Contaminant release from sediments:

a mass flux approach

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Abstract

With the predicted climate change it is expected that the chances of flooding increase. During flood events sediments will suspend and if sediments are polluted, contaminants can be released to water. Also under gentle flow regimes, when sediments are settled and form a sediment bed, transfer of contaminants to water is possible. The release of contaminants from the sediment –particles and bed– to the aqueous phase is the first step in a sequence of processes. When this step is the rate limiting process we speak of mass transfer limitation. In this thesis the release of (mainly) dieldrin from field aged sediment was studied using the SPEED reactor we developed for this purpose. In this reactor parameters like mixing intensity and water flow –or dilution– rate can be controlled and low aqueous concentrations of contaminants can be quantified. Dieldrin release from the sediments was assessed for different situations: simulating a flood event and simulating more gentle flow conditions. In line with the variable discharge rates in rivers, we performed experiments with different flow rates and assessed the release of dieldrin in time.

We found that the release of dieldrin from suspended particles –the flood event– to the aqueous phase is controlled by diffusion within the particles. Analogue to Ficks 1st (and 2nd) law of diffusion, the concentration difference and the diffusion distance are key parameters that determine the mass flux of dieldrin within the particles. Indeed, the release rate of dieldrin from particles is faster when higher flow rates –more dilution thus lower concentrations in the aqueous phase– were applied. Additional experiments with solid phase extraction showed that the release rate of dieldrin from small particles was faster than from large particles. Using the particle size distribution (PSD) as input for our diffusion model we were able to satisfactorily describe the observed release with initially rapid desorption followed by slow desorption. Dieldrin release from sediment beds –gentle flow condition– is more complex as an additional diffusion resistance is introduced in the bed itself (interstitial pore water). The diffusion resistance of the bed generally overrules the diffusion resistance of the particles. Only when dieldrin in the interstitial pore water is about exhausted, diffusion resistance of the individual particles control the release of dieldrin from the sediment bed.

We conclude that in aquatic environments with some mixing, like rivers, harbors, and the marine environment, the size of sediment particles is a key parameter that determines the release rate of dieldrin and other hydrophobic organic contaminants from sediment to the aqueous phase. Sediment properties –like PSD, contaminant concentration, and organic matter content– and properties of the receiving system, e.g. interaction/mixing and dilution determine whether this release of contaminants will lead to risks.

Contents

1

General introduction

1.1. Scope of this thesis

In Europe, large areas exist where terrestrial or aquatic systems are polluted with different classes of pollutants. Due to a growing awareness of environmental problems, direct emissions of contaminants towards the atmosphere, the water system, and to soils are reduced. However, especially soil and sediment systems need time to improve their environmental quality. Active remediation of these compartments is complicated and often expensive, as soils, sediments, and groundwater were polluted by numerous spills and landfills resulting in a diffuse pollution. These contaminated areas represent steady and long-term potential sources of regional contamination of groundwater, surface water, and sediments. Risks can arise to ecosystems, human health, and spreading of contaminants by means of transport of contaminated (ground)water, soil, and sediments towards other receptors. When a contaminant is persistent, meaning that it is resilient towards degradation, it can be transported over long distances [1]. Persistent contaminants that received a lot of attention during the last decades are the Persistent Organic Pollutants (POP), including contaminants like PCBs, dioxins, DDT, and drins (aldrin, dieldrin, and endrin) [2]. Together with other contaminants like Polycyclic Aromatic Hydrocarbons (PAH) and Hexachlorocyclohexane (HCH), these compounds are often lumped as Hydrophobic Organic Contaminants (HOC).

The discovery of the first contaminated sites, around 30 years ago, resulted in the development of contaminated land policies in most industrialized countries. Initially, national policies for contaminated land reflected the way that the countries first perceived the problems. The first is the perspective of protection; relating the impact of contamination on human health and environmental quality. The other is the spatial planning perspective; managing the impact of contaminated land on the way land is used. The major trend is to address the environmental and spatial planning aspects simultaneously [3]. Simple, generic quality criteria for soil, sediment, and (ground)water do not suffice and a more holistic approach is required. Knowledge is needed on a multidisciplinary level about physical/chemical aspects, toxicology, hydrology and biology, but also spatial planning, economics, social aspects, and many more themes. This holistic approach is now a fundament of risk based management of contaminated land and (ground)water and enables site specific risk assessments. The EU water framework directive for example makes it necessary to assess the water body as a system of processes. In order to establish sufficient water quality for the function given to it, hydrodynamic, chemical, and ecological processes should be balanced and, ultimately, improved.

