Solvent	Method	1st step[b] (%)	after 2 steps (mg (kg d.m.)$^{-1}$)	
NMP	microwave 130°C 1 hr.	99.8	648 ± 22	1
methanol/toluene	microwave 100°C 1 hr.	97.1	486 ± 9	3
acetone/water	microwave 100°C 1 hr.	99.1	612 ± 18	2

[a] Multiple Range Test: number of the group to which an extraction method belongs; significance level between extraction methods: 0.0%. [b] PAH concentration (%) after the first step as percentage of the total PAH concentration after two steps.

The relatively low extraction yield resulting from the use of methanol/toluene for extracting the sediment may be due to the low solubility of water in this mixture. As a result of this low solubility, the solvent can hardly penetrate through the water into the sediment pores and organic matter. Low extraction yields for solvents that are not miscible with water were also found by Haase et al. [5]. NMP is completely miscible with water, which may contribute to the high extraction yields. Another reason for the success of NMP in the extraction of soils and sediments may be the high capacity of this solvent to dissolve organic matter. NMP dissolves most of the organic matter contained in coal [15,16], which may be a result of its capacity to let coal swell [17]. It is also capable of solving the organic matter contained in soil and sediment, because observation showed that an NMP solution is always black after extraction of samples, while it is initially clear and colourless.

Table 2.6 The average removal (% and mg (kg of dry matter)$^{-1}$) of the EPA-PAHs, including sample standard deviation, measured in the industrial soil after one and two extraction steps

Extraction Method		**PAH removal**	
Solvent	Method	1st step[a] (%)	after 2 steps[b] (mg (kg d.m.)$^{-1}$)
NMP	microwave 130°C 1 hr.	100	91 ± 20
methanol/toluene	microwave 100°C 1 hr.	98.9	89 ± 23
acetone/water	microwave 100°C 1 hr.	96.5	114 ± 10

[a] PAH concentration (%) after the first step as percentage of the total PAH concentration after 2 steps. [b] Significance level between extraction methods: 40.7%

Since the Dutch draft NEN method was chosen as a starting point, the extraction yields for the soil, sediment and sludge as a result of using the Dutch draft NEN method (Table 2.1) were compared to those as a result of using NMP and a mixture of 80 vol.% acetone and 20 vol.% water in the microwave oven (Tables 2.4, 2.5 and 2.6). For the sludge and sediment, the draft NEN method gave significantly lower extraction yields than the two methods using the microwave oven. Extraction of the industrial soil with acetone/water gave significantly higher yields than the NEN method, but there was no difference between the extraction yields resulting from using NMP and the NEN method.

Finally, the PAH composition of the sample extracts derived by using the draft NEN method and the results of the extractions using NMP and acetone/water in the microwave oven were compared. For the single PAHs, the average recoveries (in percentages of total PAH concentration) resulting from these three extraction methods, including sample standard deviations, are shown in Table 2.7. Because the low standard deviations indicate that the extraction method had no effect on the PAH composition of the sample extracts, the PAH composition was mainly based on the origin and history of the samples.

Table 2.7 The recoveries (% of total PAH concentration) of single PAHs, including sample standard deviation; the average recoveries of three methods: draft NEN, NMP and a mixture of 80 vol.% acetone and 20 vol.% water in the microwave oven

PAH	Industrial soil	Harbour sediment	Extraction sludge
Phenanthrene	10.7 ± 0.8	16.0 ± 0.8	2.4 ± 0.4
Anthracene	5.1 ± 1.4	7.5 ± 0.2	
Fluoranthene	22.0 ± 0.7	30.3 ± 1.0	13.2 ± 1.1
Pyrene	12.7 ± 1.7	19.2 ± 0.3	17.2 ± 2.0
Benzo[a]anthracene	9.7 ± 0.5	10.9 ± 2.1	7.9 ± 1.0
Chrysene	10.5 ± 0.6	n.d.[a]	9.1 ± 0.8
Benzo[b]fluoranthene	8.9 ± 0.4	4.7 ± 0.1	8.5 ± 0.09
Benzo[k]fluoranthene	3.1 ± 0.3	1.9 ± 0.4	1.7 ± 1.0
Benzo[a]pyrene	7.0 ± 0.4	4.6 ± 0.1	16.8 ± 0.3
Benzo[ghi]perylene	4.8 ± 0.8	2.3 ± 0.03	13.1 ± 1.3
Indeno[123-cd]pyrene	5.4 ± 0.3	2.6 ± 0.04	10.1 ± 0.2

[a] n.d. = not determined, because the chrysene peak was polluted with an unidentified compound for extraction with acetone/water. The average concentration of chrysene was 41.6 mg (kg d.m.)$^{-1}$ for the draft NEN method (= 7.5% of total PAH conc.) and 48.4 mg (kg d.m.)$^{-1}$ for extraction with NMP in the microwave oven (= 7.5% of total PAH conc.).

2.4 Conclusions

The best method for extracting PAHs from the three types of samples used was found to be extraction using NMP in a microwave oven at 130°C for one hour. For the harbour sediment and extraction sludge, this method resulted in the highest recoveries, and it was one of the best methods for extracting PAHs from the industrial soil. Furthermore, a second extraction step using NMP turned out to be unnecessary, because at least 99.8% of the PAHs were extracted in the first step. The second best method was extraction with a mixture of 80 vol.% acetone and 20 vol.% water (including the water present in the soil) in a microwave oven at 100°C for one hour. For the harbour sediment, the latter method gave significantly higher recoveries than using methanol/toluene, and for the industrial soil it resulted in high recoveries, which were, however, not significantly higher than those resulting from using NMP and methanol/toluene. For the harbour sediment and extraction sludge, the Dutch draft

NEN method, which was chosen as a starting point, resulted in significantly lower extraction yields than the method using NMP in the microwave oven.

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Chapter 3

Selection of a solvent and the achievement of optimum process conditions for the extraction of spiked pyrene and benzo[a]pyrene from soil

Abstract

To develop a process for the remediation of contaminated soil based on extraction with organic solvents, acetone, methanol, ethanol, propanol and butanol were compared as regards the removal of spiked pyrene and benzo[a]pyrene from sand, silt and clay. Acetone was found to be the most appropriate solvent of the solvents tested, because it showed high extraction efficiencies and these efficiencies remained high when the soil contained water or water was added to the extraction solvent. Furthermore, equilibrium was reached within five minutes and aging of spiked pyrene had no effect on the extraction efficiency of acetone. For acetone, maximum efficiencies were obtained with 10 to 20 vol.% water in the extraction solvent for the extraction of air-dried soil. Extraction of wet sand with acetone resulted in a maximum efficiency at about 15 wt% water in the sand. The higher extraction efficiency of a mixture of acetone and water compared to that of pure acetone is discussed based on interaction of solvent and soil components.

The extraction efficiency of pyrene was not linearly correlated to the solubility of pyrene in the pure solvents. For the extraction of pyrene and benzo[a]pyrene from sand, silt and clay with pure acetone and mixtures of acetone and water, the efficiencies were not correlated either to the solubility of pyrene and benzo[a]pyrene in the extraction solvent. A linear relationship was found only between the extraction efficiency and the polarity of the solvent molecules.

3.1 Introduction

Extraction with organic solvents is an attractive technique for the cleaning of clayey soils, peat soils, sediments and residual sludges from soil washing plants contaminated with organic compounds of high molecular weight, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls [1]. The main aim of the research regarding solvent extraction is to develop an optimum solvent extraction process for the remediation of soils, sediment and sludges contaminated with PAHs.

First, an appropriate solvent has to be selected. The solubility of PAHs in the extraction solvent is especially important for this selection, because it is a measure of the driving force for the transport of PAHs from the soil to the extraction solvent. Other requirements for the solvent are a high selectivity for PAHs, easy separation of the solvent and the cleaned soil, and efficient recovery of the solvent after extraction. From an environmental and social point of view, the solvent should be acceptable, biodegradable and of the lowest possible toxicity. Less acceptable solvents are, for instance, toluene, benzene and dichloromethane [1].

The extraction efficiency for the removal of contaminants from soil depends not only on the solubility of contaminants in the extraction solvent, but also on the ability of the solvent to penetrate into the soil particles and reach the contaminants. The water solubility of the solvent and the swelling behaviour of soil organic matter (SOM) may be important for penetration into soil. Swelling is thought to make the organic matter more accessible to contaminants and should result in higher sorption rates [2, 3, 4].

The water solubility of the solvent is important for the solvent extraction process, because soil, sediment and sludge always contain water. If the solvent is completely miscible with water, the water layer around soil particles will dissolve and will no longer act as a barrier to the transport of contaminants. In practice, for the extraction of wet soils, solvents soluble in water achieve a higher extraction efficiency than those which are not soluble in water [5]. However, drying of soil before solvent extraction would increase the total costs of the process. Therefore, an appropriate solvent should also show high extraction efficiencies if the soil contains water.

Another effect of water in the soil or extraction solvent is a decreasing solubility of PAHs in the extraction solvent with increasing water content. Often, an exponential decrease in solubility with increasing water content is found [2]. Therefore, the distribution coefficient K_s of PAHs in soil and extraction solvent (K_s = concentration in soil/concentration in solvent) is also thought to decrease exponentially with increasing water content.

This effect is described by the cosolvency model [2]:

$$\log K_s = \log K_w - \sigma f_s \tag{3.1}$$

where K_s is the distribution coefficient of PAHs in soil and water with cosolvent (mol kg^{-1}), K_w the distribution coefficient of PAHs in soil and pure water (mol kg^{-1}), σ the ability of the solvent to increase the contaminant solubility in the solvent (-), and f_s the volume fraction of organic solvent in the total liquid volume (-). The result is a log-linear relation between the distribution coefficient K_s and the organic solvent fraction f_s. Parameter σ represents the slope of the linear relation.

Solvents that meet all the mentioned requirements for extraction of organic contaminants from soil are acetone and alcohols of low molecular weight. Extraction with acetone is used in several analytical pretreatments for the determination of the concentration of PAHs in soil and sediments [6, 7, 8]. Acetone is often used mixed with hexane [9, 10, 11]. Methanol is the most frequently used alcohol in pretreatments for soil analysis. It is mostly used in combination with benzene [12] or potassium hydroxide for saponification [7, 13].

The objectives of the present investigation were to choose a suitable solvent for the extraction of spiked pyrene and benzo[a]pyrene from three different types of soil, considering the effect of several process conditions and aging of the contaminants on the extraction efficiency, and to determine optimal values for the process conditions for extraction with the solvent chosen. The process conditions of interest were: amount of water added to the extraction solvent, amount of water in the soil, and extraction time. The effect of the solubility of the PAHs in the extraction solvents and the effect of swelling of SOM on the extraction efficiencies were also investigated. The extraction experiments were carried out using sand, silt and clay spiked with pyrene and benzo[a]pyrene.

3.2 Materials and Methods

3.2.1 Soil Samples

Typical sandy, silty and clayey soils were collected in the Netherlands at Kielekampsteeg in Wageningen, south of Groesbeek, and in the Ingense veld south of Rhenen, respectively. The three soils were air-dried and sieved at a cut-off diameter of 2 mm. Their composition is given in Table 3.1.

Table 3.1 Composition of the soil samples used [14]

	Sand	Silt	Clay
% of moisture (g (g dry matter)$^{-1}$)	0.98	0.93	4.2
% of organic matter (g (g dry matter)$^{-1}$)	4.1	2.4	2.2
% of mineral particle size distribution (g (g dry matter)$^{-1}$)			
< 2 μm	3.9	8.1	44.1
2 - 50 μm	11.8	72.6	49.1
50 – 2,000 μm	84.3	19.3	6.8

3.2.2 Sample preparation

Spiking of the soils with pyrene and benzo[a]pyrene. The air-dried sand, silt and clay were spiked with 100 mg of pyrene per kg of dry soil and 100 mg of benzo[a]pyrene per kg of dry soil. In the case of aging of soil samples, the samples were only spiked with 100 mg of pyrene per kg of dry soil. The spiking was carried out by dissolving 400 mg of each PAH in 1 litre of acetone, and pouring this solution over 4 kg of soil. After homogenisation of the soil, the acetone was slowly evaporized at room temperature over a period of at least two days.

Varying water content in soil. Air-dried sand containing about 1 wt% water (Table 3.1) and spiked with pyrene and benzo[a]pyrene was dried at 105°C for 24 hours to obtain spiked sand with 0% water. Water was added to the air-dried spiked sand to obtain water concentrations of 15 wt% and 29 wt%. These samples were kept at room temperature for three days before extraction.

Aging. The air-dried sand, silt and clay samples spiked with 100 mg of pyrene per kg of dry soil were kept in the dark at 7°C for three months to prevent biological and/or chemical degradation of the spiked PAHs.

3.2.3 Extraction experiments

Spiked soil samples were extracted for 30 minutes with several pure solvents and with mixtures of acetone/water and methanol/water containing varying amounts of water. The extraction efficiency of spiked sand with varying water content values was determined by extraction with methanol and acetone. Finally, the effect of extraction time and aging of spiked pyrene on the extraction efficiencies of acetone was studied.

Extraction with pure solvents. The air-dried spiked sand (20 g) was extracted with 50 ml of acetone, methanol, ethanol, 1-propanol, 2-propanol or 1-butanol in a rotary tumbler (25 rpm, rotating diameter: 50 cm) for 30 minutes at 20°C in triplicate.

Varying water content values in the extraction solvent. The air-dried spiked sand (20 g) was extracted in triplicate with mixtures of methanol/water (50 ml) or acetone/water (25 ml) in a rotary tumbler (25 rpm) for 30 minutes at 20°C. The air-dried spiked silt and clay (20 g) were also extracted with mixtures of acetone/water (25 ml) in a rotary tumbler for 30 minutes at 20°C. The solvent mixtures contained 20, 40, 60, 80 or 100 vol.% acetone or methanol, and the remainder was water.

Varying water content values in the soil. The spiked sandy samples (20 g of dry matter) with varying water content values were extracted in triplicate with pure methanol and acetone (50 ml) in a rotary tumbler (25 rpm) for 30 minutes at 20°C.

Extraction time. The air-dried spiked sand, silt and clay (20 g) were extracted with a mixture of 80 vol.% acetone and 20 vol.% water (25 ml) in a rotary tumbler (25 rpm) at 20°C for several periods, ranging from 5 to 30 minutes.

Aging. The aged sand, silt and clay samples (20 g) were extracted in triplicate with acetone/water mixtures in a rotary tumbler (25 rpm) for 30 minutes at 20°C. The solvent mixtures contained 20, 40, 60, 80 or 100 vol.% acetone.

3.2.4 Determination of solubility in mixtures of acetone and water

Pure pyrene or benzo[a]pyrene crystals were added to 5 ml of an acetone/water mixture in a HPLC-bottle. The amount of crystals exceeded the solubility, because they still could be seen after shaking and heating. The HPLC-bottles with solution were closed and heated for about 5 hours at 30°C. Then the bottles were kept in a thermostatic water bath at 20°C for at least 24 hours. Next, a sample was taken from the saturated solution with a calibrated syringe and put into a known volume of pure acetone. The resulting solution was diluted, if necessary, and then injected into the HPLC for determination of the PAH-concentration. To account for volume increase caused by addition of the PAHs to the solution, the density of the saturated solution was measured by weighing a calibrated volume of solution. The solubilities of pyrene were measured six times in pure acetone and three times in acetone/water mixtures with 90 vol.% acetone to 10 vol.% acetone with steps of 10%. Benzo[a]pyrene was measured in triplicate in pure acetone and mixtures with 85, 70 and 60 vol.% acetone.

3.2.5 Determination of the PAH concentration in extraction solvents

After extraction of the soil samples, a sample of the extraction solvent was centrifuged for 2 minutes at 10,000 rpm and the supernatant was injected into the HPLC. To determine the solubility of benzo[a]pyrene in the solvent samples, the mobile phase in the HPLC-column (flow rate: 1 ml min^{-1}) consisted of pure acetonitril. For all other solvent samples, adequate separation of the injected components was achieved using a mobile phase consisting of a mixture of 90 vol.% acetonitril and 10 vol.% water. The concentration of both PAHs was determined by UV detection. Depending on the height of the peaks in the chromatograms, pyrene was detected and quantified at 254, 306 or 335 nm, and benzo[a]pyrene at 200, 254 or 298 nm.

3.2.6 Statistical analysis of extraction efficiencies

For the extraction experiments, the extraction efficiency was defined as the percentage of the initial amount of pyrene and benzo[a]pyrene (100 mg per kg of dry soil) extracted from the soil. All extraction experiments were carried out in triplicate, and sample standard deviations were calculated from the extraction efficiencies measured in triplicate. A standard deviation is the square root of $\Sigma(Y_i-Y_a)^2/3$, where Y_i is the measured extraction efficiency, and Y_a the average efficiency. Analysis of variance was carried out with a significance level of 5% to determine whether there were significant differences in extraction efficiency between pyrene and benzo[a]pyrene and among the types of solvent, the types of soil, and the levels of the other varied process conditions.

3.3 Results and discussion

3.3.1 Extraction experiments

The extraction efficiencies of six pure solvents and the effect of water in the extraction solvent and the soil were studied for the selection of an appropriate solvent for further research into the practical application of the solvent extraction process. Furthermore, the effect of extraction time and the aging of soil spiked with pyrene on the extraction efficiencies of acetone/water mixtures was determined.

In the extraction experiments using soil spiked with pyrene and benzo[a]pyrene, the average extraction efficiency of pyrene was always significantly higher than that of benzo[a]pyrene, except for the extraction of sand with pure solvents.

Extraction with pure solvents. Figure 3.1 gives the average extraction efficiency (%) of pyrene and benzo[a]pyrene with a sample standard deviation for the extraction of air-dried spiked sand with six types of pure solvents. Methanol significantly shows the highest extraction efficiencies of pyrene (102%) and benzo[a]pyrene (92%). The efficiencies of acetone and ethanol are second best and do not differ significantly from each other. The order of decreasing extraction efficiencies is for the other three solvents: 1-propanol, 1-butanol and 2-propanol, with significantly different efficiencies. For these three solvents and acetone, no significant difference between the efficiencies of pyrene and benzo[a]pyrene exists, whereas for methanol and ethanol the efficiency of benzo[a]pyrene is significantly lower.

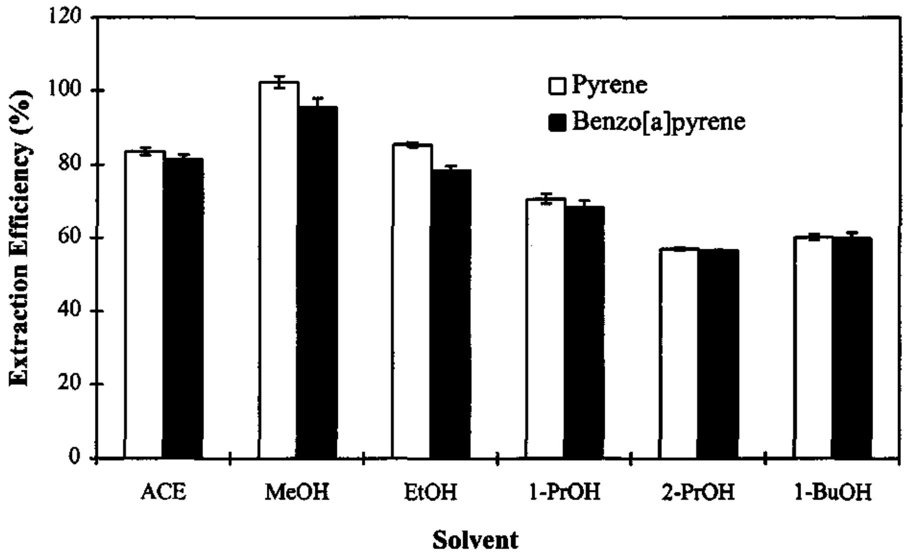

Figure 3.1 **Experimentally observed extraction efficiency (%) of pyrene and benzo[a]pyrene for the extraction of spiked sand with several pure solvents (ACE=acetone, MeOH=methanol, EtOH=ethanol, PrOH=propanol, BuOH=Butanol)**

Varying water content values in the extraction solvent. The experiments with varying water content in the extraction solvent were carried out with methanol and acetone. Figure 3.2 shows the extraction efficiency with a sample standard deviation for pyrene and benzo[a]pyrene for the sand as a function of the solvent concentration in the acetone/water and methanol/water mixtures. Third-order polynomes were fitted through the measured efficiencies to gain an impression of the optimal solvent concentration. For the total range of solvent concentrations, the average extraction efficiency of acetone is significantly higher for pyrene and benzo[a]pyrene than that of methanol. However, the extraction efficiencies of pure methanol are significantly higher than those of pure acetone, which was also concluded from the previous experiments using six types of pure solvent. The highest extraction efficiency for both PAHs was achieved with pure methanol. The maximum extraction efficiency of acetone was reached for pyrene at 85 vol.% acetone and for benzo[a]pyrene at 88 vol.% acetone, which was concluded by determination of the maximum of the fitted third-order polynomes.

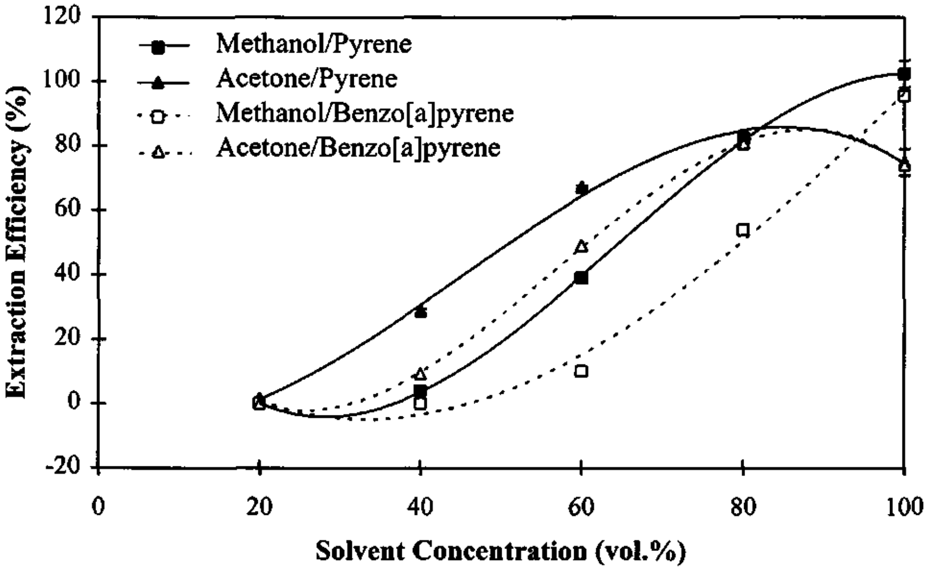

Figure 3.2 **Experimentally observed extraction efficiency (%) of pyrene and benzo[a]pyrene for the extraction of sand as a function of the methanol and acetone concentration with fitted third-order polynomes**

In Figure 3.3, the average extraction efficiency of pyrene for sand, silt and clay is plotted as a function of the acetone concentration. This is done for benzo[a]pyrene in Figure 3.4. Figure 3.3 additionally shows the extraction efficiencies of pyrene obtained after 3 months of storage of the spiked soil samples at 7°C (= aging experiment). The sample standard deviations of the samples containing pyrene are not shown in Figure 3.3. They ranged from 0.1% to 10%. Third-order polynomes were fitted through the measured efficiencies to gain an impression of the optimal values for the acetone concentration.

For pyrene as well as for benzo[a]pyrene the average extraction efficiencies differ significantly for the sand, silt and clay. For pyrene, it is remarkable that the sand shows the lowest extraction efficiencies, because the sand particles have the smallest specific surface area. Benzo[a]pyrene shows the lowest efficiency for extraction from the clay, which was only 53%.

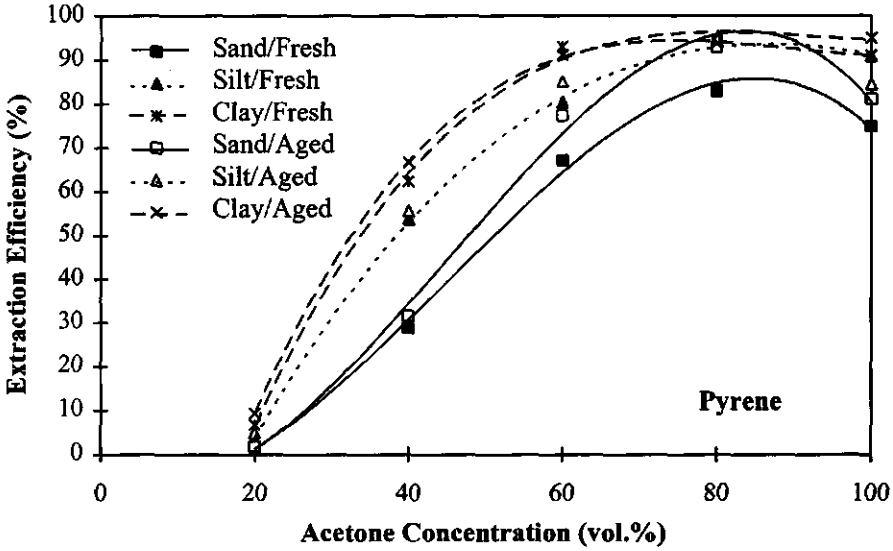

Figure 3.3 **Experimentally observed extraction efficiency (%) of fresh spiked and aged pyrene for the extraction of sand, silt and clay as a function of the acetone concentration with fitted third-order polynomes**

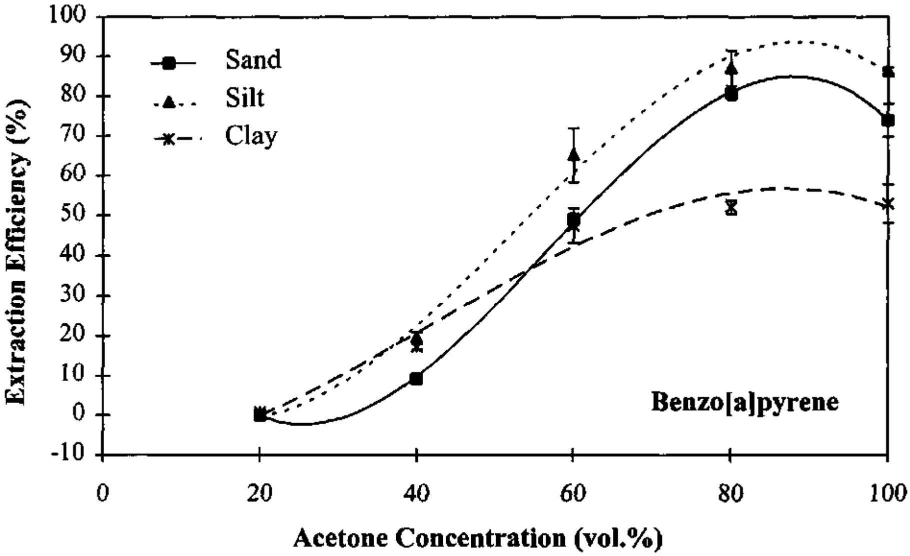

Figure 3.4 **Experimentally observed extraction efficiency (%) of benzo[a]pyrene for the extraction of sand, silt and clay as a function of the acetone concentration with fitted third-order polynomes**

The highest extraction efficiencies of pyrene were achieved with 85, 87 and 80 vol.% acetone for the sand, silt and clay, respectively, which was determined by calculating the extremities of the fitted third-order polynomes. The optimal acetone concentrations for extraction of benzo[a]pyrene are 88, 88 and 87 vol.% for the sand, silt and clay, respectively. In conclusion, for the solvent extraction process the optimal acetone content ranges from 80 to 90 vol.% of the total liquid for extraction of pyrene and benzo[a]pyrene from soil. The optimal water content therefore ranges from 10 to 20 vol.% of the total liquid.

Varying water content values in the soil. Figure 3.5 shows the average extraction efficiencies for pyrene and benzo[a]pyrene with a sample standard deviation as a function of the water content in the sand. The efficiency of methanol reaches a maximum at 1 wt% water in the sand, and acetone achieves the highest efficiencies if the sand contains about 15 wt% water. In this experiment, the results for methanol agree with those achieved in the experiment with varying water content values in the extraction solvent. Maximum efficiency is achieved with pure methanol and air-dried sand.

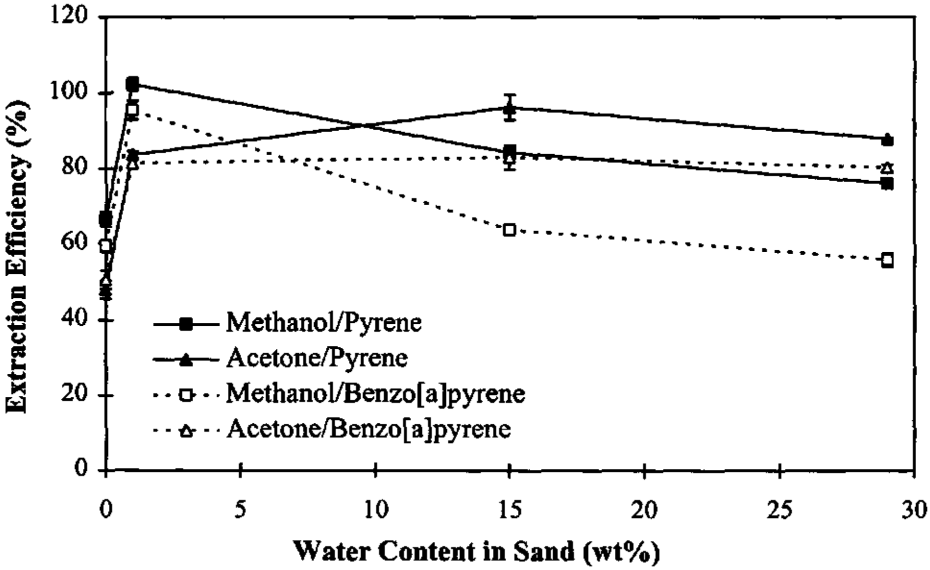

Figure 3.5 Experimentally observed extraction efficiency (%) of pyrene and benzo[a]pyrene for the extraction of sand with methanol and acetone as a function of the water content in the sand

For acetone, the pyrene extraction efficiency is highest if the sand contains 15 wt% water. The benzo[a]pyrene extraction efficiency does not show a clear optimum in the range of 1 to 29 wt% water in the sand. In summary, for extraction with acetone the maximum extraction efficiencies for pyrene and benzo[a]pyrene are reached at about 15 wt% water in the sand.

When the sand was heated for 24 hours at 105°C, the extraction efficiency of acetone and methanol for pyrene and benzo[a]pyrene was lowest. This low extraction efficiency may be due to polymerization reactions of pyrene and benzo[a]pyrene on the soil surface, probably resulting into PAHs of higher molecular weight [15]. As a result, their concentrations in the sand were lower at the beginning of the extraction process and lower PAH amounts could be extracted from the sand.

Selection of a solvent. For a solvent extraction process for contaminated soil, acetone is the best solvent, because the extraction efficiencies of acetone are sufficiently high even if the contaminated soil contains water. In general, methanol shows lower average efficiencies, except for pure methanol when used to extract PAHs from air-dried soil. However, methanol is not an appropriate extraction solvent for an extraction process for contaminated soils and sediment, because in practice soil and sediment always contain water and drying as a pretreatment step would result in higher costs.