Contaminant concentrations in soil, sediment, groundwater and surface water and contaminant fluxes between these compartments play a role in the assessment of risks linked to the water body. The fate of a contaminant is subject to transport phenomena, environmental conditions (pH, salinity, temperature, etc.) and properties of the contaminant itself (intrinsic degradability, affinity towards water, etc.). Field experiments with sediments in an English lake [4] and a south Swedish river [5] showed for example the remobilization of PCB's into surface water. At high flow rates, the concentrations of the distinct components approached the concentrations of precipitation. At low flow rates with coinciding high temperatures concentration of PCB's increased, indicating desorption of PCB from sediment. Although some correlation was found between flow rate and PCB concentration many aspects are not clear. In general, the processes responsible for transport of pollutants from or to sediments in real sites are yet poorly understood because of its complexity [6]. To predict fate and transport of HOC in contaminated aquatic systems like rivers, lakes, harbors, etc., a mechanistic understanding of the static and dynamic sorption and desorption processes is essential [7, 8]. This complexity makes risk assessment and an efficient risk reduction at least challenging.

The general question can thus be stated as "what is the contribution of sediments contaminated with HOC towards risks in a dynamic aqueous environment?" In this thesis the release of HOC from sediments under various hydrodynamic conditions is explored in order to improve risk assessment and to help selecting appropriate risk reduction measures. Based on experimental data a model is constructed that enables us to predict the transport of contaminants from sediments to the aqueous phase and that helps to understand the underlying physical processes.

1.2. Contaminant release from sediments

In the aqueous environment, HOC can exist in a variety of forms: as a dissolved component, as a colloidal phase or associated with sedimentary material. The distribution of HOC between these various phases is a central issue as it strongly influences contaminant concentrations in bed and suspended sediment, and the aqueous phase. It therefore has a strong effect on sediment and water quality. This distribution controls the equilibrium state of a system and also plays a major role in the kinetics [8]. In spite of the general consensus that organic, sedimentary material is the primary sorbent for HOC in wet soils and sediment, the sorption and desorption mechanisms are still subject of discussion [9].

The distribution of HOC between water and soils or sediments has historically been described by linear partitioning models [10-12]. Since the 1980's many publications demonstrated that sorption phenomena cannot simply be described by partitioning. Observations show that sorption is non-linear, competitive, and not reversible, also called hysteresis [12-24]. These finding implied that not all contaminants present in soils or sediments are available to exert adverse effects to organisms or are available for degradation. In the different papers, availability and bioavailability are both used, but the potential of a contaminant to be transported into the aqueous phase is overall leading, also in this thesis. Although the research groups observed similar behavior of contaminant sorption and/or desorption the theoretical framework is different. Roughly the different frameworks are as follows:

1. Sorption retarded pore diffusion (SRPD) [24]. Molecular diffusion in pore water is retarded by local sorption on pore walls. Rates are expected to be inversely dependent on the particle radius, on the tortuosity and constrictivity of pores, and on the affinity of the contaminant to the pore walls.
2. Organic matter diffusion (OMD) [21, 25]. This hypothesis is based on the discovery of a glass transition for purified humic acid, and the biphasic sorption behavior [26]. It was furthermore found that organic cosolvents increased the mass transfer rate through swelling of soil organic matter (SOM); making it more rubbery. Mass transfer rates are expected to be inversely dependent on the organic matter content and on the affinity of the contaminant to SOM.
3. Entrapment of sorbed particles in the humic organic matrix (high energy sites) or voids is described by many research groups to be rate limiting [15]. Pignatello [13, 27] proposed a similarity of voids present in soil and voids present in glassy polymers according to Fujita's free-volume theory. Their hypothesis is based on analogies between soils and glassy polymers regarding slow sorption behavior, increasing sorption non-linearity, and thus increasing site sorption with increasing contaminant-soil contact time and the occurrence of competition in sorption between HOC's. Hysteresis is explained by inelastic expansion of holes (voids) and/or creating new holes during hole filling with HOC. Since relaxation to the original state is slow, the enhanced free volume results in greater affinity for solute and greater non-linearity [18].

Differences between these frameworks manifest on a micro scale: single particles or smaller. Several aspects seem to be generally valid: contaminants present in low amounts are strongly bound to sediments as well as to other sorbents, desorption rates are not constant, and prolonged contact between contaminants and sediments reduces the fraction of contaminants that can rapidly be released from the sediment. On a larger scale, sediment suspension or sediment beds like we studied, these frameworks converge to a dynamic part (diffusion or mass transfer) and a static part (equilibrium). It depends on both the properties of the contaminated sediment and the receiving aqueous phase how fast the release of contaminants will be and what concentration will be reached. However insufficient information and data is present to truly understand the processes and predict exposure under field conditions.

1.3. Outline of this thesis

This thesis first addresses the relation between the release of a hydrophobic organic contaminant (HCH) from sediment particles and its subsequent degradation (Chapter 2). Contaminant release from a suspension of field aged sediment containing a POP (dieldrin) is studied in more detail in chapters 3 and 4. For this purpose a reactor was designed where hydrodynamic conditions could be controlled and where (very) low concentrations of dieldrin could be measured. In chapter 3 experiments are elaborated where the release of dieldrin from field aged sediment was measured under various hydrodynamic regimes. A thorough sediment characterization was conducted to explore governing factors that affect the contaminant release rate. In chapter 4 the experimental results from chapter 3 are successfully described with a bi-disperse radial diffusion model that predicts the release of dieldrin from two groups of particles: with small and large diameters. In chapter 5 a more complex system was simulated. Dieldrin release from sediment particles present in a sediment bed is studied and successfully modeled using an extension of the model described in chapter 4. Chapters 6 and 7 address potential emission control strategies that can be used to reduce the mass flux of contaminants to the aqueous phase. These strategies are in line with the source – pathway – receptor approach commonly used in risk assessment and risk reduction. The results of chapters 2 – 7 are summarized and discussed in chapter 8.

2

Availability and biodegradation of HCH

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2.1. Introduction

In highly industrialized mega sites like the Rotterdam/Antwerp harbor (NL/B), the sediments of the rivers received a high load of different organic components. Among these organic components were Persistent Organic Pollutants (POP). Since the 1970's the direct flow of these materials to the water system is reduced due to a growing application of wastewater treatment and an international restriction in the use of persistent pesticides [28]. These developments lead to improvement of the water quality as such; however surface water quality is enduringly affected by the low environmental quality of the sediment in these water systems [4, 29]. Secondary contamination of the surface water by contaminated sediment is however not only depending on the concentration of pollutant in the sediment. Characteristics of the sediment itself as well as processes like sequestration (aging) and biotransformation/biodegradation can account for changes in secondary contamination, mostly resulting in reduced availability and thus a reduced hazard for the surface water [16, 23].

Generally the first step in any environmental legislation is based on exhaustive extraction and analyses of samples followed by a comparison of appropriate target and risk values. This approach leads to an overestimation of risk, as part of the organic pollutants is strongly bound to geosorbents and within a certain timeframe not available for biota and transport to other compartments. This phenomenon is observed and studied within different fields of research e.g. ecotoxicology and environmental technology. In this paper the term potential availability is used to describe the mass of contaminants that can be released from the sediment to the aqueous phase within a limited timeframe. A method now widely used to quantify potential available concentrations is the Tenax Solid Phase Extraction (SPE) originally developed by Pignatello [30] and modified by Cornelissen [23]. With this method additional information can be obtained to select management options regarding to risks of the present situation and risk reduction by mitigative measures. Anaerobic degradation of all isomers of HCH was demonstrated by Middeldorp [31]. The relation between availability and biodegradability, as described by Volkering [32], is schematically presented in figure 2-1.