The preference of acetone for the solvent extraction process is confirmed by the high extraction efficiencies of acetone which were found in the research into the analytical determination of PAHs (Chapter 2). Regarding the extraction of PAHs from an aged sandy soil, higher extraction efficiencies were observed for acetone than for methanol and ethanol.

Extraction time. Because acetone was chosen as the most appropriate solvent for the solvent extraction process, the extraction kinetics of acetone were studied. For this purpose, spiked pyrene and benzo[a]pyrene were extracted from sand, silt and clay as a function of the extraction time with a mixture of 80 vol.% acetone and 20 vol.% water. For the sand, extraction efficiencies were determined after 5, 10, 20 and 30 minutes of extraction. As no significant difference was found between the extraction efficiencies of the sand for the four sampling points, the silt and clay were extracted only after 5 and 30 minutes. For the silt and clay, no significant difference was found either between the extraction efficiencies after 5 and 30 minutes. It was therefore concluded for all spiked soils that after 5 minutes of extraction the extraction time has no significant effect on the extraction efficiency for pyrene and benzo[a]pyrene. This means that equilibrium is reached within approximately 5 minutes. This short extraction time indicates that during spiking of soil no transport of the contamination into the soil particles occurs and that the PAH contamination is probably adsorbed only onto the surface area of the soil particles.

For pyrene, extraction of the sand showed significantly lower efficiencies than that of the silt and clay. As far as benzo[a]pyrene is concerned, significantly lower extraction efficiencies were obtained for clay than for silt and sand. The lowest efficiency for benzo[a]pyrene was obtained for extraction of the clay with an average efficiency of only 55%. These results agree with the results obtained during the experiments using mixtures of acetone and water with varying water content values (see, for example, Figures 3.3 and 3.4).

Aging of spiked pyrene. Figure 3.3 shows the average extraction efficiency of fresh and aged pyrene extracted from the sand, silt and clay using mixtures of acetone and water as extraction solvent. For the aged pyrene, the fitted third-order polynomes show maximal extraction efficiencies for 84, 79 and 75 vol.% of acetone for the sand, silt and clay, respectively. The optimal acetone percentages for the aged silt and clay are lower than those for the fresh spiked silt and clay mentioned in the subsection about the varying water content values in the extraction solvent. However, these differences are not significant for the extraction of silt and clay, because analysis of variance did not reveal significant differences between the efficiencies for fresh and aged spiked pyrene. On the contrary, the extraction efficiency for the fresh spiked pyrene in sand was significantly lower than that of the aged pyrene, which cannot be explained. In summary, aging of pyrene at 7°C for three months has no negative effect on the efficiency of pyrene extraction from the three soils. Therefore, the distribution of PAHs in the air-dried soil is not affected by storage for three months at 7°C.

3.3.2 Extraction efficiency and solubility of pyrene in pure solvents

It is expected that the solubility of PAHs in the extraction solvent has a strong effect on the extraction efficiency. Therefore, the existence of a relationship between the extraction efficiency and solubility of pyrene was studied for the extraction of pyrene from sand with pure acetone, methanol, ethanol, propanol and butanol (Figure 3.1). Table 3.2 shows the extraction efficiency for pyrene, the solubility of pyrene in the pure solvents, and the molecular weight and density of the solvents used.

Linear regression of the extraction efficiency as a function of the solubility of pyrene and the logarithm of the solubility does not result in linear correlations, as the correlation coefficients are below 0.03. Therefore, it can be concluded that no linear or log-linear relation exists between the extraction efficiency and the solubility of pyrene in the pure solvents. For extraction of pyrene with these solvents, its solubility is apparently not the limiting factor. The effect of the solvent on the properties of the soil substances is probably more important for the extraction efficiency than the solubility of pyrene.

Table 3.2 Extraction efficiency for pyrene extraction from sand, and properties of the solvents used

Solvent	Extr. Efficiency of pyrene [a] (%)	Molecular Weight M_s [b] ($g\ mol^{-1}$)	Density 20°C [b] ρ_v ($kg\ l^{-1}$)	Solubility of pyrene 26°C [c] SB_i ($10^{-2}\ mol\ mol^{-1}$)	SO_i [d] ($g\ l^{-1}$)
Acetone	84 ± 1.0	58.08	0.7899	3.61	103
Methanol	100 ± 1.7	32.04	0.7914	0.149	7.46
Ethanol	85 ± 0.6	46.07	0.7893	0.317	11.02
1-Propanol	71 ± 1.3	60.10	0.8035	0.426	11.57
2-Propanol	57 ± 0.3	60.10	0.7855	0.29	7.69
1-Butanol	60 ± 0.8	74.01	0.8098	0.622	13.8

[a] Extraction efficiencies with sample standard deviations for extraction of sand with pure solvent (Fig. 3.1); [b] Source: [16]; [c] Source: [17]; [d] Solubility SO_i [g of pyrene (l of solvent)$^{-1}$] is calculated from solubility SB_i [mol of pyrene (mol of pyrene + mol of solvent)$^{-1}$] by:
$SO_i = (SB_i \times M_i)/[(1-SB_i) \times M_s/\rho_v]$, where M_i is the molecular weight of pyrene (= 202.26 [16]), M_s is the molecular weight of the solvent, and ρ_v is the density of the solvent ($kg\ l^{-1}$).

3.3.3 Solubility of pyrene and benzo[a]pyrene in mixtures of acetone and water

Figure 3.6 shows the logarithm of the solubility of pyrene and benzo[a]pyrene in mixtures of acetone and water as a function of the acetone concentration. The logarithm of the pyrene solubility is linearly related to the acetone concentration with a correlation coefficient of 0.97. The linear relationship between the logarithm of the benzo[a]pyrene solubility and the acetone concentration has a correlation coefficient of 0.87. These correlation coefficients suggests a log-linear relationship between the solubility and the solvent concentration, as was reported by, for instance, Fu and Luthy [18]. However, Figure 3.6 shows that the measured points are not randomly distributed around the regression lines; the log-linear relationships therefore have to be used with caution. This applies especially to benzo[a]pyrene, because its solubility seems to strongly decrease below 70 vol.% of acetone (Figure 3.6).

Figure 3.6 shows that the solubility of pyrene and benzo[a]pyrene is higher in 100 vol.% acetone than in 80 vol.% acetone. Therefore, the solubility in the extraction solvent cannot account for the small decrease in extraction efficiency of pyrene and benzo[a]pyrene from 80 to 100 vol.% acetone (Figures 3.3 and 3.4). Figure 3.6 also shows that the solubility of benzo[a]pyrene in the acetone/water mixtures is more than four times lower than that of pyrene. The lower solubility of benzo[a]pyrene probably explains the lower extraction efficiency of benzo[a]pyrene found in most experiments using acetone.

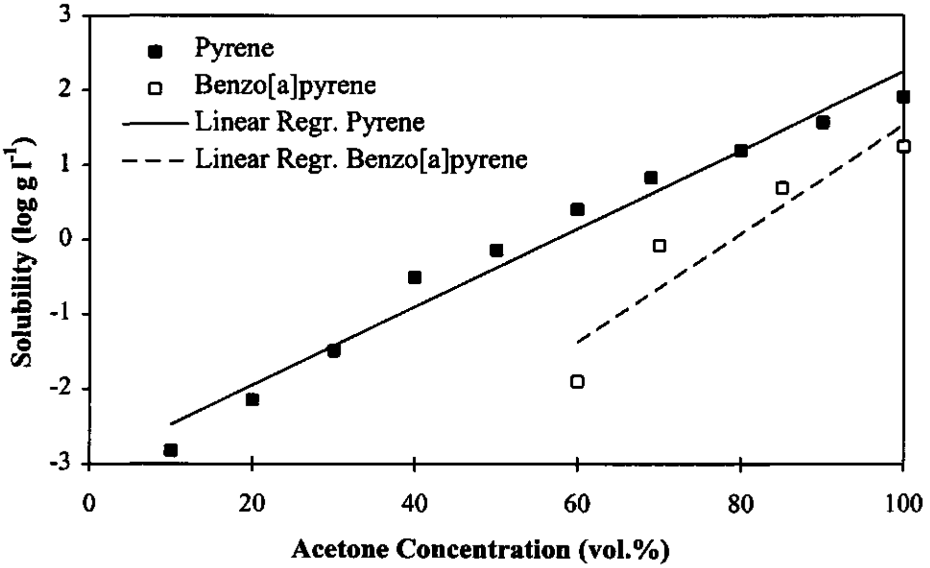

Figure 3.6 **Logarithm of the solubility (log g l^{-1}) of pyrene and benzo[a]pyrene in mixtures of acetone and water as a function of the acetone concentration with fitted linear regression lines**

3.3.4 Cosolvency model

The effect of the methanol and acetone concentration in the extraction solvent on the extraction efficiency of pyrene and benzo[a]pyrene was studied using the cosolvency model [2]. This model assumes a log-linear relationship (equation 3.1) between the distribution coefficient (K_s) and the solvent concentration. The distribution coefficient (mol kg^{-1}) is defined as the PAH concentration in the soil (mol kg^{-1}) divided by the PAH concentration in the extraction solvent (mol mol^{-1}). A condition for a log-linear relationship between K_s and the solvent concentration is the existence of a log-linear relationship between the solubility of the PAHs in the solvent/water mixture and the solvent concentration.

The cosolvency model was used to describe the results of the experiments carried out with mixtures of methanol/water and acetone/water as a function of the solvent concentration, as shown in Figure 3.2. The K_s values were calculated from the measured extraction efficiencies for pyrene and benzo[a]pyrene obtained after an extraction time of 30 minutes. As mentioned above, it can be assumed that after 30 minutes an equilibrium exists between the PAH concentration in the solvent and that in the soil. The logarithm of the K_s values is shown in Figure 3.7 as a function of the solvent concentration. For the extraction of pyrene with 100% methanol, no K_s values could be calculated, because the extraction efficiency was close to 100%, which would lead to an inaccurate calculation of the pyrene concentration in the soil.

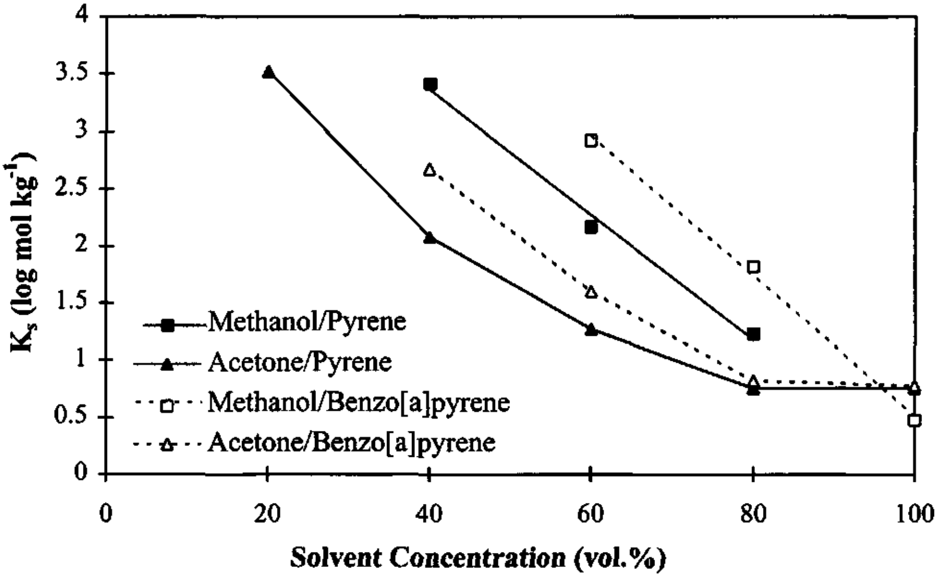

Figure 3.7 **Logarithm of the distribution coefficients (log mol kg^{-1}) of pyrene and benzo[a]pyrene between sand and mixtures of methanol/water or acetone/water as a function of the solvent concentration**

If mixtures of methanol and water are used, the values for log K_s of pyrene and benzo[a]pyrene show a linear relationship with the methanol concentration. The correlation coefficients of both regression lines are above 0.99.

For mixtures of acetone and water, the values for log K_s of pyrene and benzo[a]pyrene are not linearly correlated to the acetone concentration (Figure 3.7). For pyrene, log K_s shows a linear relationship with the acetone concentration from 20 vol.% to 60 vol.% acetone. The correlation coefficient of this relationship is 0.97. For benzo[a]pyrene, the relationship between log K_s and the acetone concentration is linear until 80 vol.% acetone with a correlation coefficient of 0.99. Therefore, the cosolvency model applies to mixtures of methanol and water, but not to those of acetone and water above an acetone concentration of 60 vol.%.

The results obtained with the cosolvency model for mixtures of methanol/water and acetone/water for pyrene and benzo[a]pyrene agree with those reported by Nkedi-Kizza et al. [19]. For the sorption of anthracene from mixtures of methanol and water onto four soils, they found a log-linear relationship between K_s and the methanol concentration. For mixtures of acetone and water however, the relationship between K_s and the acetone concentration was not log-linear. Nkedi-Kizza et al. [19] suggest that the deviations from the log-linear relationship are caused by effects of the solvent on the soil organic matter. The cosolvency model does not account for these effects.

Another explanation for the absence of a log-linear relationship between K_s and the acetone concentration is derived from the solubility of pyrene and benzo[a]pyrene in mixtures of acetone and water. As mentioned before, an important condition of the cosolvency model is that a log-linear relationship exists between the solubility of the PAHs in the acetone/water mixture and the acetone concentration. However, it was doubted whether such a relationship exists in the previous subsection, because the measured solubilities are not randomly distributed.

3.3.5 Relation between extraction efficiency, swelling of SOM and molecular interactions

From the above discussion it can be concluded that no clear relationship exists between the extraction efficiency or distribution coefficient (K_s) and the solubility of pyrene and benzo[a]pyrene in the extraction solvent, except for extraction solvents containing methanol and water. This is probably due to interactions occurring between the extraction solvent and soil substances, which are discussed in the following subsections.

Swelling of soil organic matter. An important effect of organic solvents on soil is thought to be swelling of soil organic matter (SOM), which results in higher sorption rates [2, 3, 4]. This swelling is thought to be strongest if the solubility parameter (δ_t) of the soil organic matter has a value close to that of the solvent [3, 20, 21]. The solubility parameter is based on the cohesive energy density of materials and was originally defined by Hildebrand and Scott. This parameter is a measure of the internal energy of a material and was intended for nonpolar, nonassociating systems [22]. Table 3.3 lists values of the solubility parameter (δ_t) and those of the partial solubility parameters for water and the solvents used. The partial solubility parameters are an indication of the ability of a material to interact by dispersion (δ_d), to form polar interactions (δ_p), and to form hydrogen (H) bonds (δ_h).

Table 3.3 Experimentally observed extraction efficiency (%) of pyrene and benzo[a]pyrene and solubility parameters of water and the solvents used

Solvent	Extraction efficiency (%)		Solubility parameters ((MPa)$^{1/2}$)			
	Pyrene	Benzo[a]p.	Total δ_t	Dispersion δ_d	Polar δ_p	H-bonding δ_h
Acetone	84 ± 1.0	81 ± 1.2	20.0	15.5	10.4	7.0
Methanol	100 ± 1.7	95 ± 2.5	29.7	15.1	12.3	22.3
Ethanol	85 ± 0.6	79 ± 1.2	26.6	18.8	8.8	19.4
1-Propanol	71 ± 1.3	68 ± 1.8	24.5	16.0	6.8	17.4
2-Propanol	57 ± 0.3	57 ± 0.06	23.5	15.8	6.1	16.4
1-Butanol	60 ± 0.8	60 ± 1.6	23.1	16.0	5.7	14.5
Water			47.9	15.5	16.0	42.3

Source: [23]

The solubility parameter of soil organic matter is hard to determine, because the structure of this matter is very complex and mostly unknown. In fact, the solubility parameter was originally defined for non-polar solvents and should not be applied to such a highly complex organic structure as soil organic matter [22]. During the present investigation, the solubility parameters (δ_t) of the six organic solvents were compared to the extraction efficiency for the extraction of pyrene and benzo[a]pyrene from sand with these six pure solvents (Table 3.3). However, no linear correlation was found between the δ_t values of the six solvents and the extraction efficiency. The correlation coefficients are 0.33 for pyrene and 0.26 for benzo[a]pyrene.

It is very doubtful whether the solubility parameter can be used to predict the degree of swelling of SOM. Experiments carried out by Schuerch [20] and Lyon and Rhodes [24] did not show a relationship between the solubility parameter of the solvent and the degree of swelling of SOM in that solvent. Schuerch found an abruptly decreasing solubility of lignin compounds in alcohols with increasing chain length, although the solubility parameters of the larger alcohols were more similar to those of the lignin compounds (about 22 (MPa)$^{1/2}$). Lyon and Rhodes [24] did not find a correlation between the swelling of peat organic matter and cellulose in about 40 solvents on the one hand, and the solubility parameters of the solvents on the other. They suggest that swelling of SOM is largely attributable to site-specific chemical interactions of the donor-acceptor type between the solvent and the components of the organic matter. Such site-specific interactions lower the net free energy of the swollen state of SOM for some solvents. An example of a donor-acceptor interaction is an H-bond. Schuerch [20] found, for instance, that the swelling of lignin compounds increased as the H-bonding capacity of the solvent increased.

For the spiked soils used, it is doubtful whether swelling of SOM has a strong influence on the extraction efficiency, because the PAHs are adsorbed onto the surface area of the soil particles, as was concluded before. It is not likely that during extraction with a solvent the PAHs move into the swollen SOM because of the high extraction capacity of organic solvents.

Molecular interactions. Another important interaction between a solvent and soil substances may be the competition of the solvent and PAH molecules for (ad)sorption sites on the soil substances. The competition of solvent molecules will be more successful if many interactions occur between the sorption sites and solvent molecules. The sorption sites contain mostly polar groups, such as $-COO^-$ and $-OH$, which are able to form H-bonds [25]. Therefore, formation of H-bonds and polar interactions are thought to play an important role in the interaction of solvent molecules with soil substances.

The ability of solvent molecules to form H-bonds and to participate in polar interactions is expressed by the partial solubility parameters δ_h and δ_p (Table 3.3). The value of δ_p for the pure solvents is linearly correlated with the extraction efficiency with a correlation coefficient of 0.91 for pyrene and one of 0.94 for benzo[a]pyrene. The values of δ_h and δ_d are not linearly correlated to the extraction efficiency, because the correlation coefficients are below 0.1. In conclusion, polar interactions between the extraction solvent and soil substances are probably most important for competition with PAHs, whereas the formation of H-bonds and dispersion play a minor role.

For mixtures of acetone and water, the extraction efficiency was highest when the extraction solvent contained 10 to 20 vol.% water. An explanation for this phenomenon may be that water molecules compete more successfully with the PAHs for (ad)sorption sites on the soil substances than acetone molecules do. Addition of water increases the total polarity and the total H-bonding capacity of the acetone/water mixture. Acetone molecules can accept only H-bonds, but water molecules can both donate and accept H-bonds and are more polar. Therefore, the number of interactions between the soil substances and molecules of the acetone/water mixture increase, when water is added. This also appears from an increase in the values of δ_p and δ_h of an acetone/water mixture with increasing water content. The solubility parameter of a binary mixture is thought to be volume-wise proportional to the solubility parameters of the pure solvents [22]. The δ_p and δ_h values of an acetone/water or methanol/water mixture are therefore higher than those of pure acetone or pure methanol, because water has higher δ_p and δ_h values than acetone and methanol have (Table 3.3). However, addition of water will also decrease the solubility of pyrene and benzo[a]pyrene in the extraction solvent (Figure 3.6), which results in a decreassing PAH desorption and decreasing extraction efficiency. In conclusion, by adding water the PAH desorption and the extraction efficiency are negatively influenced by a decreasing solubility of the PAHs in the extraction solvent and positively influenced by an increasing competition of acetone and water molecules with PAHs for (ad)sorption sites. These two opposite effects probably lead to the highest extraction efficiency for 10 to 20 vol.% water in the mixture of acetone and water.

3.4 Conclusions

For the remediation of contaminated soil using the solvent extraction process, acetone is the best solvent compared to methanol, ethanol, propanol and butanol. The most important advantage of acetone is that the extraction efficiencies are high even if the contaminated soil contains water. Methanol shows lower extraction efficiencies compared to acetone, except for the extraction of air-dried sand with pure methanol. However, methanol is not a suitable solvent for the process, because in practice soil always contains water, and drying as a pretreatment step will result in higher costs.

For the extraction with acetone, the maximum extraction efficiency is reached with 10 to 20 vol.% water in the extraction solvent for air-dried sand, silt and clay. When water is added to the sand, the maximum extraction efficiency is achieved with about 15 wt% water in sand for the extraction with pure acetone. In the three soils spiked with pyrene and benzo[a]pyrene, the extraction efficiency of a mixture of 80 vol.% acetone and 20 vol.% water no longer changes after an extraction time of about 5 minutes. Therefore, an equilibrium is reached within 5 minutes, which indicates that during spiking of the soil no transport of contamination into the soil particles occurs. The PAH contamination is probably bound only to the surface area of the soil particles. Furthermore, aging of pyrene in the sand, silt and clay did not have a negative effect on the extraction efficiency, from which it was concluded that the distribution of PAHs in air-dried soil is not influenced by storage for three months at 7°C.

The extraction efficiency of pyrene was not correlated to the solubility ($g\ l^{-1}$) of pyrene in pure acetone, methanol, ethanol, 1-propanol, 2-propanol and 1-butanol for the extraction of sand. In addition, for the extraction of pyrene and benzo[a]pyrene from the three air-dried soils with pure acetone and mixtures of acetone and water, the efficiencies were also not correlated to the solubility of pyrene and benzo[a]pyrene. The highest extraction efficiency was achieved with a mixture of 80 vol.% acetone and 20 vol.% for both PAHs, whereas the solubility of these PAHs in pure acetone is higher than in a mixture of 80 vol.% acetone and 20 vol.% water.

The cosolvency model was used to study the effect of the methanol and acetone concentration in the extraction solvent on the extraction efficiency for pyrene and benzo[a]pyrene. For methanol, the distribution coefficients (K_s) of pyrene and benzo[a]pyrene were found to be log-linearly correlated to the methanol concentration. However, the distribution coefficients in mixtures of acetone and water showed no log-linear relationship with the acetone concentration above acetone concentrations of 60 vol.% and 80 vol.% for pyrene and benzo[a]pyrene, respectively. Two explanations were proposed for the absence of a clear relationship between the extraction efficiency, the distribution coefficient, the solubility of pyrene and benzo[a]pyrene, and the acetone concentration: a) swelling of soil organic matter, which makes the organic matter more easily accessible for PAHs and results in higher sorption rates, b) competition between solvent molecules and PAHs for sorption sites on the soil substances. For both mechanisms, polar interactions between the solvent molecules and soil substances may be important, because a linear relationship was found between the extraction efficiencies of the six pure solvents and the polar partial solubility parameters (δ_p) of the solvents.

Finally, addition of water to an extraction solvent (e.g. acetone) may have two opposite effects on the PAH desorption and the extraction efficiency. The desorption and efficiency will decrease because of the decreasing solubility of the PAHs in the extraction solvent, but on the other hand the water molecules will probably show strong competition with PAHs for sorption sites. This leads to the highest extraction efficiency for the extraction of pyrene and benzo[a]pyrene for 10 to 20 vol.% water in the mixture of acetone and water.

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Chapter 4

Removal of PAHs from aged sludge and sediment by multiple subsequent extraction steps with acetone/water mixtures

Abstract

Aged sludge, sieve fractions of this sludge and aged sediment all contaminated with polycyclic aromatic hydrocarbons (PAHs) were extracted seven times with acetone/water mixtures with a volume ratio of 4:1 and 3:2. The extraction procedure with a 4:1 mixture of acetone and water was found to be sufficient to reach the Dutch target level of PAHs for clean soil in sludge (= 2.6 mg per kg of dry matter). In the sediment, the target level of PAHs (= 1.2 mg per kg of dry matter) was almost achieved. The initial total PAH concentrations in the sludge (about 1,000 mg per kg of dry matter) and in the sediment (about 650 mg per kg of dry matter) were reduced by more than 99%. Most PAHs remaining in the samples extracted seven times with a 4:1 mixture of acetone and water were of a relatively low molecular weight: phenanthrene, anthracene and fluoranthene. These three PAHs showed to be most difficult to remove from the solids at low concentrations. Extraction with a 3:2 mixture of acetone and water showed lower extraction efficiencies and higher residual concentrations in sludge and sediment.

Based on the results of the seven extraction steps, desorption isotherms for the PAHs in the samples were calculated. The desorption isotherms of the individual PAHs and the sum of EPA-PAHs in the sludge and sediment could be accurately described with Freundlich isotherms. For the sieve fractions of the sludge the PAH composition and the desorption isotherms of the PAHs showed almost no differences, and therefore separate treatment of contaminated sieve fractions is not an efficient remediation strategy.

4.1 Introduction

The desorption of contaminants like polycyclic aromatic hydrocarbons (PAHs) is a critical factor in the development of a solvent extraction process for remediation of aged soils, sludges and sediments. The solvent extraction process is thought to be especially suited for remediation of residual sludges from soil washing plants, because these sludges contain high amounts of contamination and are regarded as chemical wastes. Disposal of chemical waste is expensive and therefore, cleaning of these sludges for reuse is expected to be worthwhile. Besides residual sludges, contaminated sediments obtained from dredging of harbours and rivers are of interest for remediation with solvent extraction. Biological remediation of these sediments is difficult because of the high clay content, and thermal treatment is expensive because of the high water content. Solvent extraction seems an appropriate remediation method for contaminated sediments as high extraction efficiencies were obtained by the solvent extraction process of Resources Conservation Company for two aged sediments contamined with PAHs and polychlorinated biphenyls, using triethylamine as extraction solvent [1]. However, a remediation method for contaminated soil, sediment or sludge can only be considered successful in the Netherlands if the Dutch target levels established for clean soil can be achieved or if they can be cleaned up to the requirements for building materials.

A suitable solvent for extraction of PAHs from soil, sludge and sediment is acetone, because it shows high extraction efficiencies for these substances [2], is less toxic than other organic solvents used in industry, and is easily biodegradable [3]. Another advantage of acetone is that a small amount of water in the sludge or sediment has no negative effect on the attainable extraction efficiencies [3].

To demonstrate whether the Dutch target levels for clean soil can be obtained by extraction with acetone the desorption of PAHs from aged contaminated sludge and sediment into the organic solvent has to be studied. In general, most research on the (ad)sorption and desorption behaviour of PAHs is carried out using spiked soils in slurries of water. For such systems, two mechanisms for the sorption of nonpolar organic compounds—such as PAHs—present in a water phase have been proposed: partitioning and hydrophobic adsorption [4]. In the case of hydrophobic adsorption, the PAH molecules accumulate at external or internal surfaces of the soil substances. They are adsorbed at hydrophobic active sites, such as aliphatic side chains, fats and aromatic lignin-derived substances with a high carbon content and few polar groups [5]. For hydrophobic adsorption the size of the external and/or internal surface area is important [6]. The driving force of hydrophobic adsorption is the strong excluding force applied by water molecules. Partitioning refers to the homogeneous distribution of PAHs throughout the organic-matter phase and water phase, such as the partitioning of PAH molecules between two immiscible liquid phases [4]. In soil/water slurries, (de)sorption isotherms of non-ionic organic contaminants are mostly related to the organic matter content or organic carbon content of the soil and to the water solubility of the contaminants [4,7]. Such a relationship is considered to indicate that partitioning is the main sorption mechanism [3].

A model often applied for the description of (de)sorption isotherms of contaminants in soil or slurry systems is the Freundlich equation [6]:

$$S = K * C_l^n \tag{4.1}$$

where S is the PAH concentration in the solids (mg (kg of dry matter)$^{-1}$), C_l is the PAH concentration in the extraction solvent (mg l^{-1}), and K and n are constants. The values of K and n can be determined by curve fitting. The value of K is an indication of the (ad)sorption energy and entropy, and n is an indication of the distribution of the interaction energy over the (ad)sorption sites [6]. K is also known as the sorption capacity, and n as the sorption intensity. Although the Freundlich equation is an empirical equation, it usually describes the (de)sorption behaviour quite well [7].

For remediation of contaminated soil by washing, soil is often separated in size fractions because the initial concentrations, the physical state of the contaminants and the sorption capacity of the solids in the size fractions vary [8,9]. Often, the sand fraction (particle diameter > 63 µm) contains almost no contaminants, whereas the clay and silt fractions contain large amounts of contaminants because of the large surface area and sorption capacity [10]. Therefore, it can be profitable to develop a remediation strategy for contaminated solids based on the properties of the particles like size, organic matter content and sorption capacity.

The (de)sorption behaviour of PAHs depends not only on the properties of the solids but also on their affinity for the extraction solvent, which is apparent from their solubility in this solvent. PAHs have low water solubility, because they are non-polar and cannot form hydrogen bridges. Acetone is far less polar than water. Therefore, the solubility of, for instance, anthracene, fluoranthene, pyrene and benzo[ghi]perylene in pure acetone is a factor of at least 10^5 higher than their water solubility [11,12,13]. Consequently, the solubility of PAHs in acetone decreases if water is added to the acetone. However, preliminary experiments showed that for aged contaminated soils present in an acetone/water mixture with a volume ratio of 4:1 the extraction efficiency of PAHs was somewhat higher than or equal to their extraction efficiency in pure acetone.

In this investigation the aim was to determine whether the Dutch target levels established for clean soil could be reached in a contaminated aged sludge and sediment by performing multiple extraction steps with acetone/water mixtures. In addition, the amount of extraction solvent needed to reach these target levels was determined. Based on the results of the multiple extraction steps desorption isotherms of PAHs were calculated for the aged sludge, size fractions of this sludge, and the aged sediment to investigate the desorption behaviour. Finally, based on the extraction efficiencies and desorption isotherms a remediation strategy for the sludge and sediment was determined.

4.2 Materials and methods

4.2.1 Samples

Two samples were used: residual sludge from a Dutch soil washing plant (hereafter referred to as "sludge" or "SG"), and sediment from Amsterdam's Petroleum Harbour (hereafter referred to as "sediment" or "SDM"). The sludge had been delivered after being dewatered using a sieve belt press; its dry matter content was 52% (kg kg^{-1}), and its organic matter content 26% (kg (kg of dry $matter)^{-1}$). A sample of the sludge (SG) was split into a clay (<20 μm), silt (20-63 μm) and sand fraction (>63 μm) by sieving with water for seven hours. The dry weight and organic matter content of each fraction were determined (see Table 4.1). The dry matter content of samples was determined by heating at 105°C, and their organic matter content by heating at 500°C, after which the loss of weight was determined. Table 4.1 shows also the particle diameter of the sieve fractions. The mean particle diameter was chosen as the midst diameter of fraction SG<20 and SG20-63. In SG>63 almost all particles had a diameter between 63 and 180 μm [14], and therefore the mean diameter was chosen to be 120 μm.

The sediment had a dry matter content of about 35% (kg kg^{-1}) and an organic matter content of 12% (kg (kg of dry $matter)^{-1}$). The content of mineral particles smaller than 2 μm in the sediment was 17%, and the content of particles ranging from 63 to 2000 μm was 41% (kg (kg of dry $matter)^{-1}$) [14].

Table 4.1 The particle size of the sludge after sieving with water, the dry weight content and the organic matter content

Sample	Particle diameter		Mass fraction	Organic matter content
	Range (μm)	Mean (μm)	(kg (kg dry $matter)^{-1}$)	(kg (kg dry $matter)^{-1}$)
SG>63	63-1,000	120	0.36	0.36
SG20-63	20 - 63	42	0.25	0.23
SG<20	0 - 20	10	0.39	0.27
SG	0-1,000			0.26

4.2.2 Desorption procedure

Desorption isotherms were determined for the sum of the 16 EPA-PAHs and the individual EPA-PAHs, which comprise pyrene and the 15 PAHs given on the EPA list of priority pollutants. These isotherms were determined by extraction with an acetone/water mixture with a volume ratio of 4:1 for the complete sludge (SG 4:1), the sieve fractions of this sludge (SG<20, SG20-63, SG>63), and the sediment (SDM 4:1). Samples of the complete sludge (SG 3:2) and the sediment (SDM 3:2) were also extracted with an acetone/water mixture with a volume ratio of 3:2. The water already present in the sludge and sediment samples was taken into account when calculating the volume ratios. A volume ratio of 4:1 was chosen, because preliminary experiments with the sludge and sediment showed maximum extraction efficiencies at this ratio. When using acetone/water mixtures with a volume ratio of 3:2, the extraction efficiency will be lower and the residual PAH concentration will be higher, but probably less acetone is needed for the extraction process. A volume ratio of 4:1 for the mixture of acetone and water is equal to a mixture of 80 vol.% acetone and 20 vol.% water. An acetone/water mixture with a volume ratio of 3:2 corresponds to a mixture with 60 vol.% acetone and 40 vol.% water.

The desorption procedure was as follows. In a centrifuge tube (250 ml), wet sludge or sediment (10 g of dry matter) and 90 ml of an acetone/water mixture were mixed at 20°C for one hour using a rotary tumbler (25 rpm, rotation diameter: 50 cm). The added acetone/water mixture had been adjusted so that the total amount of liquid in the tubes had an acetone/water volume ratio of 4:1 or 3:2. After extraction, the tube was centrifuged (using an IEC Centra-4B centrifuge) at 4500 rpm for six minutes, which always resulted in a clear supernatant. As much supernatant as possible was removed (about 75 ml) and fresh solvent was added to obtain again 90 ml of extraction solvent. Next, the tube content was mixed for one hour and centrifuged for six minutes.

This desorption procedure was carried out seven times, because during preliminary extraction experiments with an acetone/water mixture of 4:1 it was found that about seven extraction steps were needed to reach the Dutch target levels in the sludge. This had been calculated from the decrease in PAH concentration in the solids after two extraction steps. To calculate the mass balance, the tube (including contents) was weighted after each removal or addition of solvent. The experiments were carried out in duplicate, except for the experiment using the complete sludge and an acetone/water mixture with a ratio of 4:1, which was carried out in triplicate.

Preliminary extraction experiments showed that for the sludge the PAH concentration in the extraction solvents no longer increased after an extraction time of 30 minutes during the first and second extraction step. Extraction from the sediment lasted longer: the state of equilibrium was reached within one hour during the first extraction step. Therefore, one hour of extraction time was assumed to be sufficient to reach equilibrium in each extraction step.

4.2.3 Analytical procedures

Pretreatment of solvent extracts. The PAH concentration in the supernatants removed during the desorption procedure was determined by HPLC after concentration or dilution of the supernatants. Supernatants were concentrated by transferring the PAHs into petroleum ether (40-60°C), namely by extraction of the acetone/water phase with petroleum ether in a separation funnel. Such extraction was carried out twice. Next, the petroleum-ether phases were concentrated in a Kuderna Danish apparatus. Finally, the PAHs in the concentrated petroleum-ether phase were transferred into acetonitrile by stripping the residual petroleum ether with nitrogen. The acetonitrile solution was injected into the HPLC.

The sample extracts, which needed no concentration, were centrifuged at 10,000 rpm for three minutes. The supernatants were diluted with fresh extraction solvent, if necessary, and directly injected into the HPLC, since further treatment showed no improvement of results [2].

Determination of residual PAH concentration. All samples extracted seven times with acetone/water mixtures were dried at room temperature to remove the acetone. Subsamples were taken from the dried material to determine its dry matter content, which was done by heating the samples at 105°C. Next, 5 g of the material dried at room temperature was extracted with 20 ml of N-methyl-2-pyrrolidinone (NMP) in a Teflon microwave vessel placed in a microwave oven at 130°C (CEM, MDS-2100) for one hour. This method was the most efficient method for extracting PAHs from this sludge and sediment [2]. After extraction with NMP, the sludge and sediment samples were assumed to contain negligible amounts of PAHs. Since the PAH concentration in the samples extracted with a 4:1 mixture of acetone and water was very low, NMP extracts were combined and concentrated by transferring the PAHs into petroleum ether according to the procedure detailed in the subsection above. For the sludge samples extracted with a 4:1 mixture of acetone and water the residual concentration was determined in a mixture of these samples, and therefore SG 4:1, SG>63, SG20-63 and SG<20 have the same residual concentration.

The sludge and sediment samples extracted with a 3:2 mixture of acetone and water were extracted with NMP in duplicate. The resultant NMP extracts were centrifuged at 10,000 rpm for three minutes, and the supernatants were directly injected into the HPLC.

The residual PAH concentration in the solids after seven extraction steps consisted of the PAH concentration in the NMP extracts determined by HPLC minus the average quantity of PAHs dissolved in the acetone/water mixture which was left behind in the solids after the seventh extraction step.

Determination of the PAH concentration in solvent extracts by HPLC. The concentration of the 16 EPA-PAHs in the solvent extracts was determined by separation in an HPLC column (Vydac 5, C18 Rev. phase) followed by the use of a photo diode array detector (Waters 991). The 16 EPA-PAHs were identified in the resultant chromatograms by visual comparison between the spectra of peaks for the samples and standard chromatograms for the 16 EPA-PAHs. In the extracts of the sludge, 10 of the 16 EPA-PAHs could be identified: phenanthrene (PHE), fluoranthene (FLU), pyrene (PYR), benzo[a]anthracene (B[a]A), chrysene (CHR), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), benzo[ghi]perylene (B[ghi]P), and indeno[123-cd]pyrene (IND). The extracts of the sediment contained the same PAHs as well as anthracene (ANT). Finally, the concentrations of the identified EPA-PAHs were derived from the chromatograms at a wavelength of 254 nm.

4.2.4 Target levels

In the Netherlands, the target level for clean soil is based on the concentration of the 10 VROM-PAHs [15]. Of the identified PAHs mentioned in the previous section, PYR and B[b]F are no VROM-PAHs. The target level for the sum of VROM-PAHs depends on the organic matter content and is 1 mg (kg of dry matter)$^{-1}$ for soil with 10% organic matter. The target level is 2.6 mg (kg of dry matter)$^{-1}$ and 1.2 mg (kg of dry matter)$^{-1}$ for the sludge and sediment, respectively.

4.2.5 Calculation of desorption isotherms

The mass balance of the sum of EPA-PAHs or of an individual PAH in the first extraction step is given by:

$$W \ast S^0 = W \ast S^1 + V_l^1 \ast C_l^1 \qquad (4.2)$$

where W is the quantity of dry matter (kg), S the concentration of the sum of EPA-PAHs or of an individual PAH in the solids (mg (kg of dry matter)$^{-1}$), C_l the concentration of the sum of EPA-PAHs or of a individual PAH in the extraction solvent (mg l^{-1}), and V_l the total volume of solvent (l) in this extraction step. Superscript 0 refers to the initial situation, and superscript 1 refers to the situation existing after the first extraction step. The mass balance in the subsequent extraction steps is given by:

$$W \ast S^i + x^i \ast V_l^i \ast C_l^i = W \ast S^{i+1} + V_l^{i+1} \ast C_l^{i+1} \qquad (4.3)$$

where superscript i refers to the situation existing after extraction step i, and x^i is the volume fraction of the total volume of solvent (V^i_l) remaining in the solids after extraction step i. To calculate the PAH concentration in the solids, first the initial concentration in the solids (S^0) needs to be calculated, using the following equation:

$$S^0 = S^7 + (x^7 * V_l^7 * C_l^7 + \sum_{i=1}^{7} (1 - x^i) * V_l^i * C_l^i) / W \tag{4.4}$$

where S^7 is the residual PAH concentration in the solids determined by extraction with NMP in the microwave oven. The PAH concentration in the solids after the first extraction step (S^1) is calculated using a rearranged version of equation (4.2):

$$S^1 = (W * S^0 - V_l^1 * C_l^1) / W \tag{4.5}$$

The PAH concentration in the solids after subsequent extraction steps is calculated using a rearranged version of equation (4.3):

$$S^{i+1} = (W * S^i + x^i * V_l^i * C_l^i - V_l^{i+1} * C_l^{i+1}) / W \tag{4.6}$$

For each experiment, the concentration of the sum of EPA-PAHs and that of each individual PAH in the solids (S^i) after step i was calculated.

To describe the desorption isotherms, the Freundlich equation was chosen (equation 4.1), because very little is known about the character of the sorption. The Freundlich equation was used in a logarithmic form in order to obtain a linear relationship between C_l and S:

$$\log S = \log K + n \log C_l \tag{4.7}$$

The best fitting Freundlich equations with parameters K and n were determined for the sum of EPA-PAHs and individual PAHs by linear regression with least sum of squares.

4.3 Results and discussion

4.3.1 Initial and residual concentrations in sludge and sediment

Sum of EPA-PAHs. Table 4.2 shows the initial (S^0) and residual (S^7) concentrations of the sum of EPA-PAHs measured in the samples. As far as the sludge fractions are concerned, the average initial PAH concentration in fraction SG>63 is twice as high as that in fraction SG<20. However, separate remediation of sieve fraction SG<20 on basis of the initial PAH concentration seems not profitable because the initial PAH concentration in SG<20 and the other sieve fractions is still high.

For the three sieve fractions the relationship between the initial PAH concentration (Table 4.2), the mean particle diameter and the organic matter content (Table 4.1) was studied by linear regression. A weak positive correlation exists between the mean particle diameter and the initial PAH concentration as the correlation coefficient is 0.87. The initial PAH concentration increases with increasing particle size and thus with decreasing size of the external surface area. This questions hydrophobic adsorption as the main sorption mechanism of PAHs in the sludge because hydrophobic adsorption depends on the size of the adsorption surface area [6]. However, in the sludge particles the PAHs may be adsorbed mostly to the internal surface and less to the external surface. In this case the internal porosity is important for the sorption process. The initial PAH concentration was not correlated to the organic matter content either, since this relationship had a correlation coefficient of 0.4. From these results it can be concluded that partitioning does not seem to be the main sorption mechanism, as partitioning is expected to depend on the amount of organic matter [4,7]. It is also possible that hydrophobic adsorption nor partitioning determines the sorption process because the PAHs may be present as solid phase in the pores or are absorbed into coal or tar particles [16].

Table 4.2 Average initial and residual concentrations of the sum of EPA-PAHs (mg (kg of dry matter)$^{-1}$)

Sample	Concentration	
	Initial (10^3 mg kg^{-1})	Residual (mg kg^{-1})
SG 4:1	1.0 ± 0.05	1.7
SG>63	1.4 ± 0.1	1.7
SG20-63	1.1 ± 0.06	1.7
SG<20	0.69 ± 0.05	1.7
SG 3:2	0.94 ± 0.03	93 ± 8
SDM 4:1	0.64 ± 0.03	2.2
SDM 3:2	0.68 ± 0.1	25 ± 2

In the sludge and sediment samples extracted with a 3:2 mixture of acetone and water, the residual concentration of the sum of EPA-PAHs is 55 times and 11 times higher than that in the sludge and sediment samples extracted with a 4:1 mixture of acetone and water, respectively. This effect will be mostly due to the solubility of the PAHs in the extraction solvent which decreases with increasing water content.

As mentioned before, the target level related to the sum of VROM-PAHs is 2.6 mg kg^{-1} for the sludge and 1.2 mg kg^{-1} for the sediment. The residual concentration of the 10 VROM-PAHs in the sludge and sediment extracted with a 4:1 mixture of acetone and water is 1.6 mg kg^{-1} and 2.0 mg kg^{-1}, respectively. Thus, the target level is only reached in the sludge extracted with a 4:1 mixture of acetone and water. However, after one or two additional extraction steps the target level can also be reached in the sediment extracted with a 4:1

mixture of acetone and water. The residual PAH concentrations in sludge and sediment after seven extraction steps with a 3:2 mixture of acetone and water are still substantially higher than the target levels.

Content of individual PAHs. Table 4.3 shows the distribution of the individual PAHs as the average weight percentages of the initial concentration of the sum of EPA-PAHs in the sludge and sludge fractions extracted seven times with a 4:1 mixture of acetone and water. Table 4.3 shows that each size fraction of the sludge contains almost the same percentages of individual PAHs, whereas the initial PAH concentrations are quite different (Table 4.2).

Table 4.3 Average initial content values of the individual PAHs (% of total concentration of EPA-PAHs)

PAH	SG>63	SG 20-63	SG<20	SG 4:1
PHE	3.5 ± 0.8	1.9 ± 0.2	2.2 ± 0.1	2.6 ± 0.6
FLU	11 ± 2	11 ± 0.6	8.3 ± 0.2	11 ± 0.3
PYR	18 ± 3	19 ± 1	11 ± 0.5	17 ± 1
B[a]A	7.8 ± 1	7.8 ± 1	5.4 ± 0.5	6.3 ± 0.6
CHR	9.0 ± 0.8	9.5 ± 0.6	7.9 ± 0.4	8.7 ± 1
B[b]F	9.0 ± 0.1	8.2 ± 0.4	11 ± 0.4	9.1 ± 0.5
B[k]F	2.4 ± 0.7	3.0 ± 0.1	2.0 ± 0.1	2.3 ± 0.8
B[a]P	16 ± 0.3	15 ± 1	21 ± 1.0	17 ± 0.5
B[ghi]P	15 ± 1	15 ± 0.4	19 ± 3	16 ± 2
IND	9.4 ± 0.3	9.6 ± 0.1	12 ± 2	11 ± 0.5

Table 4.4 shows the distribution of the individual PAHs as the average weight percentages of the initial and residual concentrations of the sum of EPA-PAHs in the sludge and sediment samples extracted with mixtures of acetone and water with a ratio of 4:1 and 3:2.

The initial concentrations in the two sludge samples have almost the same PAH composition and the same holds for the two sediment samples. In the sediment, the initial percentage of PAHs of low molecular weight (PHE, ANT, FLU and PYR) is high: about 68%. Only about 15% of the PAHs contained in the sediment are of high molecular weight (B[b]F, B[k]F, B[a]P, B[ghi]P and IND), while in the sludge these PAHs comprise more than 46% of the PAH concentration. Table 4.4 shows that the residual concentrations in SG 4:1, SDM 4:1 and SDM 3:2 comprise high percentages of PAHs of relatively low molecular weight: PHE, ANT and FLU. In SG 4:1 even half of the residual PAH concentration is composed of FLU. SG 3:2 contains only 26% of PHE and FLU, and 59% of B[a]P, B[ghi]P and IND. On the contrary, B[b]F and B[k]F can not be determined in all samples anymore after seven extractions with acetone/water mixtures.

Table 4.4 Average initial and residual content values of the individual PAHs (% of total concentration of EPA-PAHs)

PAH	SG 4:1		SG 3:2		SDM 4:1		SDM 3:2	
	Initial	Resid.	Initial	Resid.	Initial	Resid.	Initial	Resid.
PHE	2.6 ± 0.6	27	3.9 ± 0.1	6.3	15 ± 0.1	28	13 ± 2	28
ANT	-	-	-	-	7.8 ± 0.1	19	7.4 ± 1	16
FLU	11 ± 0.3	48	14 ± 0.1	20	27 ± 1	31	28 ± 5	27
PYR	17 ± 1	8.7	16 ± 2	5.7	19 ± 0.3	11	19 ± 4	9.3
B[a]A	6.3 ± 0.6	6.5	6.3 ± 0.03	3.4	6.9 ± 0.07	5.1	8.7 ± 3	6.0
CHR	8.7 ± 1	7.1	8.5 ± 0.09	5.5	8.6 ± 3	4.9	9.5 ± 2	8.6
B[b]F	9.1 ± 0.5	0.0	8.7 ± 0.5	0.0	3.7 ± 0.06	0.0	4.4 ± 1	0.0
B[k]F	2.3 ± 0.8	0.0	3.2 ± 0.4	0.0	1.8 ± 0.05	0.0	2.0 ± 0.5	0.0
B[a]P	17 ± 0.5	3.4	15 ± 0.2	17	4.3 ± 0.09	1.4	4.0 ± 2	5.7
B[ghi]P	16 ± 2	0.1	11 ± 0.04	23	2.7 ± 0.3	0.0	2.0 ± 0.6	0.0
IND	11 ± 0.5	0.0	8.7 ± 0.2	19	2.6 ± 0.2	0.0	2.4 ± 0.5	0.0

Extraction efficiencies. Table 4.5 shows the extraction efficiencies for the sum of EPA-PAHs and the individual PAHs as well as the molecular weight, the solubility in water and the logarithm of the octanol/water partition coefficient (log K_{ow}) for the individual PAHs. For the samples extracted with a 4:1 mixture of acetone and water, the extraction efficiencies of the sum of EPA-PAHs are higher than 99% in both sludge and sediment. The PAHs of low molecular weight (PHE, ANT and FLU) show a slightly lower extraction efficiency in these samples.

Almost equally high extraction efficiencies for removal of PAHs were obtained in seven sequent extraction steps by the Basic Extractive Sludge Treatment (BEST) process of Resources Conservation Company for extraction of two aged sediments [1]. In this process triethylamine was used as extraction solvent at temperatures varying from -2°C to 77°C. The extraction efficiencies of the 11 EPA-PAHs ranges from 92.6 to 98.5% for sediment A (initial concentration: 377 mg kg^{-1}) and from 99.5 to 99.9% for sediment B (initial concentration: 26,002 mg kg^{-1}). The residual concentrations for the sum of the 11 EPA-PAHs were 11.6 mg kg^{-1} and 85.2 mg kg^{-1} for sediment A and B, respectively, which is higher than the residual concentrations measured in this investigation for a 4:1 mixture of acetone and water (Table 4.2). However, the extraction process with 4:1 mixtures of acetone and water is not necessarily better than the BEST process because no information is available about the applied solid/liquid ratios in the BEST process. The reported advantage of the BEST process is the use of triethylamine, which is miscible with water at temperatures below 10°C and immiscible with water above 55°C [1]. These properties are exploited during the solvent recovery cycle of the process. However, probably much energy is needed to cool down the solvent below 10°C for dewatering of the sediment in the first two extraction steps and to heat up the solvent to 43°C or 77°C for the other five extraction steps. Extraction with a mixture of acetone and water can be carried out at room temperature and previous dewatering of the solids is not necessary. However, probably more energy is needed for the recovery of clean acetone.

Table 4.5 Extraction efficiencies (%) of the sum of EPA-PAHs and the individual PAHs for the sludge and sediment samples, and physical properties of the individual PAHs

PAH	Extraction Efficiencies (%)				Mol.wt[a]	Sol. Wa.[b]	log K_{ow}[c]
	SG 4:1	SG 3:2	SDM 4:1	SDM3:2	(g mol^{-1})	($\mu g\ l^{-1}$)	(-)
EPA	99.8	91.0	99.7	96.5			
PHE	98.3	86.3	99.4	92.6	178	1290	4.46
ANT	-	-	99.2	92.7	178	73	4.54
FLU	99.2	87.2	99.6	96.6	202	260	5.33
PYR	99.9	96.5	99.8	98.2	202	135	5.98
B[a]A	99.8	94.9	99.7	97.5	228	14	5.61
CHR	99.9	94.0	99.8	96.8	228	2	5.61
B[b]F	100.0	100.0	100.0	100.0	252	1.2	6.57
B[k]F	100.0	100.0	100.0	100.0	252	0.55	6.84
B[a]P	100.0	89.9	99.9	95.0	252	3.8	5.98
B[ghi]P	100.0	82.9	100.0	100.0	276	0.26	7.23
IND	100.0	81.9	100.0	100.0	276	0.62	7.66

[a] Mol. wt = molecular weight, source: [13]; [b] Sol. Wa. = solubility in water at 25°C, source: [13]; [c] source: [1]

Meckes et al. [1] found lower extractions efficiencies for PAHs of low molecular weight, like PHE and ANT, compared to PAHs of higher molecular weight as was also found in this investigation. Meckes et al. reported a relationship between the extraction efficiency and some physical characteristics of the PAHs, like molecular weight, the solubility in water and the value of log K_{ow} [1]. By linear regression the relationship between these three PAH properties and the extraction efficiencies of the individual PAHs (Table 4.5) was studied. For SG 4:1 the highest correlation coefficient (0.92) is found for the solubility of the PAHs in water, while the extraction efficiencies of SG 3:2 show no relationship with the PAH properties at all. Both sediment samples show the highest correlation with the value of log K_{ow}. The correlation coefficients are 0.83 and 0.82 for SDM 4:1 and SDM 3:2, respectively. However, conclusions about important PAH properties have to be drawn with caution because these PAH properties are mutual correlated. For instance, the molecular weight is weakly linear related to the value of log K_{ow} and to the logarithm of the solubility in water with correlation coefficients of 0.87 and 0.86, respectively. In addition, the relationships do not explain the lower extractability of the PAHs of low molecular weight and do not provide insight in the desorption processes. A property that may give more insight in the desorption processes is the solubility of the PAHs in the extraction solvent. However, the solubility in a 4:1 mixture of acetone and water is only known for a few PAHs. Another characteristic of the PAHs providing insight in the extractability is the desorption isotherm of the PAHs, which is discussed in the next subsection.

4.3.2 Desorption isotherms

Table 4.6 shows for all samples the values of K and n of the best fitting Freundlich isotherm for the sum of EPA-PAHs. The correlation between C_l and S can be described accurately by the log-linear Freundlich isotherm, as the correlation coefficient (R^2) is higher than 0.86 for all samples.

Table 4.6 The best fitting Freundlich desorption isotherms of the sum of EPA-PAHs for all samples, based on the formula: $\log S = \log K + n \log C_l$, with correlation coefficient R^2 and determined with least sum of squares

Parameters	SG>63	SG20-63	SG<20	SG 4:1	SG 3:2	SDM 4:1	SDM 3:2
log K	0.783	0.803	0.780	0.762	1.87	0.806	1.473
K	6.06	6.35	6.03	5.78	74.1	6.40	29.7
n	0.691	0.561	0.762	0.730	0.385	0.386	0.439
R^2	0.939	0.982	0.971	0.956	0.995	0.863	0.950

Sludge and sludge fractions. For the sludge and the sieve fractions extracted with a 4:1 mixture of acetone and water the best fitting value of K is almost equal (Table 4.6). By linear regression it was derived that the values of K and n of the sum of EPA-PAHs (Table 4.6) are not related to the mean particle diameter and the organic matter content (Table 4.1), because all correlation coefficients are below 0.5. Therefore, no conclusions can be drawn about the (de)sorption mechanism of PAHs in the sludge.

Figure 4.1 shows the calculated average equilibrium curves of the sum of EPA-PAHs in the solids (S) and the fitted log-linear Freundlich isotherms as a function of the PAH concentration in the extraction solvent (C_l) for the sludge and the three sieve fractions.

A high value of n means that the PAH concentration in the solids rapidly decreases with decreasing concentration in the solvent. Consequently, high n values are preferable for the cleaning of solids, as at such values large amounts of PAHs will be desorbed from the solids. The SG<20 fraction shows the highest n value (Table 4.6), which means that the PAH concentration in this fraction decreases more rapidly than that in the other fractions. Therefore, in SG<20 low S values can be reached more easily than in the other fractions, and at high values of C_l and S the PAH concentration in SG<20 will be higher than that in the other fractions. However, the sieve fractions show small differences in n value and the fitted Freundlich isotherms do not differ much as can be seen in Figure 4.1.

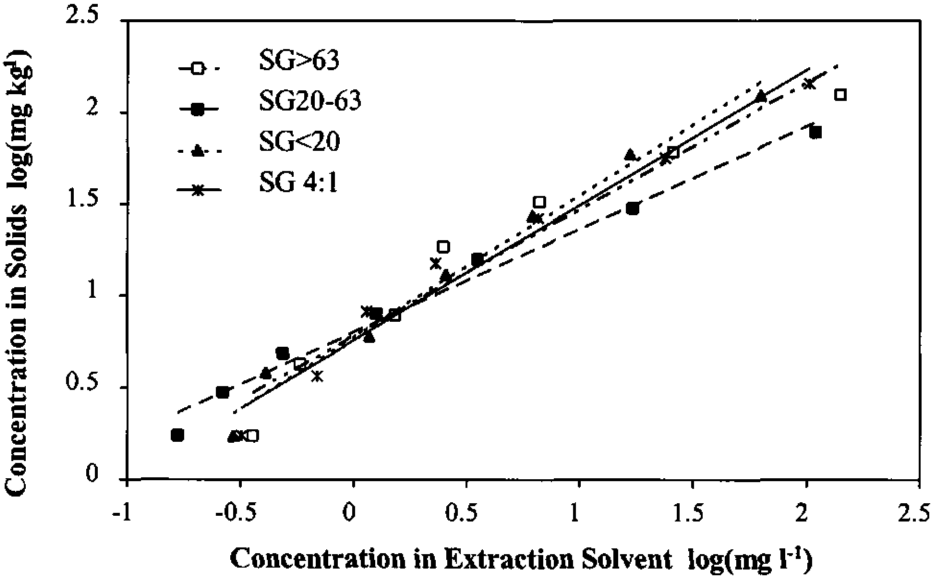

Figure 4.1 **Desorption isotherms of sum of EPA-PAHs in sludge and sieve fractions**

Figure 4.2 shows the desorption isotherms of five individual PAHs in SG20-63. These five PAHs are presented because they give an overall picture of the behaviour of all PAHs.

The desorption isotherm of B[a]P shows initially higher S values compared to PHE, FLU and PYR, but the B[a]P concentration in the solids decreases more rapidly because of a higher n value. This results in a low residual percentage of B[a]P, whereas PHE and FLU have high residual percentages (Table 4.4). The high sorption intensity n of the PAHs of high molecular weight (B[a]P, B[ghi]P and IND) results in low or zero residual percentages (Table 4.4). B[b]F and B[k]F show not only high n values but also relatively low K values, resulting in zero residual concentrations in all samples.

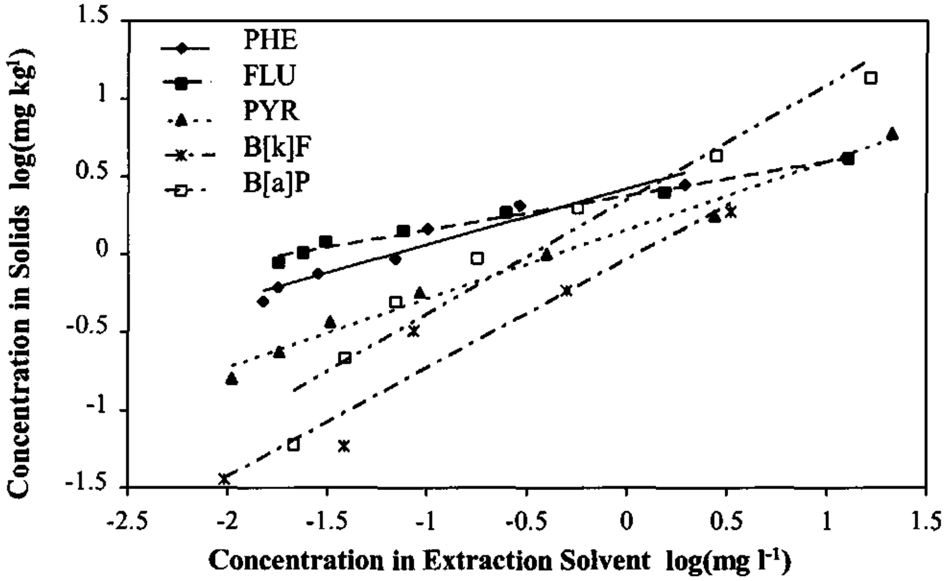

Figure 4.2 Desorption isotherms of five PAHs in SG20-63

Figure 4.3 shows the K (Figure 4.3a) and n values (Figure 4.3b) for the sum of EPA-PAHs and individual PAHs in the sludge samples extracted with a 4:1 mixture of acetone and water. The individual PAHs (X-axis) are given in the order in which they emerge from the HPLC. SG<20 shows the highest sorption capacities (K) for the individual PAHs, except for B[ghi]P, the sorption capacity of which is higher in SG>63 and SG 4:1. The sorption intensities n are also highest in SG<20 with a maximum for B[b]F.

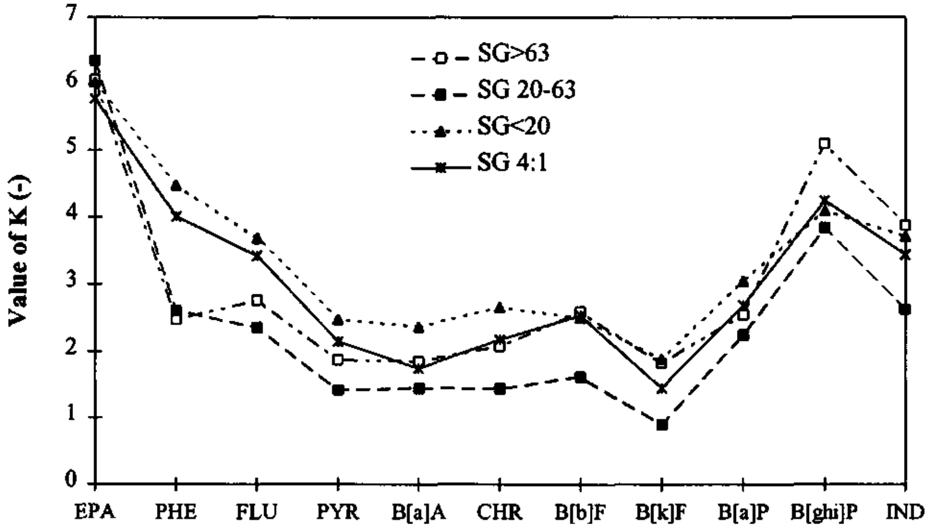

Figure 4.3a Value of K for sum of EPA-PAHs and individual PAHs

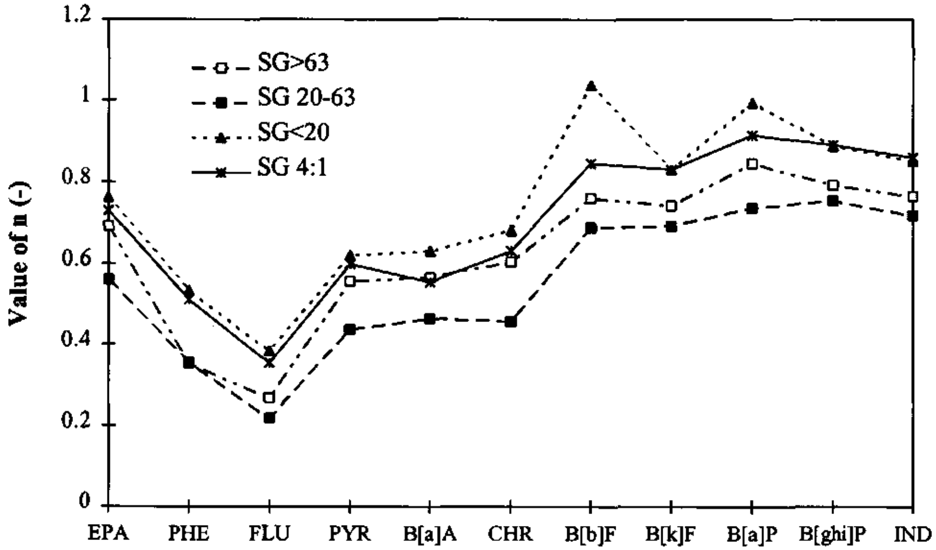

Figure 4.3b Value of n for sum of EPA-PAHs and individual PAHs

For the four samples, K and n show almost the same trend. In general, sorption intensity n increases with increasing molecular weight of the PAHs (Figure 4.3b) with the lowest value of n for FLU. From linear regression it was concluded that the molecular weight is weakly linear correlated with the values of n, because the correlation coefficients ranged from 0.66 to 0.81 for the sludge and sludge fractions.