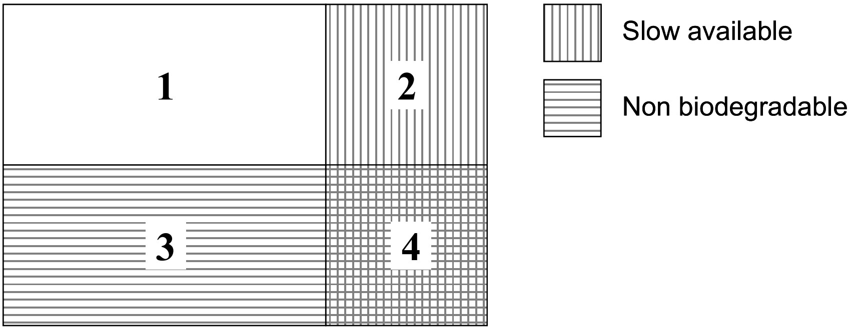

Figure 2-1: relation between availability and biodegradability [32]

Biodegradable contaminants (e.g. HCH, 2-4 ringed PAH, volatile TPH) are positioned in groups 1 and 2 whereas persistent pollutants (e.g. DDT, drins, 5+ ring PAH) are positioned in groups 3 and 4. We hypothesize that from a risk based perspective groups 1 and 3 are of major interest because of their availability to species possibly resulting in negative effects to these species. However as contaminants in group 1 are biodegradable, risks can decrease in time in case that the environmental conditions are favorable for degradation. Therefore we like to proof that all available HCH is biodegradable.

Groups 2 and 4 poses a lower threat compared to groups 1 and 3 as contaminants are not available in a limited time to species and negative effects are not likely to occur. From a remediation perspective knowledge about the availability of degradable contaminants (groups 1 and 2) is of importance as the availability will possibly determine the residual concentration of contaminants after biological treatment or (monitored) natural attenuation.

2.2. Materials and methods

Soil samples. Samples were taken from a HCH contaminated area in Hengelo (the Netherlands). The site was contaminated with HCH since 1948 when lindane production started at this location. The samples were collected from 0.2 – 2.0 meter below surface using a shovel and were stored in a polypropylene container at 4 ºC until use. Before any experiments were performed the samples were liquidized with approximately 20% (W/W) demineralised water and sieved over 2 mm.

HCH analysis.

HCH and its metabolites were extracted from soil samples and Tenax beads in a microwave (Milestone Ethos E, 20 minutes at 110 ºC) using 30 ml of acetone and hexane (1:1 Vol).

After extraction acetone was removed from the acetone/hexane mixture by shaking the extract with demineralised water.

Pesticides were analyzed using a Trace GC with an EP-Sil 8 CB lowbleed/MS column (50m x 0.25mm x 0.12 µm film thickness). Sample injection (1µl) was splitless (5 minutes) at a temperature of 250ºC. Helium was used as carrier gas at a constant flow (1.0 $ml\cdot min^{-1}$). The temperature program was 40 °C for 4 min, increased at a rate of 10 °C/min to 270 °C, and then held constant for 13 min. The detector, a Polaris Q, ion trap mass spectrometer (MS) had a constant temperature of 300ºC. Ionization was Electron Impact at 70 eV and detection was full scan. Calibration was multipoint, using external standards. Mass spectra were compared to the data of the NIST library (National institute for standards and technology, 1998).

Availability of HCH in soil.

Tenax solid phase extraction (SPE) was adopted from Cornelissen [23]. Samples were extracted in duplicate at a temperature of 20ºC. Samples (~1 g dry matter) were weighted into 50 ml separatory funnels together with 40 ml 0.01M $CaCl_2$ solution and 20 mg of NaN_3. After equilibration overnight 1.5 gram Tenax beads were added and funnels were horizontally shaken at 150 strokes per minute (spm). At selected times Tenax beads were refreshed and the loaded Tenax was extracted as described in the HCH analysis part. At the end of the experiment the remaining samples were extracted after removal of the supernatant by centrifugation for 10 minutes at 3000 rpm. The results of the extraction were fitted into the two-compartment model (equation 2-1) using the least sum of squares method.