For remediation of the sludge it is not worthwhile to separate the sludge in size fractions because the differences between the desorption isotherms of the fractions are minimal.

Acetone/water ratio. Figure 4.4 shows desorption isotherms of the sum of EPA-PAHs obtained by extraction of the sludge and sediment with 4:1 and 3:2 mixtures of acetone and water. The slope of the isotherm (= value of n) for SG 4:1 is almost twice as high as that for SG 3:2, SDM 4:1 and SDM 3:2, whose n values are almost equal (Table 4.6). This can also be seen in Figure 4.4, where the Freundlich isotherms of SG 3:2, SDM 4:1 and SDM 3:2 run parallel and the Freundlich isotherm of SG 4:1 is much steeper.

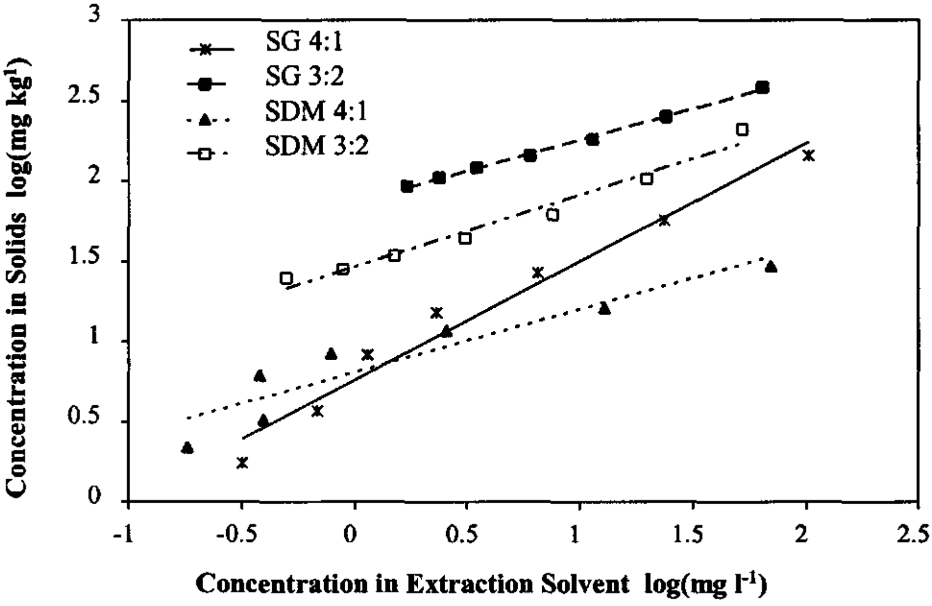

Figure 4.4 **Desorption isotherms of the sum of EPA-PAHs in sludge and sediment**

For the sludge it is less efficient to use a 3:2 mixture of acetone and water, because for SG 3:2 the n value is lower and the log K value is higher compared to a 4:1 mixture of acetone and water. As far as the sediment is concerned, for SDM 3:2 the concentration of the sum of EPA-PAHs in the solids is about 4.5 times as high as that for SDM 4:1 after the first extraction step (Figure 4.4). This is due to the high sorption capacity K for SDM 3:2, which is about 4.5 times higher than this value for SDM 4:1 (Table 4.6). The value of n is almost equal for SDM 4:1 and SDM 3:2 (Table 4.6). Consequently, the residual concentration in SDM 3:2 will be 4.5 times as high as in SDM 4:1, if the fitted isotherms are compared.

For the individual PAHs the values of K and n show almost the same trend as the K and n values for the sum of EPA-PAHs in these samples (results not shown). In SG 3:2 the K values of the individual PAHs are more than 3 times as high as in SG 4:1 and most n values are lower in SG 3:2 than those in SG 4:1. For the sediment, the sorption capacities K of the individual PAHs are about 6 times as high in SDM 3:2 as those in SDM 4:1. The n values in SDM 3:2 are equal or twice as high compared to SDM 4:1. These results confirm the conclusion that 3:2 mixtures of acetone and water are not efficient for the complete removal of PAHs from the used sludge and sediment. The n values of the individual PAHs in SDM 4:1 and SDM 3:2 are weakly linear correlated to the molecular weight of the PAHs with correlation coefficients of 0.75 and 0.86, respectively. In these two sediment samples the values of n are increasing with increasing molecular weight of the PAHs.

4.3.3 Amount of extraction solvent required for reaching the target levels

Based on the best fitting Freundlich isotherms, the amount of an acetone/water mixture required for reaching the target level of 2.6 mg kg^{-1} in the sludge and that of 1.2 mg kg^{-1} in the sediment was calculated. The initial PAH concentration (S^0) was fixed at 1000 mg kg^{-1} in the sludge and 650 mg kg^{-1} in the sediment. For one extraction step the amount of solvent (V^1_s, l kg^{-1}) required to reach the target level (S^7) is calculated by:

$$V_s^1 = \frac{S^0 - S^7}{C_l^7} \tag{4.8}$$

where C^7_l is calculated using the Freundlich equation (4.1):

$$C_l^7 = \left(\frac{S^7}{K}\right)^{1/n} \tag{4.9}$$

For calculation of C^7_l with equation (4.9) the best fitting values for parameters K and n (Table 4.6) were used.

For seven extraction steps the total amount of solvent (V^7_s) required to reduce the PAH concentration in the solids from initial concentration to the target level is calculated by:

$$V_s^7 = \sum_{i=1}^{7} \frac{S^{i-1} - S^i}{\left(\frac{S^i}{K}\right)^{1/n}} \tag{4.10}$$

where K and n are the best fitting parameters in the Freundlich isotherm (Table 4.6) and assuming that no solvent remains in the solids after an extraction step. The total amount of solvent for seven extraction steps V^7_s (see equation (4.10)) was minimized by varying the values of S^i (for i = 1 to 6) to obtain the lowest required amount of solvent.

Using a 4:1 mixture of acetone and water 33 litres per kg of dry matter are at least required to reach the target level in the sludge, and 102 litres per kg of dry matter are needed to reach the target level in the sediment in seven extractions. The amounts differ because of the lower target level established for sediment and the large number of PAHs of low molecular weight present in the sediment. If a 3:2 mixture of acetone and water is used, about 17,000 and 2,500 litres of extraction solvent per kg of dry solids are needed to reach the target level in sludge and sediment, respectively, in seven extraction steps. Consequently, a 3:2 mixture of acetone and water is unsuitable for treating the sludge and sediment investigated.

Cleaned soil, sludge or sediment can also be used as a building material, provided that the particle size distribution and organic matter content meet the technical requirements. For the sludge and sediment to be suitable as a building material, the PAH concentration should not exceed 104 and 48 mg PAHs per kg of dry matter in the sludge and sediment, respectively [15]. The maximal allowed PAH concentration in building materials depends on their organic matter content just as the target level for clean soil and sediment. The sludge has to be treated with at least 3.8 l of a 4:1 mixture of acetone and water per kg to reach the corresponding concentration in seven extractions, and the sediment has to be treated with 0.23 l per kg to reach the corresponding concentration. However, in practice the value of 0.23 l per kg for the sediment needs to be higher to obtain a homogeneous mixture of solids and extraction solvent. Treatment of the sediment to the level required for use as a building material rather than to the target level established for clean soil and sediment means a reduction in acetone consumption for seven extraction steps by a factor of 443. For the sludge, 8.7 times less of a 4:1 mixture of acetone and water is needed to reach the level required for use as a building material. Concerning the total environmental benefit of the solvent extraction process treatment of the sediment up to the requirement for building material will probably achieve a higher environmental benefit than cleaning up to the target level established for clean sediment.

4.4 Conclusions

4.4.1 Remediation of aged sludge and sediment

For removal of PAHs from the wet sludge (52 wt% of dry matter) seven extraction steps with a 4:1 mixture of acetone and water are found to be sufficient to reach the Dutch target level for clean soil. For the sediment (35 wt% of dry matter) the same extraction procedure is almost sufficient to reach the target level for PAHs. Nevertheless, it may be advantageous to use the treated sediment as a building material, because then 443 times less of a 4:1 mixture of acetone and water is needed in seven extraction steps to meet the requirements established for building materials compared to the amount of acetone needed to reach the target level for clean soil. For remediation of the aged sludge it is not worthwhile to separate the sludge in size fractions because the differences between the PAH composition and the desorption isotherms of the size fractions are small.

The residual concentrations in the sludge and sediment samples extracted with a 4:1 mixture of acetone and water contain high percentages of PAHs of relatively low molecular weight (PHE, ANT and FLU), and low or zero percentages of PAHs of relatively high molecular weight (B[b]F, B[k]F, B[a]P, B[ghi]P and IND). This is also found for extraction of PAHs from sediment by the BEST process, using triethylamine as extraction solvent. PHE, ANT and FLU will be the most difficult PAHs to remove from the solids at low concentrations which is due to relatively low values of n of the Freundlich desorption isotherms. For the sediment more acetone is needed to reach the target level than for the sludge, which is due to the lower target level established for the sediment and the initially high percentages of PHE, ANT and FLU in the sediment. The extraction efficiencies of the individual PAHs in the sludge and sediment samples extracted with 4:1 mixtures of acetone and water are higher than 98%, which is comparable to the efficiencies reached for contaminated sediments by the BEST process with seven extraction steps using triethylamine.

Extraction of the sludge and sediment samples with 3:2 mixtures of acetone and water result in residual PAH concentrations substantially higher than the target levels. In addition, the desorption isotherms for these acetone/water mixtures show high values of K and low values of n, which is not efficient for removal of PAHs. Therefore, an acetone/water mixture with a volume ratio of 3:2 is not appropriate for the extraction of PAHs from this aged sludge and sediment.

4.4.2 Desorption isotherms

The desorption isotherms of all sludge and sediment samples extracted with 4:1 and 3:2 mixtures of acetone and water show non-linear behaviour for the sum of EPA-PAHs and individual PAHs, which could be accurately described by Freundlich equations.

In general, PAHs of relatively high molecular weight (B[b]F, B[k]F, B[a]P, B[ghi]P and IND) show higher values for fitted sorption intensity n than PAHs of low molecular weight. A weak correlation is found between the n value of individual PAHs and the molecular weight. The correlation coefficients of this relationship ranged from 0.66 to 0.86 for all samples except SG 3:2, which showed a correlation coefficient of 0.23. Due to the high values of n for the PAHs of high molecular weight their percentages of the residual concentration are low after seven extraction steps with a 4:1 mixture of acetone and water. B[b]F and B[k]F show in most samples the highest sorption intensity n and a relatively low sorption capacity K, and therefore, their residual concentration was zero in all samples.

For the sieve fractions of the sludge the initial concentration of the sum of EPA-PAHs, the sorption capacity K and sorption intensity n for the sum of EPA-PAHs are not positively linearly related to the organic matter content and to the mean particle diameter (= size of the external surface area) of the sieve fractions. Therefore, no conclusions can be drawn about the (de)sorption mechanism of PAHs in the sludge. Although for desorption of PAHs from aged sludge and sediment the mechanisms are not unraveled yet, the desorption isotherms measured in this investigation provided additional insight in the extraction efficiencies.

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Chapter 5

Kinetics of PAH-desorption from aged sludge during extraction with acetone in a stirred reactor.

I. Experimental results

Abstract

The extraction behaviour of an aged sludge and fractions of this sludge was studied by measuring the PAH concentration in the extraction solvent (a mixture of 80 vol.% acetone and 20 vol.% water) as a function of time in a stirred reactor. In all samples, the desorption rates of all PAHs were initially high. For the size fractions with a particle diameter smaller than 125 μm, 90% of the PAHs were desorbed within 10 minutes and almost no differences existed between the desorption curves in these fractions. The desorption rates of the PAHs in the fraction with particle sizes greater than 125 μm were (a little) lower. After an extraction time of about 100 seconds, the PAHs of high molecular weight showed lower desorption rates compared to the PAHs of low molecular weight, and these differences were greater for the fractions with a particle diameter larger than 63 μm. Nevertheless, within 40 minutes 95% of all PAHs were extracted from each sample and thereafter, differences in desorption rate were no longer observed.

In general, the initial PAH concentration and the particle size of the fractions had little effect on the desorption rates. This may be due to the high mass transfer coefficients and high extraction capacity of the acetone/water mixture. Therefore, the differences in desorption rate are probably too small to be measured by means of the experimental set-up used.

5.1 Introduction

The desorption rate of polycyclic aromatic hydrocarbons (PAHs) is an important factor for the development of a process for the remediation of contaminated soils, sludges and sediments on the basis of extraction with organic solvents. A suitable solvent for the extraction of PAHs from soils is acetone, because it shows high extraction efficiencies for PAHs (Chapter 2), is less toxic than most other organic solvents used in industry, and is easily biodegradable [1]. The solvent extraction process is thought to be especially suited for the remediation of heavily polluted residual sludges from soil washing plants, which are regarded as chemical wastes. Because disposal of chemical waste is expensive, cleaning of these sludges for reuse (e.g. as a building material) using such an advanced treatment process as solvent extraction is expected to be worthwhile.

The desorption rate of PAHs is important for determining the time needed to reach the desired extraction efficiency. Unfortunately, most experimental and theoretical research into the (ad)sorption and desorption kinetics of PAHs is carried out using spiked soils and slurries of water and soil; the results are therefore less applicable to aged sludge and extraction with acetone. Desorption of hydrophobic organic contaminants, such as PAHs, in slurry systems is thought to depend mostly on (radial) diffusion from the solid particles. For instance, Errett et al. [2] described the sorption and desorption rates of a few PAHs in soils and mixtures of water and methanol as a result of radial diffusion. Carroll et al. [3] did this for the desorption rates of polychlorinated biphenyls regarding sediments. It was found that the determined diffusion rates and diffusion coefficients depend on the organic matter content of the soil, sludge or sediment [3-5], the particle size [3-6], and the internal porosity of the particles in combination with the tortuosity of the pores in the particles [2, 4, 6].

For intraparticle diffusion and other transport mechanisms such as transport through a film layer, the driving force is the difference between the actual PAH concentration and the equilibrium PAH concentration in the extraction solvent. The equilibrium PAH concentration depends on the distribution of the PAHs between solids and extraction solvent in a state of equilibrium. In Chapter 4, equilibrium distribution coefficients (K_d) were determined for a slurry of acetone, water and aged residual sludge contaminated with PAHs produced by a soil washing plant. In the present investigation, the same sludge was studied to determine experimentally the desorption rate of PAHs in a slurry of acetone and water as a function of particle size and organic matter content.

5.2 Materials and Methods

5.2.1 Sludge sample

The used sample was an aged residual sludge from a soil washing plant heavily contaminated with PAHs. This sludge was the overflow from the separation of a contaminated soil by means of a hydrocyclone and contained high amounts of organic matter and small (clay) particles. The sludge contained 52 wt% water, which was obtained after addition of flocculants and dewatering on a sieve belt press.

The average diameter of the particles in the sludge was about 40 μm, which was calculated from the weight percentages of the sieve fractions (see next subsection) and checked by microscopic observations.

5.2.2 Separation into fractions

The sludge was sieved with water at cut-off diameters of 20, 63 and 125 μm. This resulted in four sieve fractions: <20 μm, 20-63 μm, 63-125 μm and >125 μm with a dry mass of 39, 25, 22 and 14% of the total dry sludge matter, respectively. The sieve fractions were dewatered by centrifuging, followed by removal of the supernatant.

Thereafter, the particles in sieve fractions 20-63 μm and 63-125 μm were further separated on the basis of density and size by means of a water flow in an upflow column. The objective was to obtain organic particles in the overflow and mineral particles in the underflow of the upflow column. The applied upflow velocity of the water was calculated using Stokes' equation for sedimentation of a spherical particle in water [7]:

$$v = \frac{g(\rho_s - \rho_l)d_s^2}{18\eta} \tag{5.1}$$

where v is the sedimentation velocity of the spherical particle (m s^{-1}), g the gravitational acceleration (m s^{-2}), ρ_s the density of the particle (kg m^{-3}), ρ_l the density of water (kg m^{-3}), d_s the diameter of the particle, and η the dynamic viscosity of water (Ns m^{-2}). The upflow velocity applied corresponded to the sedimentation velocity of the smallest particles in the sieve fraction with a diameter of 20 or 63 μm consisting of pure mineral material (density = 2,500 kg m^{-3}). For the sieve fraction of 20-63 μm, the upflow velocity was 0.00032 m s^{-1}, and for the sieve fraction of 63-125 μm it was 0.0032 m s^{-1}. Stokes' equation could be applied, because for both upflow velocities Reynolds number ($=v\rho_l d_s/\eta$) was lower than 1. Particles were collected in the overflow, if the upflow velocity of the water was (slightly) higher than the sedimentation velocity of these particles. The slurries from the overflow were dewatered by centrifuging, after which the supernatant was removed. The fractions obtained from the sieve fractions of 20-63 µm and 63-125 µm by use of the upflow column are here referred to as "underflow" and "overflow".

The dry matter content values of the original sludge and the various fractions were determined by measuring the loss of weight of the samples after 24 hours of drying at 103°C. Next, the organic matter content values were determined by heating the dried samples for 24 hours at 550°C and again measuring the loss of weight.

5.2.3 Desorption experiments

In all extraction experiments with the sludge and fractions, the PAH concentration in the extraction solvent was measured as a function of time during extraction. The experimental set-up of this extraction procedure is shown in Figure 5.1.

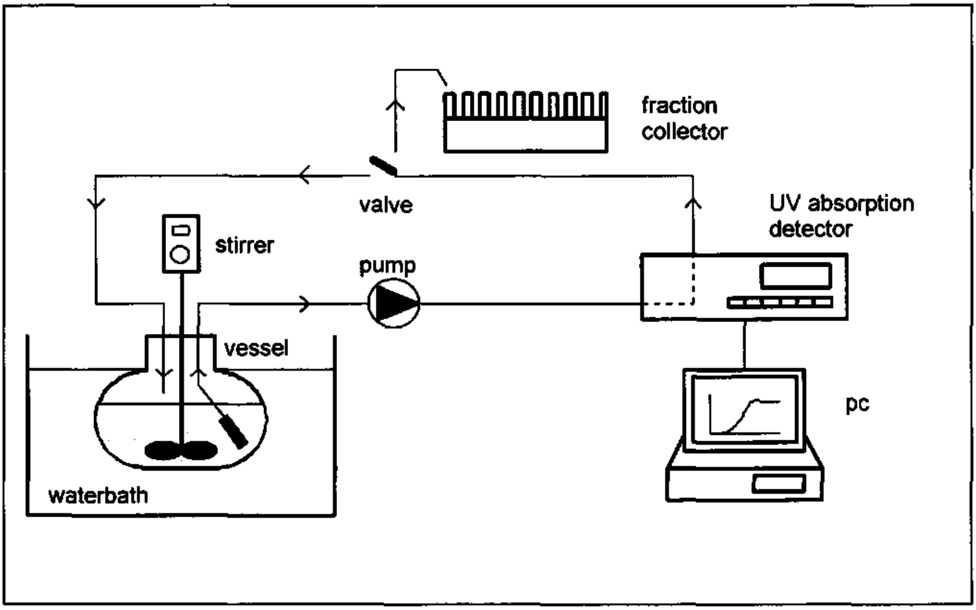

Figure 5.1 Diagram of the experimental set-up for the determination of desorption curves

In a glass vessel (250 ml), a sludge sample, acetone and water were stirred at a rate of 250 rotations per minute. Extraction solvent was pumped out of the vessel (2 ml min.$^{-1}$) through a stainless steel filter with pores of 2 µm and through stainless steel tubes with an internal diameter of 0.75 mm. Next, the extraction solvent passed an UV absorption detector and a valve and was then fed again into the glass vessel (Figure 5.1). The glass vessel was placed in a water bath of 20°C to assure a constant temperature during extraction. A sample collector was controlling the valve to collect samples of the extraction solvent at programmed time intervals for determination of the PAH concentration in the solvent by HPLC (see next subsection). The residence time of the extraction solvent in the tubes between the vessel and the sample collector was about two minutes. The UV absorption detector was connected to a personal computer, which showed the on-line UV signal on screen.

The UV absorption detector measured the absorption of the extraction solvent at a wavelength of 420 nm. This wavelength was chosen, because at lower wavelengths the UV absorption of the extraction solvent with PAHs exceeded the maximum absorption capacity of the detector and at higher wavelengths PAHs could no longer be detected. The measured UV-absorption at a wavelength of 420 nm was used as a measure for the PAH concentration in the extraction solvent and gave an indication of the state of the extraction process.

The desorption experiments were performed with wet samples of the sludge and fractions containing 5 to 8 g of dry matter. The samples were extracted for three hours with 200 ml of a mixture of 80 vol.% acetone and 20 vol.% water. The water in the samples was taken into account in the 20% water. The mixture of 80% acetone and 20% water was used, because during earlier research it was found that at this ratio the highest extraction efficiency was reached for spiked soils (Chapter 3) as well as for the used sludge. The last sample of the extraction solvent was taken 3 hours after the beginning of the extraction. The desorption experiments were performed in duplicate except for the sieve fraction of >125 μm, which was extracted just once because of lack of material.

5.2.4 Determination of the PAH concentration in solvent extracts by HPLC

The extracts collected by means of the sample collector were directly injected into the HPLC column. In these extracts, the concentration was determined of the 16 EPA-PAHs, which comprise pyrene and the 15 PAHs given on the EPA list of priority pollutants. The PAHs were separated in a HPLC column (Vydac 5, C18 Rev. phase), and their absorption spectra between 200 and 400 nm were measured by means of a photo diode array detector (Waters 991) as a function of time. The EPA-PAHs were identified in the resultant chromatograms by visual comparison between the spectra of peaks for the samples and standard chromatograms for EPA-PAHs. In the extracts, 10 EPA-PAHs could be identified: phenanthrene (PHE), fluoranthene (FLU), pyrene (PYR), benzo[a]anthracene (B[a]A), chrysene (CHR), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), benzo[ghi]perylene (B[ghi]P), and indeno[123-cd]pyrene (IND). The other six EPA-PAHs could not be identified. The concentrations of the identified EPA-PAHs were derived from the chromatograms at a wavelength of 254 nm.

5.3 Results and discussion

5.3.1 Initial PAH concentrations in the sludge and fractions

The initial PAH concentrations in the samples were calculated from the PAH concentration in the extraction solvent after three hours of extraction. This is a valid procedure, because it can be assumed that after 3 hours the PAH concentration in the solids is at equilibrium with that in the extraction solvent, and in a state of equilibrium the concentration in the solvent is much higher than that in the solids. Table 5.1 gives the initial concentration of the sum of EPA-PAHs and the measured organic matter content values in the sludge and fractions. This table shows that in the four sieve fractions the initial PAH concentration increases with increasing organic matter content. A strong positive linear relationship between the initial PAH concentration and the organic matter content in the four sieve fractions was derived by linear regression with a correlation coefficient of 0.99. It can be therefore concluded that in the sieve fractions the PAHs are mostly sorbed onto the organic matter.

Table 5.1 The organic matter content (wt% of total dry matter) and initial concentration of the sum of EPA-PAHs in sludge and fractions.

Sludge and fractions	organic matter (wt%)	initial PAH concentration (10^3 mg (kg dry matter)$^{-1}$)
Sludge	27	1.0±7%
< 20 μm	27	1.2±2%
20-63 μm	23	0.81±9%
Upflow column:		
- underflow	22	0.58±6%
- overflow	29	1.5±14%
63-125 μm	30	1.3±17%
Upflow column:		
- underflow	24	0.49±11%
- overflow	28	1.6±3%
> 125 μm	45	2.5

The sieve fractions of 63-125 μm and >125 μm have a high organic matter content (30% and 45%, respectively), which is probably due to the fact that the sludge was the overflow from a hydrocyclone in a soil washing plant. A hydrocyclone separation is based on both particle size and density, and large particles of low density are therefore also collected in the overflow of a hydrocyclone. The low density of particles may be caused by either a high organic matter content or a high internal porosity.

The initial percentages of individual PAHs in sludge and sieve fractions are shown in Table 5.2. This table shows that the sieve fraction of <20 μm contains more PAHs of high molecular weight (B[a]P, B[ghi]P, IND) and less PAHs of low molecular weight (FLU, PYR, B[a]A) than the other fractions. On the contrary, the sieve fraction of >125 μm contains less PAHs of high molecular weight (B[ghi], IND) and more PAHs of low molecular weight (FLU, PYR, CHR).

Table 5.2 Initial percentages of individual PAHs in sludge and fractions

Samples	PHE	FLU	PYR	B[a]A	CHR
Sludge	1.7±0.2	12±0.4	19±0.08	4.5±0.1	8.9±0.03
< 20 μm	1.8±0.2	8.1±0.06	13±1.7	3.4±1.3	8.4±0.9
20-63 μm	1.4±0.08	13±0.6	19±0.9	7.3±0.1	8.8±0.01
underflow	2.0±0.09	13±0.02	18±0.5	9.9±0.5	8.7±0.1
overflow	1.5±0.2	11±0.7	18±0.7	5.1±0.4	9.2±0.01
63-125 μm	2.5±0.4	13±0.8	20±0.8	8.1±0.1	9.7±0.2
underflow	2.3±0.8	16±0.5	21±0.9	6.6±0.6	9.9±0.3
overflow	1.9±0.03	13±0.6	20±0.6	9.7±0.1	9.3±0.00
> 125 μm	1.2	15	23	7.1	11

Samples	B[b]F	B[k]F	B[a]P	B[ghi]P	IND
Sludge	9.4±0.4	5.4±0.4	17±1.2	12±0.1	11±0.08
< 20 μm	11±0.05	4.6±1.6	22±0.07	17±0.8	12±1.9
20-63 μm	9.4±0.8	1.9±0.2	18±0.2	12±0.5	9.5±0.2
underflow	8.8±0.2	2.0±0.1	16±0.3	12±1.2	8.9±0.2
overflow	9.6±0.2	5.1±0.02	18±0.4	12±1.2	11±0.05
63-125 μm	8.5±0.3	2.8±0.4	15±1.1	12±0.3	9.5±0.3
underflow	8.3±0.2	3.7±0.5	14±1.7	9.4±0.2	8.9±0.8
overflow	8.4±0.2	2.0±0.09	17±0.2	10±0.2	9.3±0.5
> 125 μm	7.7	4.1	16	7.7	7.2

The percentages of the individual PAHs in the underflow and overflow of the fractions of 20-63 μm and 63-125 μm are comparable to those in the corresponding sieve fractions. Furthermore, the percentages of the individual PAHs in the underflow fractions do not differ much from those in the overflow fractions (Table 5.2), although the absolute initial concentrations of the sum of EPA-PAHs in the overflow fractions are about three times higher than the concentration in the underflow fractions (Table 5.1). Thus, separation in the upflow column has no effect on the distribution of the individual PAHs in the fractions of 20-63 μm and 63-125 μm.

5.3.2 Particle separation in the upflow column

Separation of the sieve fractions of 20-63 μm and 63-125 μm in the upflow column led to an organic matter content of 22 wt% and 24 wt% in the respective underflow fractions, while the overflow fractions contained 29% and 28% of organic matter, respectively (Table 5.1). Therefore, the aim of the separation in the upflow column, i.e. to obtain underflow fractions with a high mineral matter content and upflow fractions with a high organic matter content, was only partly achieved. The difference in organic matter content between the underflow and overflow of the fraction of 20-63 μm is only 7%, whereas for the fraction of 63-125 μm this difference is 4%.

Since the upflow column separates particles based on size and density, it is hard to predict the composition of the particles in the overflow and underflow. Figure 5.2 shows all possible compositions of particles in the underflow and overflow with respect to size and density. The two curves in Figure 5.2 were calculated by means of Stokes' equation (5.1) for the two applied upflow velocities of 0.00032 m s^{-1} and 0.0032 m s^{-1} for the sieve fractions of 20-63 μm and 63-125 μm, respectively. The curves represent the size and density of particles collected in the overflow (left-hand area of a curve) and particles remaining in the underflow (right-hand area of a curve). Figure 5.2 shows that for the fraction of 20-63 μm the density of the particles in the underflow can vary between 1,150 kg m^{-3} for the largest particles (diameter of 63 μm) and 2,500 kg m^{-3} for the smallest particles (diameter of 20 μm). For the fraction of 63-125 μm, the density of the particles in the underflow ranges from 1,380 kg m^{-3} for the largest particles (diameter of 125 μm) to 2,500 kg m^{-3} for the smallest particles (diameter of 63 μm). Based on Figure 5.2, it can be concluded that the particles in the overflow are either smaller or have a lower density than those in the underflow. The lower density of the particles in the overflow is caused by a (slightly) higher organic matter content in the overflow fractions, as mentioned before. The other reason is probably a higher internal porosity of the particles.

The initial PAH concentration in the overflow of the sieve fractions of 20-63 μm and 63-125 μm is about three times higher compared to the PAH concentration in the underflow fractions (Table 5.1). As was concluded before, the PAHs are mostly sorbed onto the organic matter in the sieve fractions. However, the amount of organic matter in the underflow and overflow cannot account for the fact that the PAH concentration in the overflow is three times higher, because the organic matter content is only 4% and 7% higher, respectively, in the overflow of the fractions of 20-63 μm and 63-125 μm compared to that in the underflow. Therefore, the properties of the organic matter in the overflow fractions must be different from those of the organic matter in the underflow fractions.

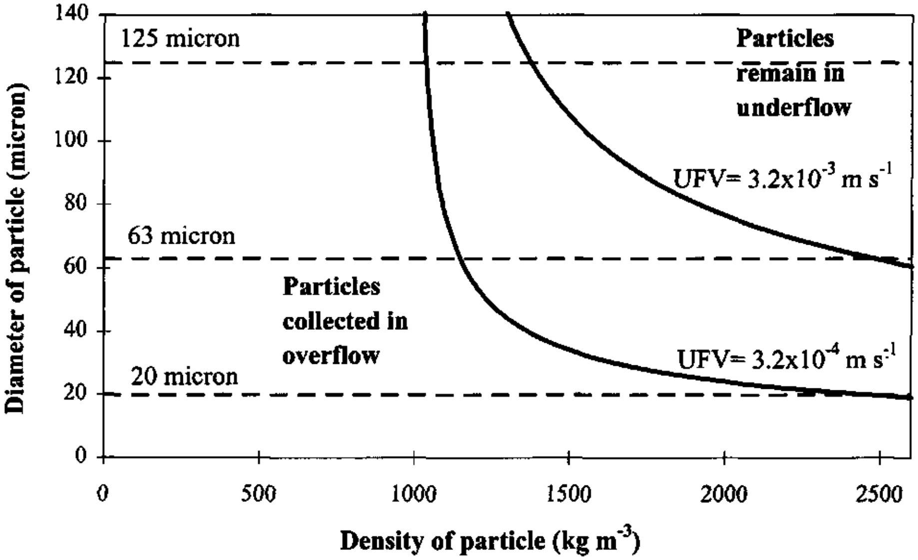

Figure 5.2 **Size and density of particles in the underflow and overflow of the upflow column for upflow velocities (UFV) of water of $3.3\text{x}10^{-4}$ m s^{-1} and $3.2\text{x}10^{-3}$ m s^{-1}**

An explanation for the difference in organic matter between the underflow and overflow fractions may be that the particles in the overflow fractions have a higher internal porosity and thus a higher specific surface area than those in the underflow fractions. This may be due to the nature of the organic matter. The polymers in organic matter can be characterized as glassy or rubbery on the basis of their internal structure [8]. According to Xing and Pignatello [8], the glassy fraction is condensed, and because of its low internal porosity this condensed organic fraction is likely to remain in the underflow of the upflow column. The glassy/condensed fraction is associated with the humic fraction of soil organic matter, which is insoluble in alkali and acid. The rubbery polymers are amorphous and swollen, and they are associated with humic acids. Because these polymers will absorb more water than the glassy polymers, they have a higher internal porosity and a higher specific surface area. Therefore, humic acids are collected probably mostly in the overflow of the upflow column.

The glassy or rubbery state of the organic matter is assumed to influence the sorption and desorption rates. Sorption onto glassy polymers is progressively more nonlinear, and desorption from glassy organic matter is also thought to be nonlinear and responsible for low desorption rates [8, 9, 10]. For the use of acetone as an extraction solvent, it is important to consider that conversion from the glassy to the rubbery state can be achieved through addition of a swelling solvent [8].

5.3.3 Comparison between on-line UV absorption and determination by HPLC

The on-line signal of the UV detector (420 nm) was compared to the concentration of the sum of EPA-PAHs measured by HPLC and using a photo diode array detector. Figure 5.3 shows for the sludge the on-line UV signal and the concentration of EPA-PAHs measured by HPLC in the extraction solvent as a function of time for duplicate experiments. For this comparison, the UV signal and the concentration were standardized, which means that all measured UV absorption values and measured PAH concentrations are presented as a percentage of the last UV absorption value measured and last PAH concentration measured, which was set at 100%.

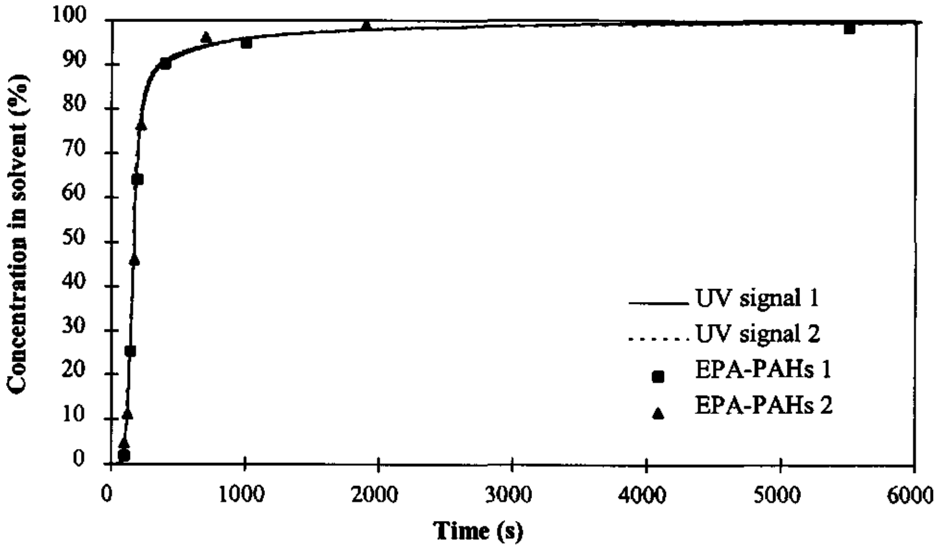

Figure 5.3 **Desorption curves according to the on-line UV signal and the sum of EPA-PAHs measured by HPLC for duplicate extraction of the original sludge**

Figure 5.3 shows that the UV signal and the measured concentrations fit very well for the original sludge. The measured PAH concentrations of the duplicate experiment and both signals of the UV detector show that the desorption experiment could also be reproduced well. However, for the other samples, the deviation between the UV signal and the measured PAH concentration was (slightly) higher, and for some samples the deviation of the duplicate experiment was also (slightly) higher. The most explicit deviation between the UV signal and the measured PAH concentration was found for the underflow of the fraction of 63-125 µm. Figure 5.4 shows both UV signals, the measured EPA-PAH concentrations and the measured IND concentrations for this fraction. The measured IND concentrations fit far better to the UV signal than the concentration of the sum of EPA-PAHs. This may be due to the fact that at the wavelength of 420 nm only IND of the 10 identified EPA-PAHs absorbs light.

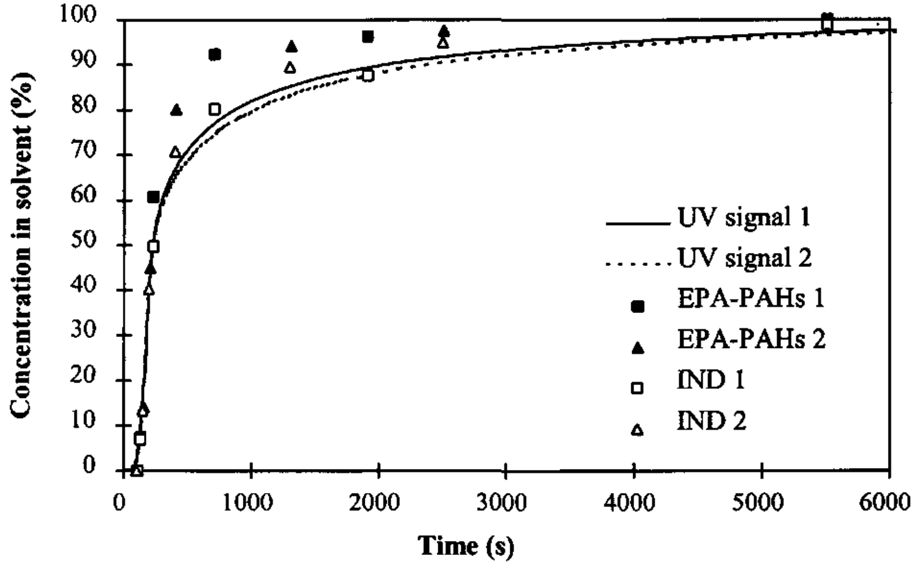

Figure 5.4 **Desorption curves according to the on-line UV signal, the sum of EPA-PAHs and IND measured by HPLC for duplicate extraction of the underflow of 63-125 µm**

However, for the other fractions and original sludge the measured concentration of the sum of EPA-PAHs fits better to the UV signals than the IND concentration. An explanation may be the interference of other components in the sludge which also absorb light at 420 nm.

In conclusion, the UV absorption at a wavelength of 420 nm is a good indication of the

PAH concentration in the extraction solvent, and therefore it also gives a good on-line description of the desorption rate. It is recommended verifying the reliability of the UV absorption signal as an indication for the on-line desorption rate for each distinct sample and each distinct extraction solvent.

5.3.4 The desorption rate of the sum of EPA-PAHs

Figure 5.5 shows the standardised concentration of the sum of EPA-PAHs in the extraction solvent (% of the initial concentration) as a function of time for sludge and sieve fractions. The results of the duplicate experiments are combined in these desorption curves, because the duplicate PAH concentrations measured in the extraction solvent could be fitted well into one desorption curve, as shown in Figures 5.3 and 5.4. The duplicate experiments (slightly) differ for the sieve fraction of 20-63 μm, and the curve shows one outlier at 285 sec. (Figure 5.5).

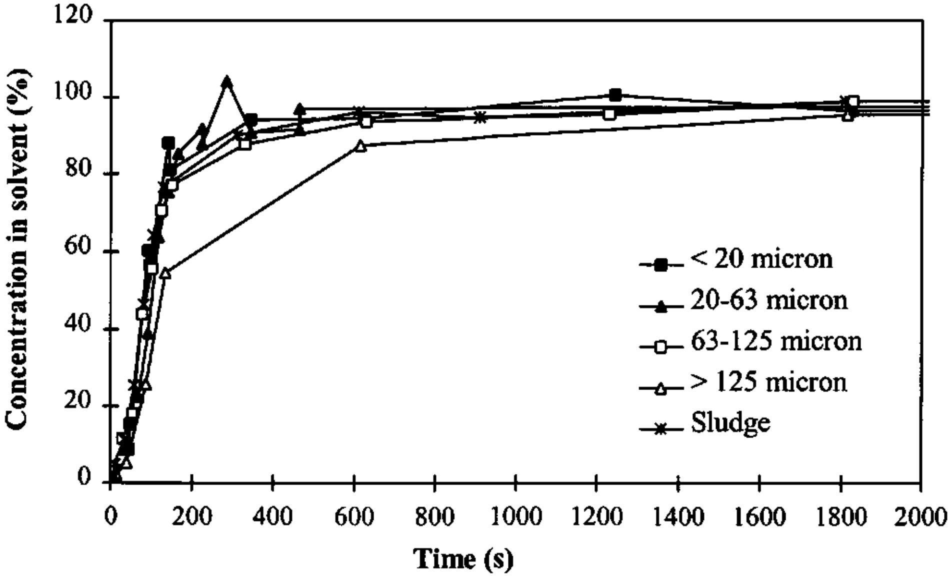

Figure 5.5 Desorption curves for the sum of EPA-PAHs for the extraction of the sieve fractions and the sludge

During the first 100 seconds of the extraction process the desorption rates of the sum of EPA-PAHs for all samples were very high and did almost not differ from each other (Figure 5.5). Within 600 seconds (10 minutes), 90% of all PAHs were desorbed from the sludge and the sieve fractions of <20 μm, 20-63 μm and 63-125 μm. For the sieve fraction of >125 μm, the desorption of 90% of the PAHs took 1,200 to 1,800 seconds.

For the fraction of 20-63 μm, the desorption rates of the sum of EPA-PAHs for the sieve fraction, underflow and overflow are shown in Figure 5.6. No differences in desorption rate are distinguishable.

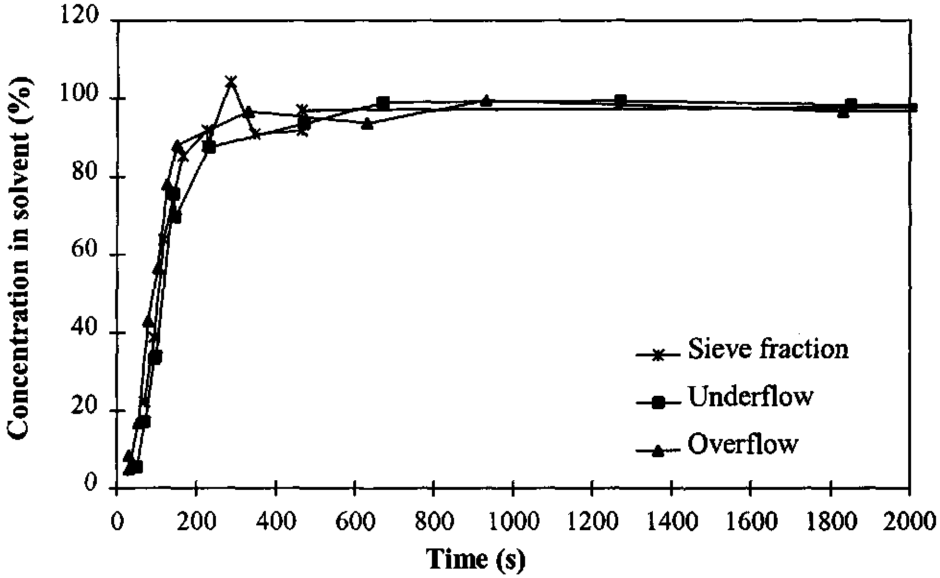

Figure 5.6 The fractions of 20-63 μm: desorption curves of the sum of EPA-PAHs

The desorption rates of the sum of EPA-PAHs for the sieve fraction, underflow and overflow of 63-125 μm are presented in Figure 5.7. The figure shows that in the time period between 100 and 600 seconds the underflow has a lower desorption rate than the sieve fraction of 63-125 μm and the overflow. The desorption rates no longer differ after 600 seconds.

The almost equal desorption rates for the underflow and overflow of sieve fractions 20-63 μm and 63-125 μm do not agree with the hypothesis that the organic matter in the underflow has a more glassy and condensed structure and that in the overflow a more rubbery and amorphous structure. It is thought that the desorption of PAHs from glassy/condensed organic matter is slower than that from rubbery/amorphous organic matter [9], but this is not clearly visible in Figures 5.6 and 5.7. However, the hypothesis cannot be rejected, because acetone may serve as a swelling solvent and convert the glassy/condensed organic matter of the underflow into rubbery/amorphous organic matter. It was already shown that acetone is capable of swelling several peat materials [11]. In general, the conversion of polymers from their glassy state to their amorphous state can be determined by calorimetric analysis while the temperature of the sample is raised. The conversion occurs at the glass transition temperature, when there is a peak in the heat flow. This was, for instance, demonstrated for humic acid by Leboeuf and Weber [9]. Acetone can probably reduce the glass transition temperature of organic matter to 20°C or lower, so that organic matter has an amorphous structure at room temperature. It is recommended applying calorimetric analysis to the organic matter in the underflow and overflow in water and acetone to determine the glass transition temperatures.

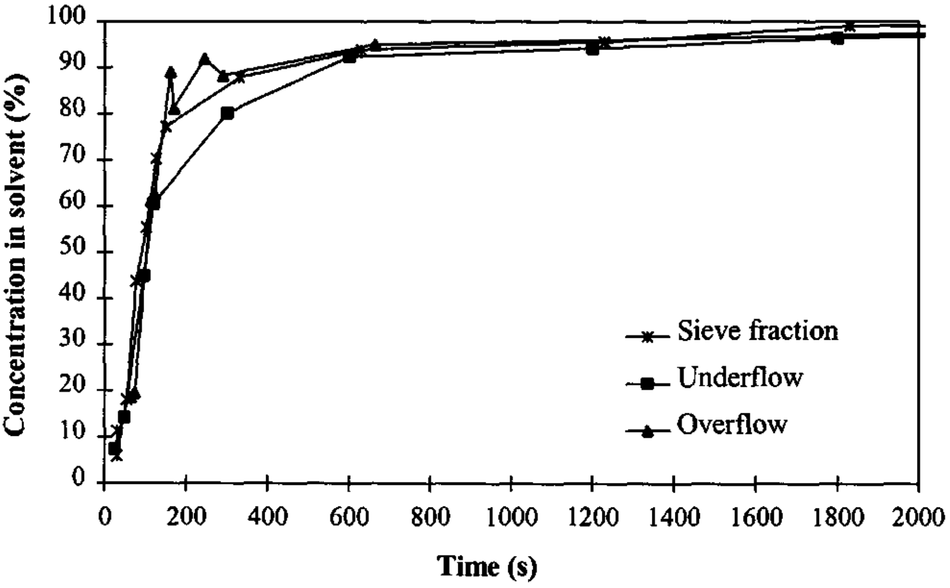

Figure 5.7 The fraction of 63-125 μm: desorption curves of the sum of EPA-PAHs

A comparison between Figures 5.6 and 5.7 shows that in the time period between 150 and 1,800 seconds the PAH concentration in the extraction solvent for the fraction of 63-125 μm is about 5% lower than that for the fraction of 20-63 μm. In Figure 5.5 is also shown that the desorption rate of the PAHs from sieve fraction 63-125 μm is slightly lower than that of the PAHs from the fractions <20 μm and 20-63 μm in the time period from 150 to 1,800 seconds. Nevertheless, within 1,800 seconds at least 95% of the EPA-PAHs were extracted from all samples (Figures 5.5, 5.6 and 5.7), and it is assumed that equilibrium is reached at this point.

In conclusion, in the sludge and the fractions with a particle diameter smaller than 63 μm the desorption rates of the sum of EPA-PAHs are similar, whereas those in the fractions of 63-125 μm and >125 μm are (slightly) lower. Particle size and initial PAH-concentration apparently have little effect on the desorption rate. This may be due to the high mass transfer coefficients and the high extraction capacity of the acetone/water mixture, which creates a strong driving force for transport. Therefore, there will be only small differences in desorption rate, which probably cannot be accurately measured by means of the experimental set-up used. This may account especially for the fractions with a particle diameter below 63 μm, because the PAHs are rapidly desorbed from these fractions in the first ten minutes (Figure 5.5). In the experimental set-up each solvent sample collected by the fraction collector contains solvent collected over a period of 30 seconds. Therefore, the measured concentration is an average over 30 seconds of extraction. In addition, it takes the extraction solvent about two minutes to travel from the extraction vessel to the fraction collector, during which it can mix in the tubes.

Another explanation for the fact that particle size has only a small effect on the desorption rates may be that PAH contamination is (ad)sorbed mostly onto the surface area of the sludge particles. If this is true, the desorption depends mainly on diffusion from the surface area and only for a small part on diffusion of PAHs from the inside of the particles, for which the particle size is expected to be quite important.

5.3.5 The desorption rate of individual PAHs

Figure 5.8 shows the desorption curves of FLU, PYR, B[ghi]P, IND and the sum of EPA-PAHs for extraction of the sludge. FLU and PYR represent the PAHs of low molecular weight, and B[ghi]P and IND represent those of high molecular weight. Figure 5.8 shows that the desorption rates of the individual PAHs initially did not differ. However, during the period between 200 and 1,000 seconds desorption of the PAHs of high molecular weight was (slightly) slower than that of the PAHs of low molecular weight. For instance, after 300 seconds the concentration of IND in the extraction solvent was about 12% lower than that of

FLU and PYR. The differences became negligible after about 1,800 seconds (30 min.), when all PAHs were desorbed for more than 95%. The same trend was observed for the PAHs in the other fractions with a particle diameter smaller than 63 μm (results not shown).

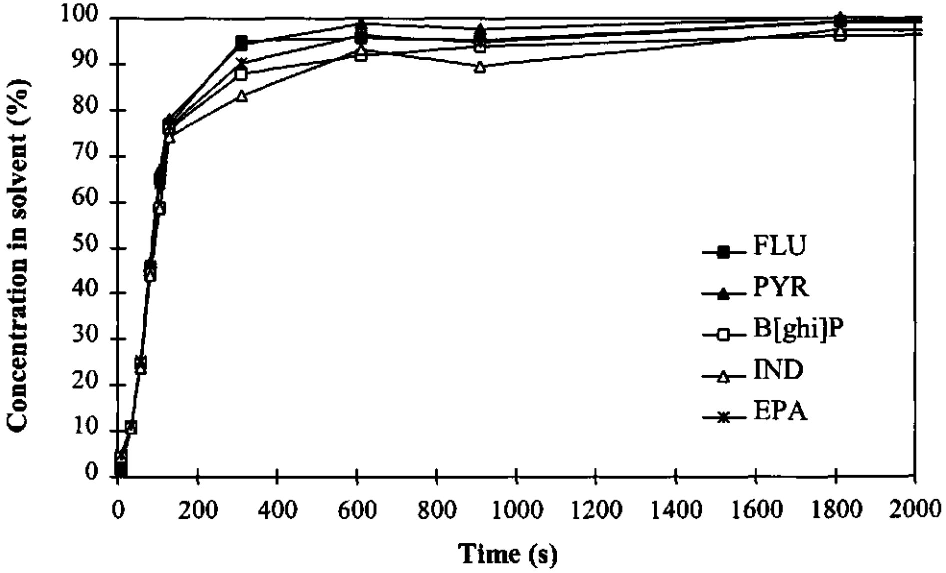

Figure 5.8 **Desorption curves for FLU, PYR, B[ghi]P, IND and the sum of EPA-PAHs for extraction of the sludge**

For the underflow of the fraction of 63-125 μm, the desorption curves for FLU, PYR, B[ghi]P, IND and the sum of EPA-PAHs are shown in Figure 5.9. For this fraction, the differences in desorption rate between the PAHs of low and high molecular weight are more pronounced than those for the fractions with smaller particles. Initially, the desorption rates of the PAHs were equal, but after 100 seconds the PAHs of high molecular weight (B[ghi]P and IND) clearly showed a lower desorption rate than the PAHs of low molecular weight (FLU and PYR). After 600 sec. (10 min.), the concentrations of FLU and PYR in the extraction solvent were as much as about 17% higher than those of B[ghi]P and IND. However, the difference between the PAHs of low and high molecular weight became negligible after about 2,400 sec. (40 min.), when at least 95% of the PAHs were desorbed (Figure 5.9). These desorption courses are almost the same for the other fractions with a particle size greater than 63 μm (results not shown).

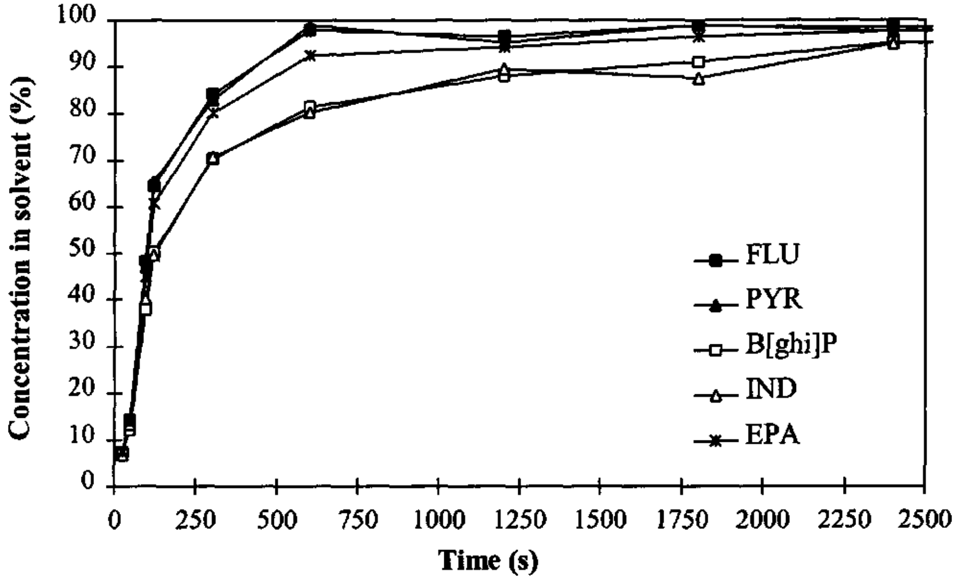

Figure 5.9 **Desorption curves for FLU, PYR, B[ghi]P, IND and the sum of EPA-PAHs for extraction of the underflow of 63-125 μm**

The lower desorption rates of the PAHs of high molecular weight may be due to a lower driving force for transport. This driving force depends on the difference between the actual PAH concentration and the equilibrium concentration in the extraction solvent. An indication of the driving force is distribution coefficient K_d, which is defined as the PAH concentration in the solids divided by the PAH concentration in the extraction solvent when thermodynamic equilibrium is accomplished. The K_d values of the individual PAHs in all samples were calculated from the last concentration measured in the extraction solvent and the corresponding PAH concentration in the solids, which were read off the desorption isotherms determined in Chapter 4. In general, the distribution coefficients of the PAHs of high molecular weight are higher than those of the PAHs of low molecular weight, which may account for the lower desorption rates of the PAHs of high molecular weight. For instance, the calculated distribution coefficients of B[ghi]P and IND are 1.5 to 6 times higher than those of FLU and PYR.

5.4 Conclusions

The initial concentration of the sum of EPA-PAHs in the four sieve fractions investigated depends primarily on the organic matter content, because the correlation coefficient between the initial PAH concentration and the organic matter content was 0.99. Therefore, in the sieve fractions the PAHs are probably sorbed onto organic matter. The organic matter in the underflow and overflow of the sieve fractions of 20-63 μm and 63-125 μm had to be of a different structure, because the two overflow fractions initially contained about three times more PAHs than the underflow fractions, whereas the organic matter content values of the underflow and overflow fractions were almost equal. An explanation for this may be that the particles in the overflow fractions have a higher internal porosity and therefore a higher specific surface area, onto which higher amounts of PAHs can (ad)sorb. It is assumed that the organic matter in the overflow consists mainly of amorphous polymers with a high specific surface area, whereas the organic matter in the underflow is condensed and has a more glassy structure.

The desorption rates of the PAHs in all samples were initially very high and did not differ from each other during the first 100 seconds of the extraction process. In the sludge and the fractions with a particle diameter smaller than 125 μm, at least 90% of the PAHs were desorbed within 10 minutes. The sieve fraction of >125 μm showed (slightly) lower desorption rates after 100 seconds than the other samples did. The particle size and/or initial PAH concentration apparently had little effect on the desorption rates. This may be due to either the high extraction capacity of the acetone/water mixture or the distribution of the PAHs in the sludge particles. The desorption was probably less dependent on the diffusion of PAHs from the inside of the particles, and mainly dependent on the diffusion of PAHs from the surface area of the particles.

Almost no differences could be observed between the desorption rates of the underflow and overflow fractions, which does not agree with the hypothesis that the organic matter in the underflow fraction and that in the overflow fraction differ in structure.

The initial desorption rates for the individual PAHs were equal, but after an extraction period of about 100 seconds the PAHs of high molecular weight had a lower desorption rate than those of low molecular weight. The differences in desorption rate were larger as the particle diameter of the fractions exceeded 63 μm. The lower desorption rates of PAHs of high molecular weight may be due to a lower driving force for transport, because the distribution coefficients in a state of equilibrium of the PAHs of high molecular weight were higher than those of the PAHs of low molecular weight.

For all samples and all individual PAHs, after about 40 minutes of extraction 95% of the PAHs were found to be desorbed from the sludge, and after this period there were no longer any differences in desorption rate. It was therefore assumed that equilibrium was reached within 40 minutes.

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Chapter 6

Kinetics of PAH desorption from aged sludge during extraction with acetone in a stirred reactor.

II. Transport models

Abstract

A radial diffusion model and a first-order reaction model were used to fit experimental desorption curves of PAHs as a function of time. These desorption curves were obtained by extraction of an aged sludge and size fractions of this sludge with a mixture of 80 vol.% acetone and 20 vol.% water. The radial diffusion model fitted the experimental data best for a situation in which it is assumed that the PAH contamination is concentrated in the core of the sludge particles at the beginning of the extraction process. For the radial diffusion model, the best fitting values of the effective diffusion coefficient (D_{eff}) increased with increasing particle size of the fractions. This may be due to the physical properties of the sludge particles, like the internal porosity. Therefore, the internal porosity of the particles in the fractions was calculated from the best fitting values of D_{eff} determined for the radial diffusion model with the PAH contamination in the core of the particles. From these calculations it can be concluded that the internal porosities increase with increasing particle size of the fractions.

6.1 Introduction

The desorption kinetics of polycyclic aromatic hydrocarbons (PAHs) are studied here as this is thought to be an essential factor in the design of a solvent extraction process for PAH contaminated sludge. In Chapter 5, the desorption of PAHs from an aged sludge and several sludge fractions was experimentally determined as a function of time. The used sample was a residual sludge from a soil washing plant and was separated in four fractions by wet sieving: < 20 μm, 20-63 μm, 63-125 μm and >125 μm. Part of the sieve fractions of 20-63 μm and 63-125 μm were separated into an overflow and underflow fraction by upflow of water in a vertical column. This was done to collect particles of low density and/or small particle diameter in the overflow and particles of high density and/or large particle diameter in the underflow. Samples of the sludge and the sludge fractions were extracted with a mixture of 80 vol.% acetone and 20 vol.% water in a stirred vessel, and the PAH concentration in the extraction solvent was measured as a function of time.

Models can be elucidative for understanding the PAH desorption and transport processes occurring during extraction. The objective of this chapter is to develop a mass transport model for the desorption of PAHs from sludge particles that properly describes the desorption curves measured.

In general, two classes of transport models can be distinguished: chemical and physical nonequilibrium models [1]. An example of a chemical nonequilibrium model is a first-order reaction model. Such a model is an empirical model and describes the sorption onto and desorption from soil as a linear first-order process with rate coefficients for sorption and desorption [2]. It can be used to describe the transport of PAHs from the surface area of the sludge particles, which was suggested to be an important transport process in the extraction system used (Chapter 5).

An example of a physical nonequilibrium model is the radial diffusion model, which describes the radial diffusion of a solute into or out of a spherical particle. This is a mechanistic model, and the parameters within the radial diffusion model are generally applicable and have a physical signification. The radial diffusion model was used by, among others, Errett et al. [3] to describe the sorption and desorption kinetics of a few PAHs in soils during extraction with mixtures of water and methanol. Ball and Roberts [4] used this model to describe the sorption kinetics of halogenated organic chemicals in sandy aquifer materials, and Wu and Gschwend [5] used it to describe the sorption kinetics of hydrophobic organic compounds in natural sediments and soils. In addition, it is hypothesised that the radial diffusion of the contaminants in the porous particles occurs through the pore fluid in the particle, and that the contaminant molecules are retarded during diffusion by partitioning *between the pore fluid and the solid phase substances in the particle* [3, 4, 5]. The measure of retardation depends on the internal porosity of the particles and the geometry of the pores.

For the choice of model, not only the sort of model but also the following considerations are important. A practical requirement is that the model preferentially should have only one unknown parameter that can be fitted to the experimental desorption curves. Besides, the model preferentially has no parameters that have not been measured for this sludge/acetone extraction system or cannot be reliably estimated. If the model has many unknown parameters, it will be hard to verify the model results.

Based on literature and the above-mentioned requirements, the radial diffusion model and the empirical first-order model were chosen for application to the experimental desorption curves.

6.2 Transport models

6.2.1 Model 1: Radial diffusion within spherical sludge particles

In the first model, transport of PAHs within a sludge particle is governed by radial diffusion. The radial diffusion of PAH molecules within a spherical particle with radius R (m) is described by [2]:

$$\frac{\partial C_s}{\partial t} = D_{eff}\left[\frac{\partial^2 C_s}{\partial r^2} + \frac{2}{r}\frac{\partial C_s}{\partial r}\right] \tag{6.1}$$

where C_s is the PAH concentration in the sludge particle (mg m^{-3}), r the distance between the centre and the actual position in the particle (m), t time (s), and D_{eff} the effective diffusion coefficient in the particle (m^2 s^{-1}).

No diffusion of PAHs occurs in the centre of the particle (r=0). This means:

$$-D_{eff}\frac{\partial C_s}{\partial r} = 0 \qquad \text{for } r=0 \tag{6.2}$$

It is assumed that the external boundary layer around the particle is not limiting for the transport of PAHs. Another assumption is that at the surface of the particle the PAH concentration within the particle (C_{se}) and the PAH concentration in the extraction solvent (C_{le} (mg m^{-3})) are at equilibrium. These concentrations are related by:

$$C_{se} = C_{le}\,K_{d1} \qquad \text{for } r=R \tag{6.3}$$

where K_{d1} is the distribution coefficient (-) for model 1.