The available fraction resembles F_{rap} whereas F_{slow} is considered to be not available in a certain timeframe.

$$S_t = F_{rap} \cdot S_0 \cdot e^{-k_{rap} \cdot t} + F_{slow} \cdot S_0 \cdot e^{-k_{slow} \cdot t} \qquad (\ 2\text{-}1\ )$$

where S_t [$mg\cdot kg^{-1}$] is the amount of contaminant still present in or on the sediment, S_0 [$mg\cdot kg^{-1}$] is the initial concentration of contaminant at t=0, F_{rap} and F_{slow} [-] are the fractions of contaminant sorbed in or on the rapid and slow desorbing domain, k_{rap} and k_{slow} [h^{-1}] are rate constants for rapid and slow desorption and t is desorption time.

Biodegradation of HCH in soil.

Microbiological degradation of HCH in the field contaminated soil was studied in batch tests. A control with autoclaved biomass was used to test abiotic degradation of HCH. Both the degradation experiment and the control were performed in triplicate.

Figure 2-2: SPME batch reactor

Approximately 150 grams (wet weight) of soil sample was weighted into a 1 liter modified Schott-flask (see figure 2-2) after which 100 ml of basal medium [33] was added. The pH in the batches was adjusted to 7.1 by using phosphoric acid. Finally the headspace was changed to N_2 (80%) and CO_2 (20%) with an overpressure of 0.1 bar. The batches were mixed using a rotary shaker (130 rpm) at 30ºC in the dark. Every week 2 ml of lactate solution was added resulting in a concentration of 0.5 g COD/l reactor.

Biodegradation of HCH was monitored by exposing a 100 µm PolyDiMethylSiloxane (PDMS) SPME fiber to the headspace for 20 hours to reach apparent equilibrium. After equilibrium was reached the fibers were injected in the GC/MS as described before.

2.3. Results and discussion

Availability of HCH in original soil sample.

Despite the age of pollution approximately 70% of HCH present in the original soil sample desorbed rapidly from the original soil sample (fig. 2-3 and table 2-1: original soil sample).

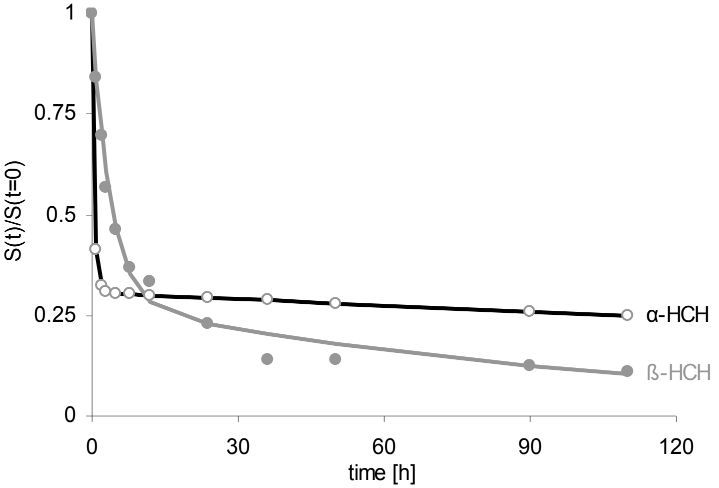

Figure 2-3: results of Tenax desorption of α-HCH and β-HCH of the original soil sample

Results of the Tenax SPE of the original soil sample as well as the soil sample after 45 days of biological degradation are summarized in table 2-1.

Table 2-1: results of two compartment model fitting parameters of Tenax SPE Extraction

	C_{HCH} [mg·kg^{-1}]	F_{rap} [-]	k_{rap} [h^{-1}]	k_{slow} [h^{-1}]
Original soil sample				
α-HCH	35 ± 2.0	0.69	1.88	0.002
β-HCH	311 ± 33	0.72	0.26	0.009
After 45 days degradation				
α-HCH	10 ± 0.4	0.43	1.51	0.005
β-HCH	207 ± 190	0.89	0.77	0.007

Biodegradation of HCH in soil.

Biodegradation of HCH in the soil samples was monitored using a headspace SPME method. In figures 2-4 and 2-5 the relative concentration of α and ß-HCH in the SPME fiber is presented as a function of time.