During extraction, a (large) number of sludge particles are present in the extraction solvent, for which equations (6.1), (6.2) and (6.3) are valid.

For an ideally mixed extraction solvent containing sludge particles, the mass balance is:

$$V_l \frac{dC_l}{dt} = -A_s D_{eff} \left(\frac{\partial C_s}{\partial r} \right) \Big|_{r=R} \tag{6.4}$$

where C_l is the PAH concentration in the extraction solvent (mg m^{-3}), V_l the total liquid volume (m^3), and A_s the total interfacial surface area of the particles in the extraction solvent (m^2).

The only unknown parameter in the radial diffusion model is the diffusion coefficient, D_{eff}. To define how D_{eff} depends on the physical properties of the particles, it is assumed that a sludge particle is an aggregate of smaller particles consisting of organic and mineral matter. A sludge aggregate with internal pores is diagrammed in Figure 6.1. Diffusion of PAHs occurs only in the pore fluid of the sludge aggregate. This diffusion depends on the diffusivity of the PAHs in the extraction solvent located in the pores, the porosity of the particle, and the geometry of the pores (e.g. tortuosity and constrictivity). Taking this into account, D_{eff} can be defined as [2]:

$$D_{eff} = \frac{\varepsilon D_l f(\varepsilon, \tau)}{(1-\varepsilon) K_{dl} + \varepsilon} \tag{6.5}$$

where ϵ is the internal porosity of the particle (-), D_l the diffusion coefficient of the PAHs in the extraction solvent located in the pores of the particle (m^2 s^{-1}), $f(\epsilon,\tau)$ the pore geometry factor, and τ the tortuosity of the pores.

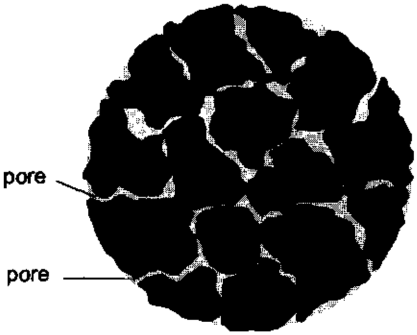

Figure 6.1 **Schematic presentation of a cross section of a sludge particle with internal pores according to the radial diffusion model (model 1)**

As suggested in Chapter 5, the initial distribution of the PAH contamination throughout the entire particle may influence the desorption rates. Therefore, three physical states of the initial PAH distribution in the particle were evaluated for the radial diffusion model. The three variants are shown in Figure 6.2:

a. The PAHs are homogeneously distributed throughout the entire particle.

b. The PAHs are homogeneously distributed throughout the entire core of the particle. It is assumed that the PAHs in the outmost layer of the particle were completely degraded or were diffused from the outmost layer.

c. The PAHs are homogeneously distributed throughout the entire outmost layer of the particle, which consists of organic matter. The mineral core contains no PAHs.

For each variant, initial and boundary conditions are defined in the following section.

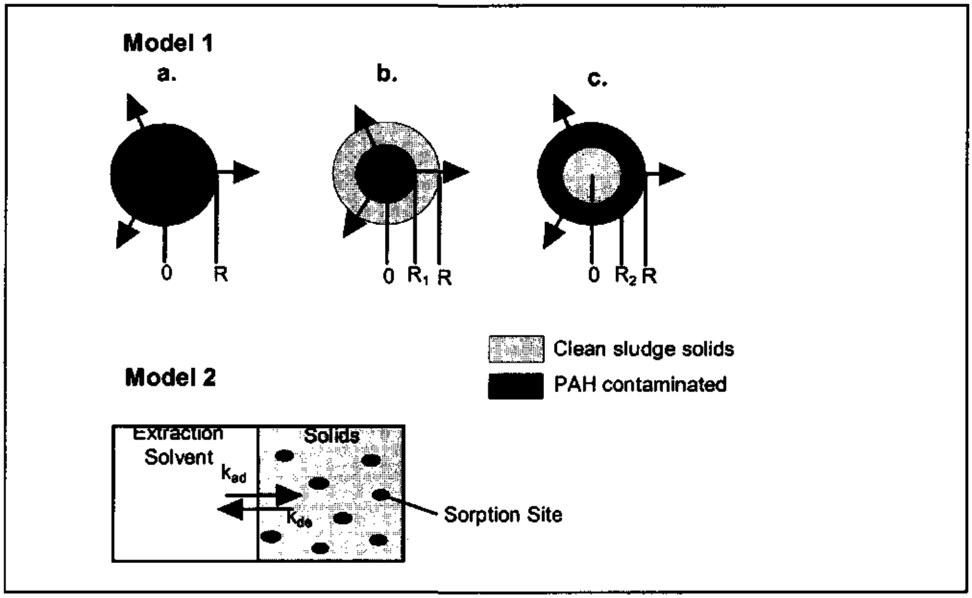

Figure 6.2 Diagrams of model 1 (radial diffusion of PAHs from a sludge particle) and model 2 (sorption and desorption of PAHs as a first-order reaction with k_{ad} and k_{de} as rate constants for adsorption and desorption, respectively)

Model 1a: PAHs distributed homogeneously throughout the entire sludge particle.

For this model, equations (6.1) to (6.5) apply in combination with the following initial conditions in the particle and the extraction solvent:

$$C_s = C^0_s \qquad \text{for } t=0 \text{ and } 0 \leq r \leq R \qquad (6.6)$$

$$C_l = 0 \qquad \text{for } t=0 \qquad (6.7)$$

where C^0_s is the initial PAH concentration in the sludge particle (mg m^{-3}).

Model 1b: the core of the sludge particle is contaminated with PAHs.

The outmost layer of the particle is not contaminated with PAHs. For model 1b, the equations (6.1) to (6.5) apply in combination with the following initial conditions in the particle and the extraction solvent:

$$C_s = C^0_s \qquad \text{for } t=0 \text{ and } 0 \leq r \leq R_1 \qquad (6.8)$$

$$C_s = 0 \qquad \text{for } t=0 \text{ and } R_1 < r \leq R \qquad (6.9)$$

$$C_l = 0 \qquad \text{for } t=0 \qquad (6.10)$$

where R_1 is the radius of the contaminated core.

Model 1c: the outmost organic matter layer of the particle is contaminated with PAHs.

This model assumes that PAHs cannot diffuse into the mineral core. Radial diffusion occurs only in the organic matter layer:

$$\frac{\partial C_s}{\partial t} = D_{eff}\left[\frac{\partial^2 C_s}{\partial r^2} + \frac{2}{r}\frac{\partial C_s}{\partial r}\right] \qquad \text{for } R_2 \leq r \leq R \qquad (6.11)$$

where R_2 is the radius of the mineral core (m). No diffusion occurs at the mineral/organic matter interface. This means:

$$-D_{eff}\frac{\partial C_s}{\partial r} = 0 \qquad \text{for } r=R_2 \qquad (6.12)$$

Furthermore, equations (6.3) and (6.4) apply to this model, and the initial conditions in the particle and the extraction solvent are:

$$C_s = 0 \qquad \text{for } t \leq 0 \text{ and } 0 \leq r < R_2 \qquad (6.13)$$

$$C_s = C^0_s \qquad \text{for } t=0 \text{ and } R_2 \leq r \leq R \qquad (6.14)$$

$$C_l = 0 \qquad \text{for } t=0 \qquad (6.15)$$

The differential equations (6.1), (6.4) and (6.11) were numerically solved by using finite difference methods. Next, computer programs were developed in Turbo Pascal to calculate the PAH concentrations in the particle and extraction solvent for a large number of D_{eff} values with the numerical equations. The best fitting D_{eff} value was determined by calculating the minimum sum of the squared deviations between the PAH concentrations measured in the extraction solvent (C_l) as a function of time and those calculated using the model.

6.2.2 Model 2: First-order reaction model

The first-order reaction model is an empirical model and is also known as the one-box model [5]. This model describes the adsorption of PAHs onto and their desorption from sorption sites in the sludge particles as a first-order reaction with rate coefficients k_{ad} and k_{de}. The sorption sites are assumed to be equal, i.e. they have the same characteristics and sorption energy. Another assumption is that the transport of PAHs in the sludge particles and extraction solvent is not ratelimiting. This model is presented in Figure 6.2. The mass balance for the PAH concentration in the extraction solvent C_l (mg m^{-3}) is:

$$V_l \frac{dC_l}{dt} = -k_{ad} C_l V_l + k_{de} SW \tag{6.16}$$

where t is time (s), V_l the total liquid volume (m^3), k_{ad} the coefficient for the adsorption rate (s^{-1}), k_{de} the coefficient for the desorption rate (s^{-1}), S the concentration of the PAHs adsorbed onto the soil particles (mg (kg dry matter)$^{-1}$), and W the weight of the dry matter (kg). Division of both terms in equation (6.16) by V_l and the introduction of solid/liquid ratio $X = W/V_l$ (kg m^{-3}) results in the following equation:

$$\frac{dC_l}{dt} = -k_{ad} C_l + k_{de} SX \tag{6.17}$$

At the start of the extraction process (t=0), PAHs are present only in the sludge solids, which results in the following initial conditions in the sludge solids and extraction solvent:

$$S=S^0 \qquad \text{for } t=0 \tag{6.18}$$

$$C_l=0 \qquad \text{for } t=0 \tag{6.19}$$

where S^0 is the PAH concentration adsorbed in the sludge particles at t=0 (mg (kg of dry matter)$^{-1}$). Besides, the mass balance for the total amount of PAHs in the sludge solids and extraction solvent is described by:

$$S^0 X = C_l + SX \tag{6.20}$$

An additional condition is derived from the state of equilibrium, when the PAH concentration in the extraction solvent does no longer increase with time. Then, the concentration of the PAHs adsorbed in the sludge particles (S_e) and that of the PAHs in the extraction solvent (C_{le}) are related to the distribution coefficient K_{d2} (-) by:

$$K_{d2} = \frac{S_e X}{C_{le}} = \frac{k_{ad}}{k_{de}} \tag{6.21}$$

Equation (6.21) can be rearranged to form:

$$k_{ad} = K_{d2}k_{de} \tag{6.22}$$

Combination and analytical solution of equations (6.17) to (6.20) and (6.22) results in:

$$C_l = \frac{S_0X}{(K_{d2}X+1)}(1-e^{-(K_{d2}X+1)tk_{de}}) \tag{6.23}$$

The only unknown parameter in equation (6.23) is k_{de}. Using equation (6.23), the PAH concentration in the extraction solvent was calculated as a function of time for a large number of values of k_{de}. The best fitting value of k_{de} was determined by calculating the minimum sum of the squared deviations between the PAH concentrations measured in the extraction solvent (C_l) as function of time and those calculated using equation (6.23).

6.2.3 Model parameters

To calculate the distribution coefficients K_{d1} (-) and K_{d2} (-) used in models 1 and 2, respectively, their relationship to distribution coefficient K_d (= S_e/C_{le} ($m^3\ kg^{-1}$)) described in Chapter 4 needs to be defined. These relationships are:

$$K_{d1} = K_d * \rho_s \tag{6.24}$$

$$K_{d2} = K_d * X \tag{6.25}$$

where ρ_s is the solid phase density of the sludge particles (kg m^{-3}). This density was measured by immersing a weighted sludge sample in water in a vessel with a calibrated volume. It was found to be 2,401 kg m^{-3}.

The values of distribution coefficient K_d (= S_e/C_{le}) were calculated from the desorption isotherms experimentally determined during an earlier investigation (Chapter 4). From the desorption curves (Chapter 5), the final PAH concentration measured in the extraction solvent (C_{le}) was derived in order to calculate the equilibrium PAH concentration in the solids (S_e) with the desorption isotherms. The calculated S_e value was also the residual PAH concentration in the sludge solids. Because part of the PAHs remained in the solids, the extraction solvent did not contain 100% of the PAHs at the end of the extraction process.

For model 1, the most important independent parameters besides K_d are particle radius R and initial PAH concentration S^0 in the solids. Table 6.1 shows the values of these three parameters for the sum of EPA-PAHs in all samples. For the size fractions of <20 μm, 20-63 μm and 63-125 μm, particle radius R was chosen as the midst radius in those fractions. The mean particle radius of the sludge was calculated as 20 μm based on the particle size distribution obtained by wet sieving (Chapter 5). The particle size distribution of the sieve fraction of >125 μm was studied by microscopy, and based on the observations made the average particle radius R for this fraction was calculated as 75 μm.

Table 6.1 **Values of particle radius, K_d, the initial concentration of the sum of EPA-PAHs, and the solid/liquid ratio for the sludge and fractions used in the model calculations**

Sample	Particle radius R (μm)	K_d ($m^3\ kg^{-1}$)	Init. conc. S^0 EPA-PAHs (10^3 mg kg^{-1})	solid/liquid ratio X (kg m^{-3})
Sludge	20	0.0021	1.0	40
<20 μm	5	0.0026	1.2	29
20-63 μm	21	0.0014	0.81	40
Upflow column:				
- underflow	21	0.0016	0.58	40
- overflow	21	0.0013	1.5	25
63-125 μm	47	0.0018	1.3	40
Upflow column				
- underflow	47	0.0024	0.49	40
- overflow	47	0.0017	1.6	40
>125 μm	75	0.0017	2.5	25

Other important parameters for models 1b and 1c are the radius of the contaminated core (R_1) and that of the not-contaminated mineral core (R_2), respectively (Figure 6.2). For model 1c, the percentage of the radius comprising the organic matter layer ($R-R_2$) was assumed to be 20%. This assumption was based on the reasoning that the volume of a particle consists of organic matter for about 50%, if the organic matter content of the particle is about 30 wt% and the density of the organic and mineral matter in the particle is assumed to be about 1,300 kg m^{-3} and 2,800 kg m^{-3}, respectively. If the volume of a particle consists of organic matter for about 50%, the outmost organic matter layer will cover about 20% of the radius ($R-R_2$) of the particle and the mineral core will cover 80% of the radius (R_2).

Because for model 1b no reliable assumption could be made about the contaminated part of the particle (R_1), for this model the same percentage (80%) was assumed as that assumed for model 1c. Thus, at t=0 the contaminated core comprises 80% of the radius (R_1) and 50% of the volume of the particle.

For model 2, the values of K_d, the initial PAH concentrations S^0 and the solid/liquid ratios X from Table 6.1 were used to calculate desorption curves.

6.3 Results and discussion

6.3.1 Best fitting model

Table 6.2 shows for the sum of EPA-PAHs the best fitting values of D_{eff} for the three variants of model 1 and the best fitting values of k_{de} for model 2 with the sum of squared deviations (SSQs) calculated with the best fitting values. Model 1b fits best to the experimental desorption curves for the sum of EPA-PAHs, because the SSQs of all samples are lowest for model 1b compared to the other models (Table 6.2). Model 2 has slightly higher SSQs than model 1b, whereas the SSQs of models 1a and 1c are about twice as high as those of model 1b (Table 6.2). This trend is similar for the individual PAHs (results not shown).

Table 6.2 Best fitting values of D_{eff} and k_{de} with the sum of squares for the sum of EPA-PAHs in sludge and fractions for models 1 and 2

Sum of EPA-PAHs	Best fitting D_{eff} (10^{-13} m^2 s^{-1}) model 1			Bk_{de}*(s^{-1}) model 2	Sum of squares (%^{2}) models 1 and 2			
	1a	1b	1c	2	1a	1b	1c	2
Sludge	1.4	3.0	0.23	0.0072	1516	379	1385	492
<20 µm	0.11	2.1	0.019	0.0080	2325	1091	2078	1216
20-63 µm	2.4	3.5	0.37	0.0078	1922	977	1544	1021
Upflow col:								
underflow	1.3	2.5	0.22	0.0056	2722	1189	2326	1362
overflow	1.7	3.5	0.31	0.0078	2965	1084	2572	1319
63-125 µm	7.2	16	1.3	0.0068	1761	518	1578	679
Upflow col:								
underflow	5.7	13	0.93	0.0053	753	232	755	278
overflow	9.5	16	1.6	0.0071	2348	1235	2041	1314
>125 µm	9.0	27	1.6	0.0040	792	171	687	284

* Bk_{de} = Best fitting k_{de}

Figure 6.3 shows the best fitting D_{eff} values for the sum of EPA-PAHs and the individual PAHs with model 1b for the sludge and the sieve fractions. The figure shows that D_{eff} is increasing with increasing particle radius of the sample, which was also observed for the best fitting D_{eff} values for models 1a and 1c. Furthermore, within one sample the D_{eff} values for the individual PAHs do not differ much. Only for the sieve fraction of >125 µm the best fitting D_{eff} values slightly decrease with increasing molecular weight of the PAHs (Figure 6.3). This agrees with the experimental desorption curves for the individual PAHs, which clearly show slower desorption rates for PAHs of high molecular weight especially in fractions with a particle diameter greater than 63 μm (Chapter 5).

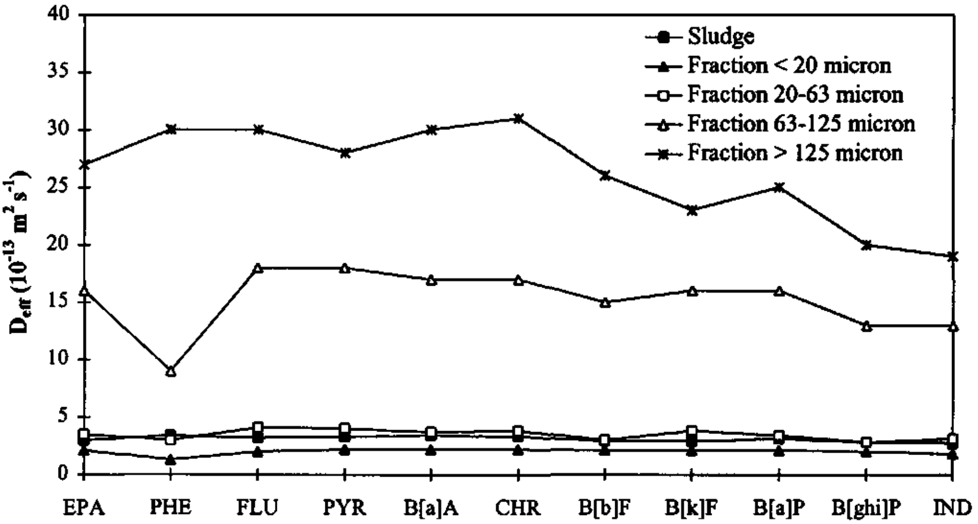

Figure 6.3 Best fitting values of Deff (m^2 s^{-1}) for the sum of EPA-PAHs and the individual PAHs in the sludge and the sieve fractions with model 1b

For the sieve fraction of 63-125 μm, desorption curves were calculated with models 1a, 1b, 1c and 2 for the best fitting values of D_{eff} and k_{de} from Table 6.2. These desorption curves are shown in Figure 6.4 together with the PAH concentrations (%) measured in the extraction solvent for the sieve fraction of 63-125 μm. As was already apparent from Table 6.2, models 1b and 2 fit the measured PAH concentrations best, and minimum differences exist between these two desorption curves.

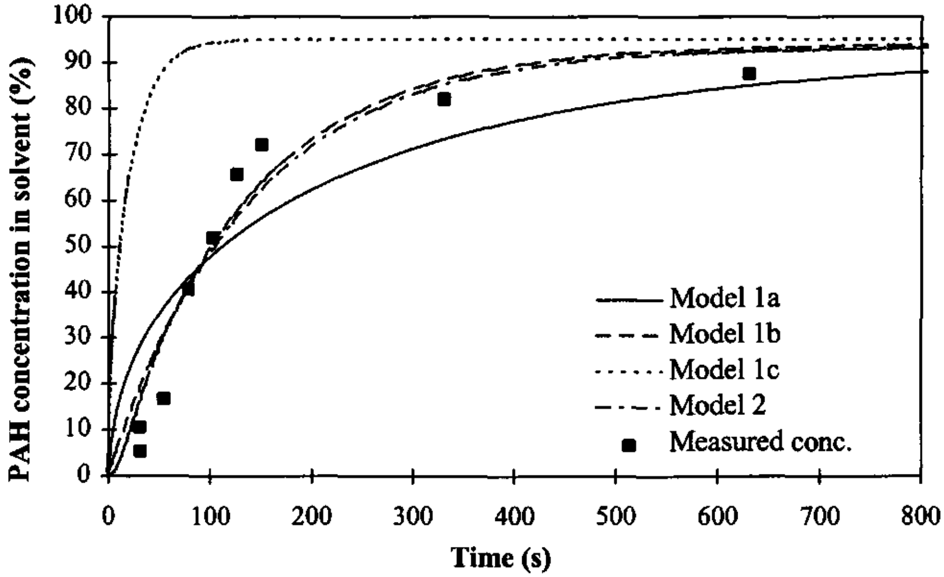

Figure 6.4 **Simulation of the PAH concentration in the extraction solvent (%) as a function of time with models 1a, 1b, 1c, 2 and the best fitting parameters for the sieve fraction of 63-125 μm**

6.3.2 Discussion of model 1b

Influence of particle radius. The good fit of model 1b suggests that the desorption of PAHs depends mainly on radial diffusion out of the sludge particles. However, the importance of particle radius (R) for radial diffusion (model 1) makes it doubtful whether model 1 applies to the experimental data. If an experimental desorption curve is fitted with model 1b and the particle radius applied in the model is increased by a factor of two, the best fitting D_{eff} increases with a factor of four.

Figure 6.5 shows the effect of the particle radius on the desorption curves calculated with model 1b. The desorption curves were calculated for $D_{eff} = 16 \times 10^{-13}$ $m^2 s^{-1}$, $K_d = 0.0018$ mg kg^{-1} and R_1 = 80% of the particle radius, which are the parameters used for fitting the experimental desorption curve of the sieve fraction of 63-125 μm. Furthermore, the desorption curves were calculated for particle radii (R) of 5, 20, 47 and 75 μm, which are the average particle radii of the samples (Table 6.1). Figure 6.5 shows large differences between the desorption curves simulated with the same value of D_{eff} but with particle radii corresponding to those of the sludge fractions.

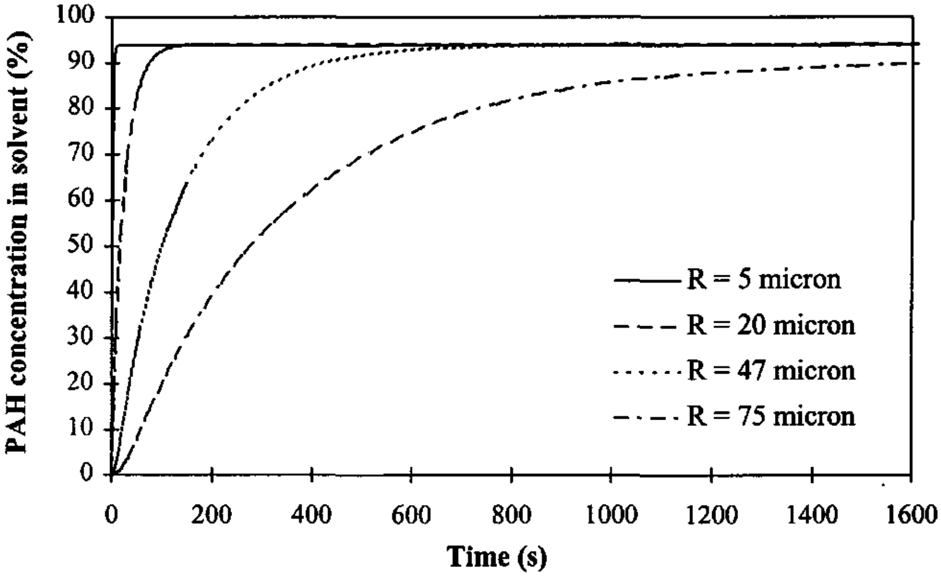

Figure 6.5 **Simulation of the concentration of the sum of EPA-PAHs in the extraction solvent (%) as a function of time with model 1b for $D_{eff} = 16x10^{-13}$ m^2 s^{-1} and particle radii of 5, 20, 47 and 75 μm**

The strong influence of the particle radius in model 1 on the desorption rate has consequences for the choice of the particle radius (R) to be used in the model calculations for the particles in sludge and the sludge fractions. In this chapter, average particle radii were used for fitting (Table 6.1). If a sample does not have an equal particle size distribution however, this can influence the desorption curves. In Figure 6.6, desorption curves were calculated with model 1b for the average particle radius (47 μm), the lowest particle radius (32 μm) and the highest particle radius (63 μm) of the sieve fraction of 63-125 μm (further: $D_{eff} = 16 \times 10^{-13}$ m^2 s^{-1}, $K_d = 0.0018$ mg kg^{-1}, R_l = 80% of the particle radius). Figure 6.6 shows that the particle size distribution within the fraction 63-125 μm influences the calculated desorption rates of model 1b.

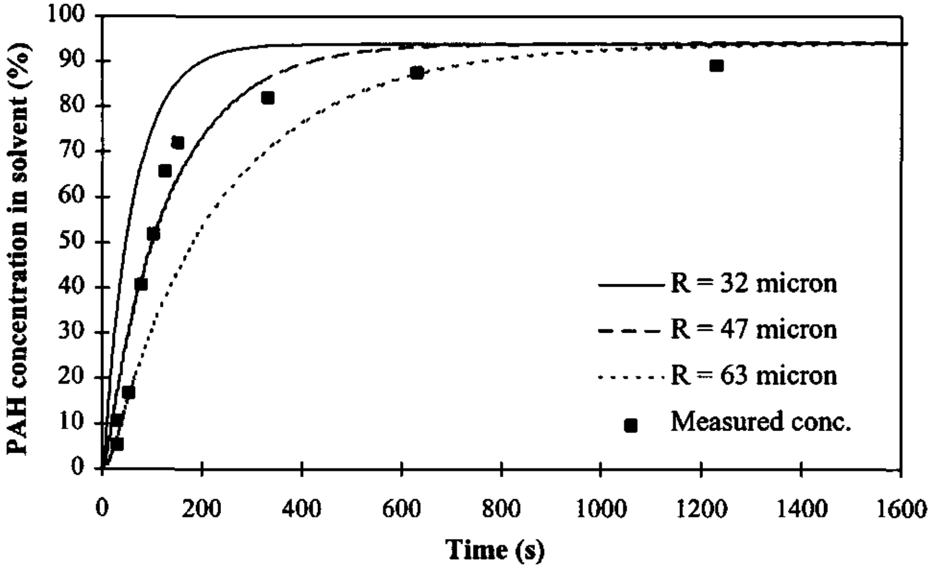

Figure 6.6 **Simulation of the concentration of the sum of EPA-PAHs in the extraction solvent (%) as a function of time with model 1b for the sieve fraction of 63-125 μm, D_{eff} = 16x10^{-13} m^2 s^{-1} and particle radii of 32, 47 and 63 μm**

As shown in Figures 6.5 and 6.6, the particle radius of the sample has a strong effect on the radial diffusion of PAHs from the sludge particles, and it was therefore expected that the experimentally determined desorption curves would also show variations with particle size. However, the latter curves show only minor differences (chapter 5) and this results in increasing values with increasing particle radius for the best fitting D_{eff} for models 1a, 1b and 1c (Table 6.2). Two explanations can be given for this phenomenon.

First, the desorption of PAHs occurs so rapidly and the value of D_{eff} is so high, that the differences between the fractions cannot be measured using the experimental set-up, as already mentioned in Chapter 5. This may account especially for the fractions with a particle diameter smaller than 63 μm, because the PAHs are rapidly desorbed from these fractions. The second explanation for the increasing D_{eff} with increasing particle size of the sludge and sludge fractions is that the fractions differ in particle properties. This is explained in the next subsection.

Internal porosity of the sludge particles. The definition of D_{eff} is given in the form of equation (6.5), which shows that D_{eff} depends on internal porosity ϵ, the diffusion coefficient in the pore fluid D_l, pore geometry factor $f(\epsilon,\tau)$, and K_{dl}. According to equation (6.24), K_{dl} depends on ρ_s and K_d. Of these parameters, D_l is equal for all fractions, because the extraction solvent is the same. Density ρ_s was measured only for the sludge (= 2,401 kg m^{-3}), and it is assumed that the sludge fractions are of similar density. Because the pore geometry factor is especially hard to determine, the porosity was calculated for two different values of $f(\epsilon,\tau)$. Factor $f(\epsilon,\tau)$ is assumed to be equivalent to unity [3] or equal to the porosity ($f(\epsilon,\tau) = \epsilon$ [5]). Based on these assumptions, internal porosity ϵ was calculated using equation (6.5) and the best fitting D_{eff} from model 1b (R_l=80%) for the individual PAHs in all samples. The average porosities calculated for the individual PAHs in the samples are given in Table 6.3. This table shows that for all samples the porosity for $f(\epsilon,\tau)=\epsilon$ is almost or more than twice as high as that for $f(\epsilon,\tau)=1$. Besides, it can be seen that the porosity increases with increasing particle radius of the fractions. It can be concluded that a higher porosity results in a higher D_{eff} value, since the value of D_l is the same for all fractions and the values of K_d are not correlated with the particle size of the fractions (Table 6.1). According to equation (6.5), besides D_l and K_d porosity is the only other parameter that can influence D_{eff}.

Table 6.3 Average porosity (vol.%) of the individual PAHs calculated with equation (6.5) and the best fitting D_{eff} of model 1b (R_l=80%)

Sample	Part. radius R (µm)	Porosity ϵ (vol.%) $f(\epsilon,\tau)=1$	$f(\epsilon,\tau)=\epsilon$
Sludge	20	0.25±0.1	4.7±1
<20 µm	5	0.019±0.00005	1.4±0.2
20-63 µm	21	0.19±0.1	4.1±1
Upflow column:			
- underflow	21	0.14±0.07	3.6±0.9
- overflow	21	0.18±0.1	4.0±1
63-125 µm	47	0.91±0.4	9.0±2
Upflow column			
- underflow	47	1.1±0.4	9.7±2
- overflow	47	0.88±0.4	8.9±2
>125 µm	75	1.6±0.8	11.6±3

The higher values of the internal porosity for $f(\epsilon,\tau)=\epsilon$ seem to be more realistic than the values calculated for $f(\epsilon,\tau)=1$. The porosities range between 1.4 and 11.6 vol.% for $f(\epsilon,\tau)=\epsilon$ (Table 6.3). Lin et al. [6] found internal porosities of 6.2% and 1.4% for a field soil and a sandy soil, respectively. For three different organic-matter fractions of soil and peat, De Jonge and Mitterlmeijer-Hazeleger [7] determined an internal porosity between 4% and 6.3%. Wu and Gschwend [5] calculated the internal porosity from the same equation as equation (6.5) for $f(\epsilon,\tau)=\epsilon$ and found values ranging from 7% to 18% for river sediments and soils.

Optimum values for the radius of the contaminated core (R_1). As mentioned before, model 1b describes the experimental desorption curves best. This model can fit the experimental curves even better if the radius of the contaminated core (R_1) is optimised. For values of R_1 ranging from 10% to 90% with steps of 10%, model 1b was fitted to the measured concentrations of the sum of EPA-PAHs. Table 6.4 gives for all samples the optimum values of R_1 (%) with the best fitting D_{eff} and SSQ.

A comparison made between the SSQs for model 1b with R_1=80% (Table 6.2) and those with the optimized R_1 (Table 6.4) shows that the SSQs strongly decrease for most samples if the value of R_1 is optimised. Model 1c was not optimised for the radius of the mineral core R_2, because the amount of minerals in the particle is a fixed percentage.

Table 6.4 Optimum values (%) for the radius of the contaminated core (R_1) for model 1b and the sum of EPA-PAHs with the best fitting D_{eff} and sum of squares

Sample	Particle radius R (μm)	Optimum value of R_1 (%)	Optimum value of R_1 (μm)	Best fitting D_{eff} (10^{-13} m^2 s^{-1})	Sum of squares (%^{2})
Sludge	20	40	8	5.5	164
<20 μm	5	10	0.5	0.40	175
20-63 μm	21	10	2.1	6.0	307
Upflow column:					
- underflow	21	10	2.1	5.2	232
- overflow	21	10	2.1	7.0	189
63-125 μm	47	50	24	26	224
Upflow column					
- underflow	47	80	38	13	232
- overflow	47	10	4.7	29	339
>125 μm	75	80	60	27	171

Because model 1b describes the experimental desorption curves best compared to models 1a, 1c and 2, the PAHs are probably distributed in the sludge particles as described by model 1b. This leads to the conclusion that no PAH contamination is present in the outer layer of the particle, because the PAH molecules have already diffused from the particles or have been degraded due to their higher availability in the outer layer. This PAH distribution results in a slow desorption rate in the first 30 seconds (see the measured concentrations in Figure 6.4), which is described well by model 1b.

Extension of model 1b. Another explanation for the good fit of model 1b may be that the slow desorption rate in the first 30 seconds is not caused by the fact that the PAHs are distributed throughout the entire particle but by the time acetone molecules need to diffuse into the sludge particles. The acetone molecules have to diffuse to the centre of the particles before diffusion of PAHs from the centre can occur. The effect of diffusion of acetone into the particle can be studied by extending the radial diffusion model. It is recommended developing a model for the combined radial diffusion of acetone into a particle and PAH contamination out of the particle with a homogeneous PAH distribution throughout the entire particle at the start of the extraction process.

6.3.3 Comparison between models 1b and 2

The alternative to the radial diffusion model is the empirical first-order rate model 2. In the latter, the particle size has no effect on the desorption rates. The best fitting values of k_{de} differ only by a factor of two (Table 6.2), and the value of k_{de} is a good indication of the desorption rates measured. This model has, however, a disadvantage in that it is empirical and model 1b fits the experimental data (slightly) better. Model 2 may fit better if the adsorption of acetone molecules onto sorption sites is taken into account. For model 2, this adsorption is comparable to diffusion of acetone molecules into the particle for model 1.

Due to the empirical character of model 2, the best fitting values of k_{de} apply only to this solvent, sludge and solid/liquid ratio. Model 2 is only suitable for predicting desorption rates for other extraction systems, if relations can be developed between the best fitting values of k_{de} and properties of the extraction system that influence k_{de}, such as type of solvent and type of sludge. As long as these relations do not exist, model 1b is preferred over model 2.

6.4 Conclusions

The mechanistic model 1b for radial diffusion fitted best to the experimental desorption curves of the sum of EPA-PAHs and the individual PAHs, because the SSQs of all samples were lowest for model 1b compared to the other models. This suggests that the desorption of PAHs depended mainly on radial diffusion out of the sludge particles. Furthermore, model 1b assumed that the PAHs accumulate in the core of the sludge particles at the beginning of the extraction process. No PAH contamination was present in the outer layer of the particles, because the PAH molecules had diffused from the particles or have been degraded due to their higher availability in the outer layer.

However, the applicability of model 1b (and models 1a and 1c) to the experimental data was doubtful because of the strong effect of the particle radius (R) on the simulated desorption curves, whereas the experimental desorption curves for the fractions did not differ much with particle size. As a result, the best fitting D_{eff} values increased with increasing particle size of the samples. The first explanation for this may be that the desorption of PAHs occured so rapidly and the value of D_{eff} was so high that the differences between the fractions could not be measured using the experimental set-up. This may account especially for the fractions with a particle diameter smaller than 63 μm, because the PAHs were rapidly desorbed from these fractions.

The second explanation was that the fractions differ in particle properties. Therefore, the internal porosity of the particles in the fractions was calculated based on the best fitting D_{eff} values for model 1b. Compared to literature data, the most realistic values for porosity were achieved if the pore geometry factor was assumed to be equal to the porosity. The porosity in the fractions ranged from 1.4 to 11.6 vol.% and increased with increasing particle size of the fractions.

As mentioned before, of the four models applied model 1b fitted the experimental desorption curves best. The deviation of this model from the experimental curves decreased even further when the radius of the contaminated core was optimised. Accumulation of the PAH contamination in the core of the particle resulted in a slow desorption rate in the first 30 seconds, which was also visible in the experimental desorption curves. However, this slow desorption rate may also be caused by the time acetone molecules need to diffuse into the sludge particles and not by the fact that the PAHs are concentrated in the core of the particle.

Because of the good fit of model 1b and the insight this model gives into the diffusion processes and physical properties of the particles, the mechanistic model 1b was preferred over the empirical first-order reaction model (model 2), which has only a predictive value for the system used.

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Chapter 7

General discussion

Abstract

The design of a solvent extraction process for the remediation of PAH contaminated soil and sludge should be based on experiments with aged PAH contaminants in soils and sludges, as different extraction efficiencies and extraction times were found compared to experiments with spiked pyrene and benzo[a]pyrene in soils. Solvent extraction with acetone is prefered because methanol and ethanol attained lower extraction efficiencies.

The proposed acetone extraction process is especially suited for remediation of sediments and residual sludges from soil classification with high water and clay contents containing barely (bio)available or biodegradable compounds.

7.1 Introduction

First, the differences and similarities observed regarding spiked soils on the one hand and aged soil, sediment and sludge on the other, as detailed in Chapters 2 to 6, are discussed. Furthermore, this general discussion deals with the technical design and feasibility of the solvent extraction process based on the results given in Chapters 2 to 6. Additionally, the design and feasibility of a solvent extraction process for the remediation of contaminated sediment by extraction with acetone is discussed.

7.2 Spiked soils versus aged soil, sediment and sludge

In the investigation, spiked soils were used as model systems. They are well defined systems, because they consist of soil substances with known types and amounts of contamination. Aged soils, sediments and sludges, however, may contain various types of contamination, and the contaminant concentrations in the solids need to be determined by analysis. The spiked soils are especially useful to gain detailed insight into the physical processes occurring during extraction. It is much more difficult to gain such insight in the case of aged solids, because it is unknown how contaminants are distributed among and in the particles and in what physical state these contaminants occur. Nevertheless, for practical application of the solvent extraction process it is necessary to use also aged soil, sludge and sediment, because there are differences between the extraction of spiked solids and that of aged solids.

The most important difference concerns the extraction time needed to achieve equilibrium between the PAH concentration in the extraction solvent and that in the solids. In the spiked soils, equilibrium is reached within 5 minutes (Chapter 3), whereas in the aged sludge equilibrium is reached for PAHs within 40 minutes (Chapter 5). This difference is assumed to be a result of the different distribution of PAHs in the solid particles after spiking compared to their distribution after an aging process of many years. After spiking, PAHs are probably bound only to the external or internal surface area of soil substances, and removal of this type of adsorbed PAHs requires only a short extraction time. For the aged sludge, it was concluded from computer simulations that PAHs are accumulated in the core of the particles at the beginning of the extraction process (Chapter 6). It may be expected that during the aging process PAHs diffuse into the solid matrix of the particles. The PAHs in the outmost layer of the particles are best available for bidodegradation and/or diffusion. Another process occurring during aging is alteration of organic matter by, for instance, biodegradation, which may cause narrowing and/or blocking of pores.

Another difference between extraction of PAHs from spiked solids and that from aged solids concerns the extraction efficiency achieved with pure acetone, methanol and ethanol. For a sandy soil spiked with PYR and B[a]P, the highest extraction efficiency was achieved with methanol and the second highest with ethanol as well as acetone (Chapter 3). Extraction of PAHs from an air-dried, aged sandy soil, however, resulted in higher extraction efficiencies for acetone than for methanol and ethanol (Chapter 2). Because PAHs are more soluble in pure acetone than in pure methanol and ethanol, solubility is probably an important factor for the extraction efficiency of aged soil, but less important for that of spiked soil. Regarding spiked soils, however, the extraction efficiency for B[a]P was in most experiments lower than that for PYR, which is probably a result of the lower solubility of B[a]P in the pure solvents. In conclusion, no clear relationship exists between the extraction efficiency for the extraction of PAHs from solids and the solubility of the PAHs in the pure solvents. Furthermore, because for only a few PAHs their solubility in organic solvents such as acetone, methanol and ethanol is known, it is not possible to determine a general relationship between the solubility of PAHs in organic solvents and their extraction efficiency.

The differences observed between spiked soils on the one hand and aged soil, sediment and sludge on the other show that it would be incorrect to design a remediation process based only on experiments with spiked soils. Experiments with aged soils, sludges and sediments also need to be carried out to check whether there are large differences between the behaviour of spiked solids and that of aged solids.

A remarkable similarity between spiked soils and aged soil, sludge and sediment is the extraction efficiency achieved with mixtures of acetone and water. For all spiked and aged solids, a maximum extraction efficiency was achieved with a mixture of about 80 vol.% acetone and 20 vol.% water. This effect was not observed for methanol and it is not related to the solubility of PAHs in the mixtures, because their solubility is higher in pure acetone than in mixtures of acetone and water. The high extraction efficiency achieved with mixtures of acetone and water is favourable for the design of the solvent extraction process, as explained in the next section.

7.3 Technical design of the solvent extraction process

Chapters 2 to 6 dealt with the choice of an appropriate solvent, the separation of solids in size fractions, and the features of the extraction step. An effect of acetone on the settlement of solid particles, which so far has not been mentioned, is also elucidated. These subjects are discussed below to determine the consequences for the design of a solvent extraction process.

Finally, the WAU acetone process is introduced and discussed [1].

7.3.1 Choice of solvent

One of the most important steps in the design of the solvent extraction process for application in practice is the choice of an appropriate solvent. Acetone is an appropriate solvent in view of its chemical and physical properties and the high extraction efficiencies achieved with it in the extraction of spiked soils (Chapter 3) as well as in that of aged soil, sediment and sludge (Chapter 2). In the extraction of an aged sludge, the Dutch target level for PAHs established for clean soil could be achieved after seven subsequent extractions with a mixture of 80 vol.% acetone and 20 vol.% water (Chapter 4). For an aged sediment, the target level could be almost achieved by following this extraction procedure. Seven subsequent extractions reduced the PAH concentration from about 1,000 mg per kg of dry matter in the sludge and from about 650 mg per kg of dry matter in the sediment to about 2 mg per kg of dry matter in both materials.

Another important property of acetone is that the extraction efficiencies are high even if the contaminated solids contain water. Because soil, sediment and sludge always contain water, it is an advantage if the solids do not have to be dewatered and/or dried before extraction. In addition, it is important that only contaminants are extracted from the solids and not other substances such as organic matter. In experiments carried out with a clean clay soil and aged contaminated sediment extracted with acetone for time periods ranging from 1 to 70 hours, less than 3 wt% of the organic matter dissolved in acetone [2, 3].

7.3.2 Separation of solids in size fractions

Before extracting contaminated solids with an organic solvent, it may be advantageous to separate the sand fraction, because this fraction is in general not (heavily) contaminated [4, 5]. The sand fraction consists of large particles with a small specific surface area, which cannot adsorb much contamination. Contaminants are sorbed for the most part in the organic fraction. In our opinion separation of sand should be recommended in combination with additional cleaning of this fraction if necessary. Thereafter, the heavily contaminated residual sludge can be treated with solvent extraction to produce a clean soil matrix.

The aged sludge investigated (Chapters 2, 4, 5 and 6) was a heavily contaminated residual sludge from a soil washing plant, from which the larger part of the sand fraction had been already removed in the washing plant. Chapters 4 and 5 demonstrated that it would not be efficient to remediate size fractions of this residual sludge separately, because the several fractions of the sludge showed hardly any differences in PAH composition, desorption isotherms or desorption kinetics.

7.3.3 Characteristic features of the extraction step

As mentioned above, for extraction with acetone the maximum efficiency is achieved with a mixture of about 80 vol.% acetone and 20 vol.% water for all investigated types of soil, sludge and sediment. Pure acetone gives slightly lower extraction efficiencies. Furthermore, Chapters 3 and 4 showed that the extraction efficiency is even high for mixtures of acetone and water containing up to 40 vol.% water. This makes acetone very suitable for the extraction of sediments and sludges with a high percentage of water. However, a mixture of 60 vol.% acetone and 40 vol.% water is less efficient for the removal of PAHs from sludge and sediment than a mixture with 80 vol.% acetone and 20 vol.% water, as shown in Chapter 4. Therefore, it is important that, if low residual concentrations have to be achieved in the solids, the last extraction step(s) is/are carried out with a mixture of acetone and water with an acetone content of about 80 vol.%.

To remediate highly contaminated sludge and sediment, about seven subsequent batch extractions with a mixture of 80 vol.% acetone and 20 vol.% water are neccessary to reach the target level of PAHs established for clean soil and sediment (Chapter 4). During each batch extraction step, clean extraction solvent was added to the solids. In practice it is more efficient to operate the extraction process in countercurrent flow in order to limit the required amount of extraction solvent. This means that the contaminated solids flowing into the extractor are extracted by solvent that is already contaminated to a rather high extent, whereas the nearly clean solids are extracted using the clean inflowing extraction solvent. Based on the desorption isotherms determined, it is possible to predict how many subsequent batch extraction steps in countercurrent flow are necessary to clean the contaminated sludge and sediment up to the target level. However, in batch as in continuously operating extractors the time of contact between solids and solvent should to be long enough to achieve equilibrium.

In the range of the target level, the residual PAH concentration in solids surprisingly depends for the most part on the presence of PAHs of low molecular weight, as concluded both in Chapter 4 and as a result of an investigation carried out by Meckes et al. [6]. It is therefore best to use the desorption isotherms of PAHs of low molecular weight for calculating the necessary number of extraction steps. It was shown that the determination of desorption isotherms is not only useful for designing purposes but also gives more insight into the desorption behaviour of PAHs of low and high molecular weight.

A crucial aspect of the solvent extraction process is the high desorption rate of PAHs. Using a mixture of 80 vol.% acetone and 20 vol.%, more than 90% of the PAHs were extracted from the aged sludge within 10 minutes. Equilibrium was reached in about 40 minutes. This means that the time of contact between sludge and extraction solvent can be relatively short. Therefore, the residence time of the solvent in the extractor can be short and the size of the extractor relatively small. To calculate the residence time, the removal rates of the PAHs of high molecular need to be used as a reference, because these PAHs need slightly more time for desorption than PAHs of low molecular weight.

7.3.4 Flocculation of particles in acetone

A remarkable effect of acetone on sludge and sediment particles is spontaneous flocculation of these particles. When acetone is added to sludge or sediment, the particles form conglomerates, resulting in a strong increase in the settling velocity of the particles. This velocity is much higher than expected for one single particle settling in acetone [1]. This phenomenon may have a large positive impact on the separation of clayey particles from the solvent.

The formation of conglomerates by sludge and sediment particles in acetone is probably an effect of the colloid properties of the particles. The diffuse double layer around the particles is probably small, because acetone has a low dielectric constant (21 C $(V{\cdot}m)^{-1}$). In comparison, the dielectric constant of water is four times as high (80 C $(V{\cdot}m)^{-1}$). Therefore, in acetone sludge and sediment particles can approach each other closely until the van der Waals attraction is strong enough to let the particles flocculate. Flocculation would occur only between small particles, because for larger particles the van der Waals attraction is not strong enough to keep the particles together.

Flocculation of particles promotes the settlement of particles in acetone and the solvent extraction process. Flocculation of particles may also occur in other organic solvents, because most organic solvents have a low dielectric constant.

7.3.5 The WAU acetone process

Based on the research into solvent extraction a complete extraction process has been developed at the subdepartment of Environmental Technology in collaboration with consulting bureau Scarabee, RIZA/POSW, TNO-MEP and Van den Herik-Sliedrecht [1, 2, 3]. Figure 7.1 shows a simplified diagram of this process. The WAU acetone process was especially designed for remediation of sediment from the Petroleum Harbour in Amsterdam, which is mainly contaminated with PAHs and mineral oil.

Contaminated sediment containing about 60 wt% of water is first mixed with practically pure acetone in a mixer. As a result, the liquid in the mixer will contain about 50 wt% acetone [1]. Next, the resultant slurry is fed into a countercurrent extractor. Such an extractor can be designed as a settling tank filled with either a packing, a modified rotating disc column or a combination of mixers and settlers simulating counter current flow. Practically pure acetone is fed to the bottom of the column, and sediment particles settle in the upward flowing extraction solvent. The total residence time of the sediment particles in the extractor is one to two hours. The settling velocity is about 1 mm s^{-1}, as established during settling experiments [1, 3]. After extraction, the sediment slurry is concentrated in a decanter centrifuge, and the separated solvent is fed back to the extractor. The resultant slurry is dried in a rotating dryer by direct contact with superheated steam. The clean sediment contains a few weight percentages of water. The acetone/water vapour escaping from the dryer is recycled to the mixer.

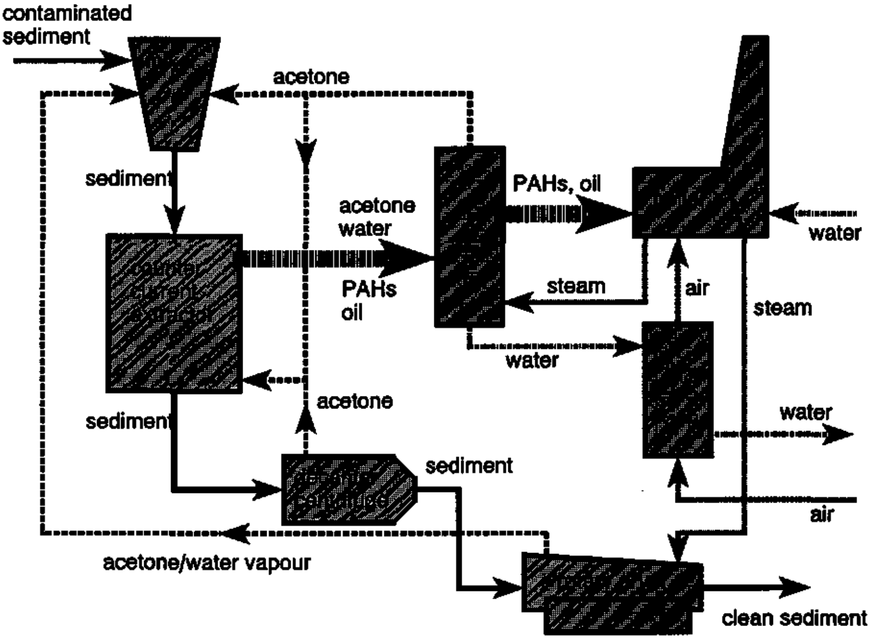

Figure 7.1 Simplified diagram of the WAU acetone process

The contaminated solvent leaving the top of the extractor contains about 50 wt% acetone, 50 wt% water, contaminants (including PAHs and oil) and possibly some entrained sediment particles, which are removed from the solvent using a lamellae separator. The contaminated solvent is separated in a distillation column into three fractions: an acetone top flow consisting of about 96 wt% acetone, a water bottom flow containing small amounts of soluble PAHs and acetone, and an oil fraction containing most of the PAHs. The acetone is reused in the mixer and extractor. The water fraction is stripped with air to remove residual amounts of acetone. Next, the water is led through an activated carbon filter and discharged. The oil fraction containing the PAHs is combusted in a burner which provides energy for the boiler. If the oil fraction contains chlorinated contaminants, combustion cannot be carried out in the plant itself because of the possible formation of dioxins. The boiler produces the energy needed for the process.

The operating costs of this solvent extraction process have been estimated at about 115 Dutch guilders for a remediation capacity of 10 tonnes of dry matter per hour. If the dry matter content of the dredged sediment is 40 wt%, the operating costs per tonne of wet sediment per hour are about 45 Dutch guilders [1].

7.4 Feasibility of the solvent extraction process

The overall feasibility of a remediation process depends on its technical, financial and environmental feasibility. This section deals only with the feasibility of a solvent extraction process based on extraction with acetone, such as the WAU acetone process.

Because the process equipment used for the WAU acetone process is based on existing techniques and apparatuses, this process can be considered technically feasible. In general, the technical feasibility of the solvent extraction process also appears from the fact that solvent extraction processes exist on a commercial scale in, for instance, the USA.

The financial feasibility of the solvent extraction process depends partly on the costs of the conventional remediation techniques employed. In the Netherlands, the commercial treatment costs of soil washing and thermal decontamination range at the moment from 60 to 150 Dutch guilders per tonne of soil depending on the type of soil and type of contamination. For biological remediation by landfarming, the estimated costs of treatment range from 60 to 120 guilders per tonne of soil [7]. The estimated operating costs of the WAU acetone process amount to 115 guilders per tonne of dry matter. It is difficult to draw any conclusion based on these figures.

Solvent extraction process can be applied to heavily PAH-contaminated sludges and sediments with high contents of clay, organic matter or water. For these sludges and sediments soil washing and biological treatment are no suitable remediation techniques. The only suitable alternative to solvent extraction is thermal treatment, but such treatment would be more expensive because of the high water content of the solids. Another advantage of the solvent extraction process compared to thermal decontamination may be that it removes hardly any organic matter from the solids. For the PAH-contaminated sludges and sediments with high clay and water content values, the solvent extraction process is probably the most suitable remediation technique compared to conventional techniques.

If the costs of the solvent extraction process are compared to those of the disposal of chemical waste, which is about 1,000 guilders per tonne, treatment with the solvent extraction process is anyway worthwhile. Heavily contaminated soils, sediments and sludges, such as the residual sludge and sediment from the Petroleum Harbour used in Chapter 4, are considered as chemical wastes.

The environmental feasibility of the solvent extraction process concerns all aspects that may influence the environment. An important aspect is whether the cleaned solids can either be used without restrictions or still contain a hazardous amount of contaminants. Chapter 4 showed that the solids probably can be cleaned below the Dutch target level of PAHs established for clean soil and sediment. Another advantage of the solvent extraction process is that its residual waste consists only of contaminants extracted from the solids. The most important reason for this small amount of residual waste is that only little organic matter is dissolved in acetone. Furthermore, even the small solid particles show a high sedimentation velocity due to the agglomeration of these particles in acetone, which provides a good separation of solvent and solids. The residual waste consisting of extracted contaminants can be easily combusted.

For the environmental feasibility of the process, it is also important that no toxic compounds are released to the environment. Therefore, the process should be operated in a closed environment. Another requirement is that the cleaned solids should not contain any solvent. This should be possible because of the high volatility of acetone and its good biodegradability.

The operating costs of the WAU acetone process comprise mostly the costs of energy consumption. These have been estimated at about 45 guilders per tonne of dry matter, which is 40% of the estimated operating costs. The energy consumption of the process is mainly due to the distillation process. Much energy is needed especially for the removal of naphthalene from the acetone flow. At a low naphthalene concentration in the contaminated sediment, the operating costs per tonne of dry matter will be lower by about 20 guilders. Aged solids generally contain little naphthalene, because this compound is well biodegradable. Nevertheless, it is important to optimise the distillation process. Furthermore, it is recommended investigating alternatives for the recovery of contaminated solvent, such as extraction of the contaminated solvent with another solvent. Such extraction is, for instance, carried out in the Low-Energy Extraction Process of ART International incorporation [8].

In conclusion, the solvent extraction process based on acetone is technically, financially and environmentally feasible, although it is recommended improving the process in order to reduce its energy consumption. It seems especially suited for the remediation of soils, sediments and sludges with high water and clay content values contaminated with barely (bio)available or biodegradable organic compounds.

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Nomenclature

A_s = total interfacial surface area (m^2)
C_l = PAH concentration in solvent (mg l^{-1} or mg m^{-3})
C_{le} = PAH concentration in solvent in equilibrium (mg m^{-3})
C^i_l = PAH concentration in solvent after extraction step i (mg l^{-1} or mg m^{-3})
C_s = PAH concentration in solids (mg m^{-3})
C^0_s = initial PAH concentration in solids (mg m^{-3})
C_{se} = PAH concentration in solids in equilibrium (mg m^{-3})
d_s = diameter of a particle (m)
D_{eff} = effective diffusion coefficient in particle (m^2 s^{-1})
D_l = diffusion coefficient in liquid (m^2 s^{-1})
f_s = volume fraction organic solvent of total liquid volume (-)
g = gravitational acceleration (m s^{-2})
k_{ad} = adsorption rate coefficient in first-order reaction model (s^{-1})
k_{de} = desorption rate coefficient in first-order reaction model (s^{-1})
K = sorption capacity, constant in Freundlich isotherm (-)
K_d = distribution coefficient over solids and solvent (m^3 (kg dry matter)$^{-1}$)
K_{d1} = distribution coefficient in radial diffusion model (-)
K_{d2} = distribution coefficient in first-order reaction model (-)
K_s = distribution coefficient over solids and solvent (mol (kg dry matter)$^{-1}$)
K_w = distribution coefficient over solids and water (mol (kg dry matter)$^{-1}$)
M_i = molecular weight of compound i
M_s = molecular weight of solvent
n = sorption intensity, constant in Freundlich isotherm (-)
r = distance from the centre to the actual position in a particle (m)
R = radius of a particle (m)
R_1 = radius of the contaminated core in a particle (m)
R_2 = radius of the mineral core in a particle (m)
S = PAH concentration in solids (mg (kg dry matter)$^{-1}$)
S^0 = initial PAH concentration in solids (mg (kg dry matter)$^{-1}$)
S^7 = residual PAH concentration in solids (mg (kg dry matter)$^{-1}$)
S_e = PAH concentration in solids in equilibrium (mg (kg dry matter)$^{-1}$)

S^i = PAH concentration in solids after extraction step i (mg (kg dry matter)$^{-1}$)

SB_i = solubility of compound i in solvent (mol mol^{-1})

sludge = residual sludge of a soil washing plant

SO_i = solubility of compound i in solvent (g ml^{-1})

solids = combination of soil, sediment and/or sludge

t = time (s)

v = sedimentation velocity (m s^{-1})

V_l = total volume of solvent (l or m^3)

V^i_l = total volume of solvent in extraction step i (l)

V^1_s = amount of solvent needed for one extraction step to reach the desired residual concentration in the solids (l (kg dry matter)$^{-1}$)

V^7_s = total amount of solvent needed for seven extraction steps to reach the desired residual concentration in the solids (l (kg dry matter)$^{-1}$)

W = quantity of dry matter (kg)

x_i = volume fraction of total volume of solvent remaining in the solids after extraction step i (-)

X = solid/liquid ratio (kg m^{-3})

Y_a = average extraction efficiency

Y_i = measured extraction efficiency

Greek symbols

δ_d = contribution of dispersion to the solubility parameter ((MPa)$^{1/2}$)

δ_h = contribution of hydrogen bonding to the solubility parameter ((MPa)$^{1/2}$)

δ_p = contribution of polar interactions to the solubility parameter ((MPa)$^{1/2}$)

δ_t = total solubility parameter ((MPa)$^{1/2}$)

ϵ = internal porosity (-)

$f(\epsilon,\tau)$ = geometry factor of pores (-)

η = dynamic viscosity (Ns m^{-2})

ρ = density (kg m^{-3})

ρ_l = density of liquid (kg m^{-3})

ρ_s = density of solids (kg m^{-3})

ρ_v = density of solvent (kg l^{-1})

σ = ability to increase the contaminant solubility in solvent (-)

τ = tortuosity of pores (-)

Abbreviations

ANT = anthracene
B[a]A = benzo[a]anthracene
B[a]P = benzo[a]pyrene
B[b]F = benzo[b]fluoranthene
BEST process = Basic Extractive Sludge Treatment process
B[ghi]P = benzo[ghi]perylene
B[k]F = benzo[k]fluoranthene
CHR = chrysene
EPA = Environmental Protection Agency of the USA
FLU = fluoranthene
HPLC = high performance liquid chromatography
IND = indeno[123-cd]pyrene
NMP = N-methyl-2-pyrrolidinone
PAHs = polycyclic aromatic hydrocarbons
PHE = phenanthrene
PYR = pyrene
SDM = sediment
SG = sludge
SOM = soil organic matter
SSQ = sum of squares (%^{2})

Summary

1 Introduction

Contamination of soils and sediments is a serious environmental problem in the Netherlands. Although several remediation methods (such as soil washing and biological and thermal treatment) are successfully being applied in practice, not all soils, sediments and sludges can be treated efficiently in technical and economic respects using these methods. This applies especially to soils, sediments and residual sludges from soil washing plants with high content values for water, clay and/or organic matter contaminated with barely biodegradable or (bio)available organic compounds. A suitable method for treating such contaminated solids may be an extraction method based on organic solvents. Several solvent extraction processes for the remediation of contaminated solids are being developed in, for instance, the USA. However, so far hardly any studies aimed at gaining more scientific and theoretical insight into such processes have been carried out. The main objective of the present investigation was therefore to study the effect of several process parameters on the efficiency of the extraction step of the solvent extraction process in order to develop an optimum process for the remediation of soils, sediments and sludges contaminated with polycyclic aromatic hydrocarbons (PAHs). The process parameters of interest were: type of solvent, extraction time, extraction procedure, water content of the extraction solvent, type of solids, size of the solid particles, and water content of the solids.

In the development of a remediation method, a critical factor is the analysis of the PAH concentration in the contaminated solids. Therefore, the first phase of the investigation consisted of selecting an efficient extraction method for determining the PAH concentration in aged soils, sediments and sludges as a basis for further research into solvent extraction of contaminated solids.

2 Extraction method for the analysis of PAHs in soil, sludge and sediment

Several extraction methods were tested for the analysis of PAHs in an aged sandy industrial soil, an extraction sludge and a harbour sediment. Extraction with N-methyl-2-pyrrolidinone (NMP) in a microwave oven at 130°C for one hour was by far the most efficient method for the extraction of PAHs from the extraction sludge and wet harbour sediment. It was also one of the most efficient methods for the extraction of PAHs from air-dried industrial soil. During the first step of a two-step extraction, at least 99.8% of the PAHs were extracted with NMP. Extraction with NMP in a microwave oven was compared to that with acetone, methanol, ethanol, a methanol/toluene mixture, tetra methyl ammonium hydroxide, and hydrolysis with KOH. These solvents were used in combination with ultrasonic treatment, rotary tumbling, Soxhlet extraction, and extraction in a microwave oven. The second best method appeared to be extraction with a mixture of 80 vol.% acetone and 20 vol.% water in a microwave oven at 100°C for one hour.

3 Selection of a solvent for the remediation process

Because the physicochemical properties of the extraction solvent have a strong effect on the design of the solvent extraction process, the selection of an appropriate solvent is of major importance. Acetone is an efficient solvent for the extraction of PAHs from an aged soil, sludge and sediment, as found during the selection of an extraction method for the analysis of PAHs in solids. It is also suitable for use in the solvent extraction process, because it is less toxic than most other organic solvents (e.g. benzene and methylene chloride), easily biodegradable and socially acceptable. Methanol, ethanol, propanol and butanol are also suitable for use in the solvent extraction process.