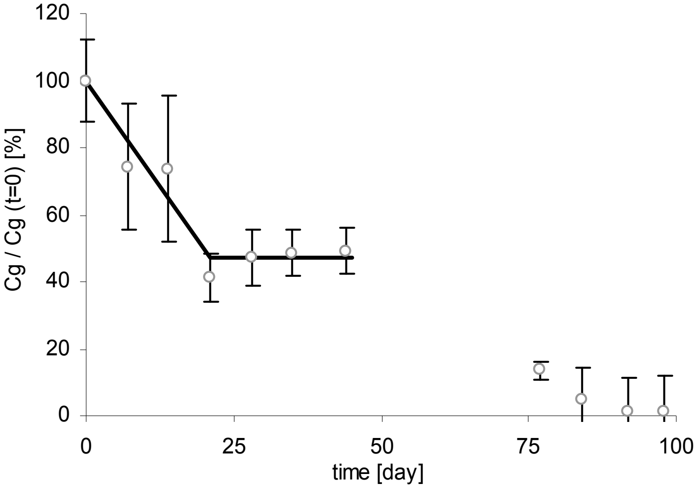

Figure 2-4: relative concentration of α-HCH analyzed by headspace SPME in time

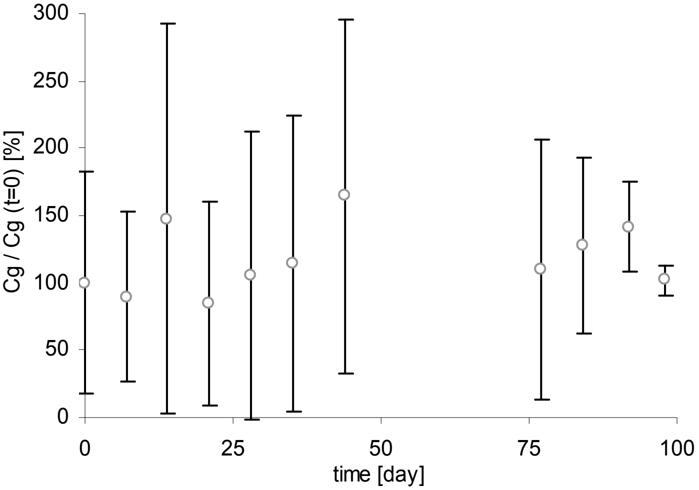

Figure 2-5: relative concentration of ß-HCH analyzed by headspace SPME in time

After one week of biological degradation different intermediates were found and could be identified by GC/MS by their mass spectra. Figure 2-6 presents a chromatogram of a SPME headspace analysis after 4 weeks of degradation including the identified components.

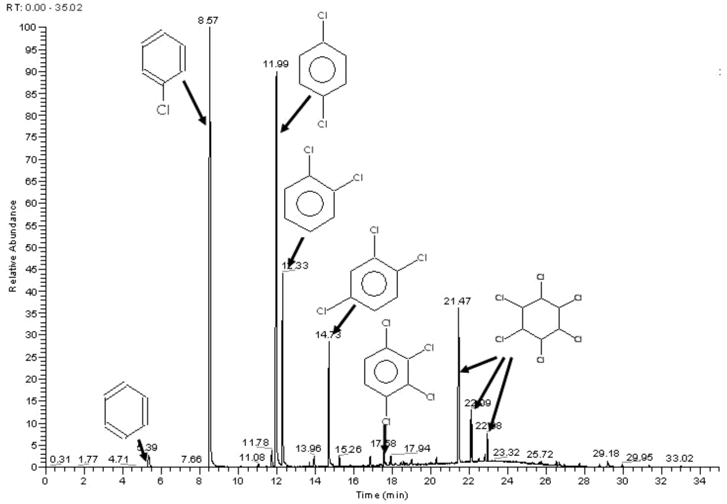

Figure 2-6: chromatogram of headspace SPME analyses after 4 weeks of biodegradation

All intermediates were monitored weekly and the results are presented in figure 2-7.

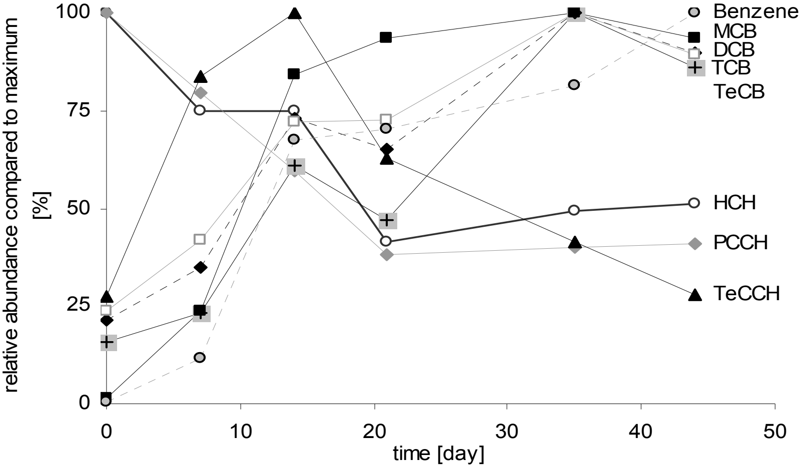

Figure 2-7: intermediates of biological degradation of HCH in time. Different isomers are lumped per group. MCB, DCB, TCB and TeCB are respectively monochloro, dichloro, trichloro, and tetrachlorobenzene and TeCCH, PCCH, and HCH are respectively tetrachloro, pentachloro, and hexachlorocyclohexane.

As can be seen in figures 2-4 and 2-7, degradation of HCH and PCCH started immediately after the start of the experiment resulting primarily in the production of TeCCH. The concentration of ß-HCH did not decrease. After three weeks the concentration of TeCCH was at a maximum and secondary products (B, MCB, DCB, and TCB) continue to be formed. After 21 days the apparent concentration of HCH remained constant although data from the availability experiments suggest that HCH is still available. Biological degradation probably stopped because of the decrease in pH values from pH 7.1 at the start of the experiments to pH 5.6 – 6.1 after sacrificing the batches. After adjusting the pH to 7.1, degradation continued until no α-HCH was detected in the headspace.

Availability of HCH in biodegraded soil sample.

After 45 days of biological degradation the remaining soil was harvested from the batch reactors and the availability was analyzed.

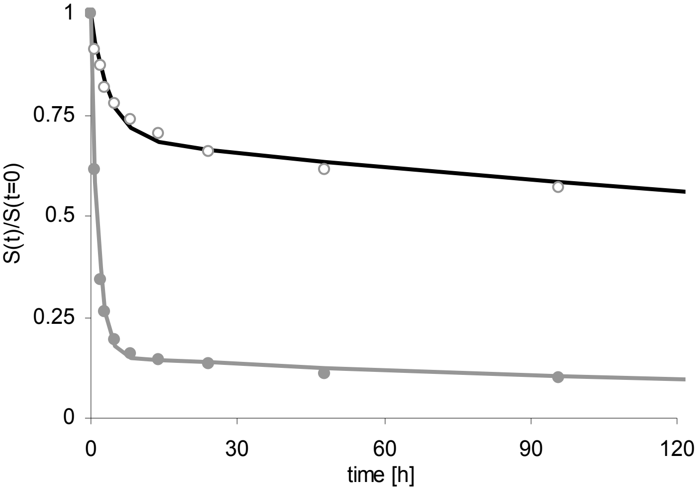

Figure 2-8: results of Tenax desorption of α-HCH and β-HCH after 45 days of degradation

The results of the availability experiment after 45 days of biological degradation (figure 2-8 and table 2-1 after degradation) show that the total concentration of α-HCH decreased from 35 to 10 mg/kg. The release rate of the rapid desorbing fraction decreased from 1.88 h^{-1} to 1.51 h^{-1}. The amount of α-HCH decreased in both the available and unavailable fraction, suggesting that redistribution of HCH occurs between rapid and slow fractions. This stretches the importance of the time aspect in the definition on potential availability as was used in this chapter. 45 days were probably more than a limited timeframe. Biodegradation of HCH was incomplete because of a decrease of pH as was discussed before. ß-HCH was not degraded as can be seen in figure 2-5. Availability data remains inconclusive because of the large variability for this compound. A combination of information of availability and biodegradability, using site specific information, can help to select appropriate control options.