Acetone and the above-mentioned alcohols were used to extract spiked PYR and B[a]P from an air-dried sandy soil. Methanol showed by far the highest extraction efficiencies, and ethanol and acetone showed the second highest efficiencies for both PAHs. However, methanol showed lower efficiencies than acetone if water was added to the extraction solvent or sandy soil. Methanol is therefore not a suitable solvent, because in practice soil always contains water and drying it as a pretreatment step would result in higher costs. In addition, the extraction efficiencies of methanol and ethanol for the extraction of 11 PAHs from aged industrial soil were significantly lower than those of acetone. This is probably due to the low solubility of PAHs in methanol and ethanol, because the solubility of ANT, FLU and PYR in pure acetone is at least ten times higher than that in methanol and ethanol. In contrast, for the extraction of spiked PYR from a sandy soil with acetone, methanol, ethanol, 1-propanol, 2-propanol and 1-butanol no relationship was found between the solubility of PYR in these solvents and the extraction efficiency. Furthermore, for the extraction of spiked PYR and B[a]P from sand, silt and clay with mixtures of acetone and water, the extraction efficiencies were not correlated with the solubility of PYR and B[a]P in the extraction mixtures. It was therefore concluded that whereas for the extraction of spiked PYR and B[a]P from soils, solubility is not the determining factor for the extraction process, for the extraction of aged soils the solubility of PAHs in the extraction solvent may be important.

Optimum process conditions were determined for the extraction of spiked PYR and B[a]P from sand, silt and clay with acetone. For acetone/water mixtures, the highest efficiencies for the extraction of PAHs from air-dried sand, silt and clay were obtained with 10 to 20 vol.% water in the extraction solvent. The highest efficiency for the extraction of PAHs from wet sand with pure acetone was obtained with about 15 wt% water in the sand. The higher extraction efficiency as a result of the addition of water can be explained based on two opposite effects: increasing competition between solvent molecules and PAHs for (ad)sorption sites, and a decreasing solubility of PYR and B[a]P in the extraction solvent.

Furthermore, within five minutes of extraction equilibrium was reached for the extraction of spiked PYR and B[a]P from sand, silt and clay with a mixture of 80 vol.% acetone and 20 vol.% water. Three-month storage at 7°C of the sand, silt and clay spiked with PYR did not influence the extraction efficiencies of acetone.

These results show that acetone is a very appropriate solvent for the extraction process.

4 Extraction efficiency for aged sludge and sediment

A remediation method for contaminated soil can be considered successful if the Dutch target levels established for clean soil can be achieved using a minimum amount of solvent. This implies that the extraction process needs to comprise more than one extraction step. Therefore, aged sludge, sieve fractions of this sludge and aged sediment all contaminated with PAHs were extracted seven times with mixtures of acetone and water with volume ratios of 80%/20% and 60%/40%.

For the aged sludge, the Dutch target level for PAHs in clean soil (= 2.6 mg per kg of dry matter) was reached in seven extraction steps with a mixture of 80 vol.% acetone and 20 vol.% water. For the sediment, the target level for PAHs (= 1.2 mg per kg of dry matter) was almost achieved. In both the sludge and sediment, the seven extraction steps resulted in a reduction of the initial total PAH concentration by more than 99%.

Concerning the residual PAHs in the samples extracted seven times with a mixture of

80 vol.% acetone and 20 vol.% water, it was observed that the residual PAH concentration comprised a high percentage of PAHs of relatively low molecular weight (PHE, ANT and FLU). These PAHs were most difficult to remove from the solids at low concentrations, whereas the residual percentages of PAHs of high molecular weight (e.g. B[b]F, B[k]F, B[a]P, B[ghi]P and IND) were low or zero.

For the PAHs in the samples, desorption isotherms were calculated based on the experimental results obtained in seven extraction steps. The desorption isotherms of the individual PAHs and the sum of EPA-PAHs in the sludge and sediment could be accurately described with Freundlich isotherms ($\log S = \log K + n \log C_l$), which included two fitted parameters: K and n. In this study PAHs of low molecular weight showed lower n values than those of high molecular weight, which resulted in relatively high residual concentrations of PAHs of low molecular weight (PHE, ANT and FLU). In most samples, B[b]F and B[k]F showed the highest n values and relatively low K values; their residual concentrations were therefore zero in all samples.

Pretreatment by separation based on particle size was found not to be useful for the efficient remediation of the sludge because the sieve fractions showed only small differences in PAH composition and PAH desorption isotherms. The treated sediment may be used as a building material. Based on the desorption isotherms, it was calculated how much of a mixture of acetone and water is needed to clean the sludge and sediment concerned in seven extraction steps up to the Dutch target level for PAHs in clean soil and to the highest PAH concentration permitted for the use of sludge or sediment as a building material (104 and 48 mg PAHs per kg of dry matter for the sludge and sediment, respectively). For the sediment, 443 times less of a mixture of 80 vol.% acetone and 20 vol.% water is needed in seven extraction steps to reach the highest PAH concentration permitted in a building material compared to treating it to the target level established for clean soil. For the sludge, this difference was a factor of 8.7. It is more difficult to achieve the Dutch target level for clean soil in the sediment than in the sludge, because the target level for the sediment is lower and the sediment initially contains higher percentages of PHE, ANT and FLU.

A mixture of 60 vol.% acetone and 40 vol.% water is less efficient for the removal of PAHs from the sludge and sediment samples than a mixture of 80 vol.% acetone and 20 vol.% water, because after seven extraction steps the residual PAH concentrations were found to be substantially higher than the target levels established for clean soil. This is due to high K values and low n values.

5 Desorption kinetics and models

Another important factor for the extraction process is the time needed to remove PAHs from the solids. Experiments were therefore carried out to measure the PAH concentration in the extraction solvent (= a mixture of 80 vol.% acetone and 20 vol.% water) as a function of time during the extraction of an aged sludge and size fractions of this sludge in a stirred reactor.

In all samples, the desorption rates for all PAHs were initially high. For the size fractions with a particle diameter smaller than 125 μm, 90% of all PAHs were desorbed within 10 minutes, and the desorption curves for these fractions were almost equal. The desorption rates of the PAHs in the fraction with a particle size larger than 125 μm were (slightly) lower. In general, after an extraction period of about 100 seconds the PAHs of high molecular weight showed lower desorption rates than those of low molecular weight. These differences were greater if the particle diameter of the fractions was larger than 63 μm. Nevertheless, within 40 minutes 95% of all PAHs were extracted from each sample, and thereafter differences in desorption rate were no longer observed. The differences between the desorption curves of the size fractions were in general small.

In the sandy, silty and clayey soils spiked with PYR and B[a]P, equilibrium was reached within 5 minutes. An aged sludge requires a longer extraction time to reach equilibrium than spiked soils due to the difference in distribution of the PAHs in the particles after spiking and after an aging process of many years. Because after spiking the PAHs are bound only to the surface of the soil substances, removal of this type of adsorbed PAHs requires little time. The difference in extraction time between aged sludge and spiked soil shows that a remediation process for aged solids cannot be developed only on the basis of experiments with spiked soils.

For the elucidation of the desorption and transport processes occurring during extraction, a radial diffusion model and a first-order reaction model were used to fit the experimental desorption curves obtained by extraction of the aged sludge and the size fractions of the sludge. For every sample and each PAH the best fitting effective diffusion coefficient and the best fitting first-order reaction coefficient were determined. The radial diffusion model fitted the experimental data best for a situation in which it is assumed that the PAH contamination is accumulated in the core of the sludge particles at the beginning of the extraction process. Such accumulation may occur by (bio)degradation or the transport of PAHs from the outer layer of particles to the liquid phase.

Because in the radial diffusion model the particle size has a strong effect on the PAH desorption rates, this model seems not very suitable for application to the experimental data, because the particle size had little effect on the experimental desorption rates. Two explanations were offered for this contradiction. The first is that mass transfer occurs very fast because of the high mass transfer coefficients and the high extraction capacity of the acetone/water mixture. Therefore, differences in desorption rate between size fractions could not be measured accurately, which applies especially to sludge particles with a diameter smaller than 63 μm. The second explanation is that physical properties of the sludge particles (e.g. their internal porosity) vary with the particle size of the fractions. The internal porosity of the particles in the fractions was calculated from the best fitting values of the effective diffusion coefficient of PAHs determined for the radial diffusion model with the PAH contamination concentrated in the core of the particles. The calculated internal porosities increased from 1.4 to 11.6 vol.% with increasing particle size of the fractions.

6 Feasibility of the solvent extraction process

Based on the results of this and other investigations a process was designed based on extraction with acetone at the subdepartment of Environmental Technology in collaboration with consulting bureau Scarabee, RIZA/POSW, TNO-MEP, and Van den Herik-Sliedrecht. This solvent extraction process, called the 'WAU acetone process', was especially designed for the remediation of contaminated sediment from the Petroleum Harbour in Amsterdam. The process comprises countercurrent extraction of contaminated solids in, for instance, a settling tank with upflowing acetone. Acetone is removed from the cleaned solids first in a decanter centrifuge and then in a rotary dryer. Contaminated acetone is recovered by distillation and reused for the extraction of solids. Because the equipment used for carrying out the WAU acetone process is based on existing techniques and apparatuses, this process is technically feasible.

The estimated operating costs for the remediation of sediment by means of the WAU acetone process are similar or lower to those of thermal decontamination. The solvent extraction process seems especially suited for the remediation of soils, sediments and sludges with high water and clay content values contaminated with barely (bio)available or biodegradable organic compounds. Biological treatment and soil washing are no suitable techniques for the remediation of such contaminated solids, and thermal treatment is more expensive because of their high water content. In this situations, the solvent extraction process will be financially feasible.

Because the solvent extraction process produces little residual waste and results in the achievement of the Dutch target levels established for clean soil, it seems also environmentally feasible.

Samenvatting

1 Inleiding

In Nederland is de verontreiniging van bodems en waterbodems een ernstig milieuprobleem. Er bestaan verschillende methoden voor het reinigen van bodems, zoals extractieve reiniging met waterige oplosmiddelen, (micro)biologische en thermische behandeling, die met succes worden toegepast in de praktijk. Het reinigen met deze methoden is echter niet voor alle soorten verontreinigde bodems technisch en/of financieel haalbaar. Dit geldt met name voor (water)bodems en restslibben van extractieve reinigingsinstallaties (extractieslibben) met een hoog watergehalte, kleigehalte of organisch stofgehalte, die verontreinigd zijn met biologisch slecht afbreekbare en/of slecht beschikbare organische stoffen. Een geschikte reinigingsmethode voor dit soort bodems en slibben is extractie met een organisch oplosmiddel of solvent. In de Verenigde Staten zijn reeds verschillende technieken op grote schaal ontwikkeld voor de reiniging van vaste stof op basis van extractie met solvents. Tot nu toe is er echter weinig onderzoek verricht dat meer wetenschappelijk en theoretisch inzicht geeft in het solvent extractieproces van verontreinigde grond en slibben. Het hier gepresenteerde onderzoek heeft als doel het bestuderen van het effect van verschillende procesvariabelen op de extractiestap van het solvent extractieproces. Met dit inzicht kan een optimaal proces ontwikkeld worden voor het reinigen van grond, waterbodems en extractieslibben, die verontreinigd zijn met polycyclische aromatische koolwaterstoffen (PAK's). In het onderzoek is het gedrag van de 16 PAK's bestudeerd die het Environmental Protection Agency uit de USA heeft geselecteerd, de zogenaamde EPA-PAK's De onderzochte procesvariabelen zijn het type solvent, de extractietijd, de extractieprocedure, het watergehalte van het extractiemiddel, het type vaste stof, de grootte van de vaste stofdeeltjes en het watergehalte in de vaste stof.

Voor het verder ontwikkelen en optimaliseren van het solvent extractieproces voor verontreinigde grond en slib is de analyse van de PAK-concentratie in de vaste stof een essentiële factor. Daarom is het eerste deel van het onderzoek gericht op de selectie van een efficiënte extractiemethode voor het bepalen van de PAK-concentratie in verontreinigde monsters van grond, extractieslib en waterbodem, waarin de PAK-verontreiniging al meer jaren aanwezig is.

2 Extractiemethode voor de analyse van de PAK-concentratie in grond, extractieslib en waterbodem

Verschillende extractiemethoden zijn getest op hun geschiktheid voor de analyse van de PAK-concentratie in drie soorten vaste stof: een zandige grond afkomstig van een fabrieksterrein, een extractieslib, en een gebaggerd havenslib. Extractie met N-methyl-2-pyrrolidon (NMP) in een magnetron bij 130°C gedurende 1 uur was verreweg de meest efficiënte methode voor bepaling van de PAK-concentratie in het extractieslib en havenslib. Deze methode was tevens één van de meest efficiënte extractiemethoden voor de zandige fabrieksgrond. Met NMP werd tenminste 99.8% van de PAK's in de vaste stof bij de eerste extractiestap verwijderd tijdens een extractieproces bestaande uit twee achtereenvolgende stappen. Het extraheren door NMP werd vergeleken met het extraheren door aceton, methanol, ethanol en een mengsel van methanol en tolueen. Daarnaast werd extractie met methanol ook uitgegevoerd in combinatie met de hydrolyse door kaliumhydroxide en tetramethylammoniumhydroxide. De extracties werden uitgevoerd in een ultrasoon bad, een end-over-end mixer, soxhlet apparaat of magnetron bij verschillende temperaturen.

Na extractie met NMP in de magnetron bleek de extractie met een mengsel van 80 vol.% aceton en 20 vol.% water in de magnetron bij 100°C gedurende 1 uur de meest efficiënte methode te zijn.

3 Selectie van een solvent voor een reinigingsproces van grond

Voor het ontwerpen van een solvent extractieproces voor het reinigen van grond zijn de fysische-chemische eigenschappen van het solvent essentieel. Daarom dient het solvent voor het proces met zorg te worden gekozen. Een geschikt solvent is bijvoorbeeld aceton omdat het hoge extractierendementen geeft, wat onder andere werd vastgesteld tijdens het onderzoek naar de analyse van de PAK-concentratie in verontreinigde vaste stof. Daarnaast is aceton minder toxisch dan de meeste andere organische oplosmiddelen zoals benzeen en dichloormethaan, wordt aceton gemakkelijk biologisch afgebroken en is het een maatschappelijk acceptabel solvent. Andere solvents die geschikt zijn voor een reinigingsproces van grond zijn methanol, ethanol, 1-propanol, 2-propanol en 1-butanol.

Aceton en de genoemde vijf alcoholen zijn gebruikt om een luchtdroge zandige grond te reinigen waaraan recent een hoeveelheid pyreen en benzo[a]pyreen was toegevoegd. Met methanol werd verreweg de grootste hoeveelheid PAK's uit het zand geëxtraheerd. Na methanol werden de hoogste extractierendementen bereikt met ethanol en aceton. Aceton gaf echter hogere rendementen dan methanol zodra water werd toegevoegd aan het zand of aan het extractiemiddel. Methanol is daarom minder geschikt voor een reinigingsproces van grond omdat in de praktijk grond altijd water bevat en het drogen van de grond zal resulteren in hogere kosten. Ook werd tijdens voorafgaand onderzoek naar de extractie van een verouderde PAK-verontreiniging uit een zandgrond vastgesteld dat methanol significant slechtere extractierendementen geeft dan aceton.

Een mogelijke verklaring voor het verschil in extractierendementen tussen de solvents is het verschil in oplosbaarheid van de PAK's in de solvents. De oplosbaarheid van bijvoorbeeld anthraceen, fluorantheen en pyreen in puur aceton is tenminste tien keer hoger dan de oplosbaarheid van deze PAK's in methanol en ethanol. Bij de extractie van recent toegevoegd pyreen uit een zandige grond met aceton, ethanol, 1-propanol, 2-propanol en 1-butanol werd echter geen verband gevonden tussen de oplosbaarheid van pyreen in de solvents en het extractierendement. Tevens werd bij de extractie van recent toegevoegd pyreen en benzo[a]pyreen uit zand, silt en klei met verschillende mengels van aceton en water geen verband gevonden tussen het extractierendement en de oplosbaarheid van pyreen in het aceton/water mengsel.

Voor extractie van een recente pyreen- en benzo[a]pyreenverontreiniging uit zand, silt en klei met aceton werden de optimale procescondities bepaald. Extractie van luchtdroog zand, silt en klei gaf de hoogste rendementen indien een mengsel van 80 tot 90 vol.% aceton en 10 tot 20 vol.% water werd gebruikt. Het toevoegen van water aan luchtdroog zand en vervolgens extractie met puur aceton leverde het hoogste rendement op indien ca. 15 gew.% water aan het zand was toegevoegd. Het toevoegen van water aan de grond of aan het extractiemiddel leverde dus hogere rendementen op, wat waarschijnlijk verklaard kan worden door het optreden van twee mechanismen die elkaar tegenwerken: de watermoleculen zorgen voor een grotere competitie bij het bezetten van de (ad)sorptieplaatsen aan de gronddeeltjes, maar daarnaast verlaagt het toevoegen van water de oplosbaarheid van de PAK's in het extractiemiddel. Verder werd bij extractie van zand, silt en klei met een mengsel van 80 vol.% aceton en 20 vol.% water evenwicht bereikt binnen een extractietijd van vijf minuten. Het nabootsen van een verouderingsproces door met pyreen verontreinigd zand, silt en klei drie maanden te bewaren bij 7°C had geen effect op de extractierendementen verkregen met aceton.

De resultaten geven aan dat aceton een geschikt solvent is voor het reinigen van grond.

4 Extractierendementen van extractieslib en waterbodems met verouderde PAK-verontreiniging

Een reinigingsmethode voor verontreinigde grond kan succesvol worden toegepast in Nederland indien de streefwaarden voor schone grond gehaald kunnen worden en daarbij zo weinig mogelijk solvent gebruikt wordt. Dit laatste houdt in dat het solvent extractieproces uit meerdere extractiestappen moet bestaan die in tegenstroom worden uitgevoerd. Om dit te onderzoeken zijn een extractieslib, zeeffracties van dit extractieslib en een waterbodem met verouderde PAK-verontreiniging zeven keer geëxtraheerd met mengsels van aceton en water in volumeverhoudingen van 80/20% en 60/40%.

Voor het extractieslib werd de Nederlandse streefwaarde voor PAK's in schone grond (= 2.6 mg per kg droge stof) bereikt na zeven extracties met een mengsel van 80% aceton en 20% water. Voor de waterbodem werd de streefwaarde (= 1.2 mg per kg droge stof) bijna gehaald. Zeven keer extraheren met een mengsel van 80% aceton en 20% water leverde een reductie van de PAK-concentratie in het slib en de waterbodem op van meer dan 99%. Van de PAK's die achterbleven in de monsters na zeven keer extraheren bestond een groot gedeelte uit PAK's met relatief laag molecuulgewicht zoals fenanthreen, anthraceen en fluorantheen. Voor concentraties rondom de streefwaarden bleken deze drie PAK's het moeilijkst te verwijderen te zijn uit het extractieslib en de waterbodem. Na zeven keer extraheren was de eindconcentratie van de PAK's met relatief hoog molecuulgewicht (benzo[b]fluorantheen, benzo[k]fluorantheen, benzo[a]pyreen, benzo[g,h,i]peryleen en indeno[1,2,3-c,d]pyreen) in het slib en sediment laag of kon gelijk gesteld worden aan nul.

Voor de geïdentificeerde PAK's in de monsters werden desorptie-isothermen berekend op basis van de experimentele resultaten van de zeven extractiestappen. De desorptie-isothermen van de individuele PAK's en de som van de PAK's konden goed beschreven worden met een Freundlich-isotherm: $\log S = \log K + n \log C_l$, waarbij S de PAK-concentratie in de vaste stof is (mg per kg droge stof), C_l de PAK-concentratie in het extractiemiddel is (mg per liter), en K en n constanten zijn, die werden berekend door de best fittende Freundlich-isotherm voor de experimentele curven te bepalen. Tijdens dit onderzoek werden voor de PAK's met lage molecuulgewichten lagere waarden voor n gevonden dan voor de PAK's met hoge molecuulgewichten. De lage waarden van n voor de laag moleculaire PAK's resulteerden in relatief hoge eindconcentraties in de monsters na zeven keer extraheren. Voor de meeste monsters werden voor benzo[b]fluorantheen en benzo[k]fluorantheen de hoogste waarden voor n gevonden en relatief lage waarden voor K. Deze twee PAK's konden geheel uit alle monsters verwijderd worden door zeven keer te extraheren.

Een voorbehandeling op basis van het scheiden van het extractieslib in fracties met verschillende deeltjesgrootte (zeeffracties) zal niet bijdragen aan een efficiënte reiniging van het slib, omdat de PAK-samenstelling en de desorptie-isothermen van de PAK's in de zeeffracties vrijwel gelijk waren. De gereinigde waterbodem zou vanuit milieuhygiënisch oogpunt beter gebruikt kunnen worden als bouwmateriaal dan voor hergebruik als schone grond. Om de waterbodem met een aceton/water mengsel (80/20 vol.%) in zeven extracties te reinigen tot de vereiste PAK-concentratie voor bouwmateriaal (= 48 mg PAK's per kg droge stof) is namelijk 443 keer minder extractiemiddel nodig dan om de waterbodem te reinigen tot de streefwaarde voor schone grond (= 1.2 mg per kg droge stof). Voor het reinigen van het extractieslib tot de vereiste PAK-concentratie voor bouwmaterialen (= 104 mg PAK's per kg droge stof) is 8.7 keer minder aceton/water (80/20 vol.%) mengsel nodig dan voor het reinigen tot de streefwaarde (= 2.6 mg per kg droge stof). Het is voor de waterbodem dus moeilijker om de streefwaarde voor schone grond te bereiken dan voor het extractieslib, wat waarschijnlijk het gevolg is van de hogere beginconcentraties van fenanthreen, anthraceen en fluorantheen in de waterbodem en de lagere streefwaarde van de PAK's voor de waterbodem. De benodigde hoeveelheden extractiemiddel voor het bereiken van de streefwaarden en de vereiste concentraties voor bouwmaterialen zijn berekend op basis van de desorptie-isothermen.

Een extractiemiddel met 60 vol.% aceton en 40 vol.% water is veel minder efficient voor het reinigen van het extractieslib en de waterbodem dan een extractiemiddel met 80 vol.% aceton en 20 vol.% water. Na zeven extracties met een mengsel van 60% aceton en 40% water was de PAK-concentratie in het slib en de waterbodem beduidend hoger dan de streefwaarden voor schone grond. Dit is een gevolg van de hoge waarden voor K en de lage waarden voor n die gevonden zijn voor de desorptie-isothermen van de PAK's.

5 Desorptie kinetiek en modellen

Een belangrijke factor in het ontwerp van een solvent extractieproces is de tijd die nodig is om de PAK's uit de vaste stof te verwijderen. In dat verband zijn er experimenten uitgevoerd om de PAK-concentratie in een extractiemiddel met 80 vol.% aceton en 20 vol.% water te meten als functie van de tijd. Daarvoor werden een extractieslib met een verouderde PAK-verontreiniging en fracties van dit slib met verschillende deeltjesgroottes geëxtraheerd in een geroerd vat.

In alle monsters waren de desorptiesnelheden in het begin hoog. In de fracties met deeltjes kleiner dan 125 μm werd 90% van de PAK's gedesorbeerd binnen 10 minuten en de desorptiecurven van de som van de EPA-PAK's van deze fracties waren vrijwel gelijk. De desorptiesnelheden van de PAK's in de fractie met deeltjes groter dan 125 μm waren (iets) lager. Na een extractieperiode van ca. 100 seconden gaven de PAK's met hoge molecuulgewichten in het algemeen lagere desorptiesnelheden dan de PAK's met lage molecuulgewichten. Het verschil tussen de hoog en laag moleculaire PAK's was groter voor de fracties met deeltjes groter dan 63 μm dan voor de fracties met kleinere deeltjes. Niettemin was binnen 40 minuten 95% van alle PAK's geëxtraheerd uit alle monsters en werden geen verschillen meer gevonden in desorptiesnelheid tussen de PAK's. De verschillen tussen de desorptiecurven van de fracties met verschillende deeltjesgrootte waren relatief klein.

Uit eerder onderzoek was gebleken dat bij extractie van zand, silt en klei waaraan recent een PAK-verontreiniging was toegevoegd, evenwicht werd bereikt binnen 5 minuten. Indien het slib met de verouderde PAK-verontreiniging werd geëxtraheerd, bleek een langere extractietijd nodig te zijn om evenwicht te bereiken dan bij een recente verontreiniging. Dit is het gevolg van een verschil in distributie van de PAK's in de vaste stof na een verouderingsperiode van jaren. Op het moment dat de PAK's aan de vaste stof worden toegevoegd, worden deze alleen gebonden aan het oppervlak van de vaste stofdeeltjes en het verwijderen van deze PAK's kost weinig tijd. Het verschil in extractietijd tussen gronden met recente en verouderde verontreiniging toont aan dat het ontwikkelen van een reinigingsproces voor grond met verouderde verontreiniging niet alleen kan gebeuren op basis van experimenten met recent verontreinigde gronden.

Voor opheldering van de desorptie- en transportprocessen die optreden tijdens extractie zijn twee transportmodellen gebruikt: het radiaal diffusiemodel en een eerste orde reactiemodel. Deze modellen zijn gebruikt om de experimentele desorptiecurven te fitten die waren verkregen door extractie van het extractieslib met verouderde verontreiniging en fracties van dit slib met verschillende deeltjesgrootte. Hierbij werden per monster en per PAK de best fittende effectieve diffusiecoëfficient en de best fittende eerste orde reactiecoëfficient bepaald. Het radiale diffusiemodel waarbij verondersteld werd dat de PAK-verontreiniging in de kern van de slibdeeltjes geconcentreerd is aan het begin van het extractieproces, resulteerde in de beste fit met de experimenteel bepaalde desorptiecurven. Het concentreren van de PAK-verontreiniging in de kern van de deeltjes tijdens veroudering is mogelijk door (biologische) afbraak of door transport van de PAK's uit de buitenste laag van de slibdeeltjes naar de vloeistoffase.

Het radiale diffusiemodel lijkt op het eerste gezicht minder geschikt voor het beschrijven van de experimentele desorptiecurven, omdat bij dit model de deeltjesgrootte grote invloed heeft op de desorptiesnelheden, terwijl dit niet optrad in de experimentele resultaten. Hiervoor zijn twee verklaringen mogelijk. De eerste verklaring is dat de transport van de PAK's uit de deeltjes erg snel is vanwege de hoge transportcoëfficienten en de grote extractiecapaciteit van het aceton/water mengsel. Daardoor is het mogelijk dat verschillen in desorptiesnelheid niet goed gemeten konden worden, wat met name geldt voor de slibdeeltjes met een diameter kleiner dan 63 µm. De tweede verklaring is dat de fysische eigenschappen van de slibdeeltjes (b.v. de interne porositeit) variëren met de deeltjesgrootte. De interne porositeit van de deeltjes in de fracties is daarom berekend aan de hand van de waarden van de best fittende effectieve diffusie coëfficienten die bepaald zijn voor het radiale diffusiemodel met de PAK-verontreiniging geconcentreerd in de kern van de deeltjes. De berekende interne porositeit nam toe van 1.4 tot 11.6 vol.% met toenemende deeltjesgrootte van de fracties.

6 Praktische haalbaarheid van het solvent extractieproces

Op basis van de resultaten uit dit proefschrift en de resultaten van aanvullend onderzoek bij de sectie Milieutechnologie, is een solvent extractieproces ontworpen op basis van aceton in samenwerking met adviesbureau Scarabee, RIZA/POSW, TNO-MEP, en Van den Herik-Sliedrecht. Dit proces: het WAU-acetonproces, is speciaal ontworpen voor de reiniging van gebaggerd slib uit de Petroleumhaven van Amsterdam. Het proces bestaat uit een tegenstroomextractie van bezinkende verontreinigde vaste stof in een opwaartse acetonstroom. Deze tegenstroomextractie kan bijvoorbeeld worden uitgevoerd in een bezinktank. Na de extractie wordt de aceton verwijderd uit de gereinigde vaste stof in een decanteercentrifuge gevolgd door een roterende droger. De verontreinigde aceton wordt na destillatie hergebruikt in het proces voor extractie van verontreinigde vaste stof. Het WAU-acetonproces is gebaseerd op toepassing van bestaande technieken en apparaten, en is daardoor technisch haalbaar.

De geschatte operationele kosten voor de reiniging van slib met behulp van het WAU-acetonproces zijn gelijk of lager dan de kosten voor reiniging met behulp van een thermische behandeling. Het solvent extractieproces lijkt vooral geschikt voor de reiniging van grond, waterbodems en slib met hoge water- en kleigehalten die zijn verontreinigd met slecht beschikbare of biologisch moeilijk afbreekbare organische verbindingen. Een (micro)biologische reinigingsmethode en extractie gebaseerd op waterige extractiemiddelen zijn hiervoor niet geschikt en een thermische behandeling is duur vanwege het hoge watergehalte. In dit soort gevallen zal solvent extractie ook financieel haalbaar zijn.

Het solvent extractieproces lijkt ook milieuhygiënisch haalbaar, omdat het vrijwel geen afval produceert en de vaste stof gereinigd kan worden tot aan de streefwaarde voor schone grond.

Dankwoord

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Erna Noordkamp

Curriculum Vitae

Op 28 augustus 1967 werd Egberdien Reina Noordkamp geboren op een boerderij in het Achterhoekse dorpje Harfsen. Van 1979 tot en met 1985 heeft ze een VWO-b opleiding gevolgd aan de Rijksscholengemeenschap in Lochem, die met succes werd afgesloten. In 1985 pakte ze haar biezen en is gaan studeren aan de Landbouwuniversiteit (LUW) in Wageningen, richting levensmiddelentechnologie. Na een afstudeervak proceskunde bij de sectie proceskunde van de LUW, een afstudeervak bedrijfskunde bij Campina-Melkunie b.v. in Eindhoven en een stage proceskunde aan de Technische Universität München-Weihenstephan in Freising behaalde ze haar bul in 1991. Daarna werkte ze 5 maanden bij Westland Kaasspecialiteiten b.v. in Huizen aan een marketing project en 6 maanden bij de sectie Zuivel en Levensmiddelennatuurkunde van de LUW aan de schuimstabiliteit van espressokoffie.

In augustus 1992 trad ze als assistent in opleiding (AIO) in dienst bij de vakgroep Milieutechnologie van de LUW, waarvan dit proefschrift het resultaat is. Tijdens haar AIO-schap heeft ze zich ingezet voor de belangen van de AIO's als bestuurslid van het Wagenings AIO- en OIO-Overleg (WAIOO) en als bestuurslid van de AIO-Raad van het Wagenings Instituut voor Milieu- en Klimaatonderzoek (WIMEK). Daarnaast heeft ze sinds 1993 de leiding over de blaaskapel 'De Rijnpijpers', waarbij ze met veel plezier euphonium speelt. In september 1998 is ze in dienst getreden als software engineer bij het Wageningse IT-bedrijf Q-Ray, dat gespecialiseerd is in het ontwikkelen van computersystemen voor bedrijven in de agrarische sector.