2.4. Conclusions

This study demonstrated that availability of HCH in the samples is high (>70%) even after extensive ageing in the field since 1948. The relative concentration of HCH remaining in the soil after each step of Tenax extraction could be fitted by a two-compartment model. A short period of fast desorption was followed by a longer period of slow desorption. The decreasing amount of α-HCH in the slow desorbing fraction, the fraction of contaminants that is supposed not to be released within a limited timeframe, stretches the clarification of this limited timeframe. The rate constant k_{slow} implies that the amount of contaminants in the slow desorbing fraction indeed decreases. Therefore a redistribution of contaminants over the different fractions might be relevant and a continuous, but slow, release of contaminants from the soil to the aqueous phase is expected. The results of β-HCH are inconclusive because of the high deviation.

High availability of HCH combined with low degradation rate can lead to serious risks for the environment. The HCH in this study could desorb from the solid matrix into the water phase and act as a secondary source of pollution. However if environmental conditions can be optimized for dechlorination, in-situ remediation might become possible.

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3

Desorption of dieldrin from field aged sediments: simulating flood events

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3.1. Introduction

With the predicted climate change it is expected that the chances of flooding increase. During flood events, sediments will resuspend and when the sediments are polluted, contaminants can be transferred to the surrounding water. Mass transfer of organic compounds like Persistent Organic Pollutants (POPs) from soils and sediments to the surrounding aqueous phase are essential regarding fate and transport of these chemicals in the aqueous environment. Equilibrium and kinetics are two different aspects in contaminant behavior in the environment but it is practically very difficult to make a distinction between them [34, 35].

The equilibrium distribution of hydrophobic pollutants between natural soils or sediments and an aqueous phase has been subject of many studies since the 1960s [10, 11, 36-38]. Sorption equilibriums are often described mathematically by linear isotherms that define contaminant concentration in the sorbed phase as function of the concentration in the aqueous phase [10, 11, 37]. This concept has been challenged by experimental isotherm data showing non-linear relations between aqueous and sorbed concentrations, and sorption hysterisis. Di Toro [39] was one of the first authors to show non-linear sorption and a fraction that was recalcitrant to desorption. He proposed a two compartment model, one compartment defined by a linear isotherm, and one compartment defined by a non-linear isotherm. This approach has been used since by many authors using non-linear isotherms like Freundlich, Langmuir, and Polanyi [18, 40-44]. Although experimental data can be mathematically described very well using these types of non-linear models there is no concise understanding of the mechanism of non-linear sorption as stated in a thorough review by Hinz [44]. At present many authors [18, 40-42, 45, 46] attribute the non-linear isotherms of especially planar contaminants to the adsorption onto black carbon or other condensed moieties in soil organic matter (SOM) and pore filling phenomena.

Mass transfer kinetics of contaminants in soils and sediments were modeled by many research groups using a variety of mass transfer models [47]. Generally the models use one or more parameters to define a concentration gradient and a parameter to define a mass transfer rate constant. A model often used nowadays is a two compartment 1st order kinetic model where the compartments describe a fast or slow desorbing fraction. Although many types of models are able to fit experimental data, only mechanistic models, like physical/diffusion models, provide insights to understand mass transfer of POPs in the sediment/water system and make it possible to predict the behavior of a contaminant [24, 48]. Application of diffusion models is however hampered by the observation of biphasic behavior, in which a rapid initial decrease in concentration of contaminants is followed by a slower decrease during desorption experiments. The introduction of an instantaneous equilibrium fraction combined with a radial diffusion model [49-53], a radial diffusion model with a concentration dependent diffusion coefficient [54, 55], or a statistical distribution of diffusion rates [56] were approaches used to fit experimental data with model calculations.

The objective of this study was to measure desorption rates of dieldrin and explore the mechanism of mass transfer from a field aged sediment suspended in a continuously refreshed aqueous phase as a function of hydraulic retention time (HRT) of the aqueous phase and thereby simulating a flood event. For this purpose a SPEED reactor (Solid Phase Extraction with External Desorption) was developed in which the HRT and hydrodynamic conditions (mixing intensity) can be controlled and low concentrations of dieldrin in the aqueous phase can be quantified.

3.2. Materials and methods

Chemicals. Tenax-TA (20-35 mesh) was purchased at Buchem b.v. (Apeldoorn, The Netherlands), acetone (p.a.), hexane (HPLC grade), NaN_3 (extra pure), and $CaCl_2$ (dried) were from Merck (Darmstadt, Germany).

Samples. Sediment samples from Broekpolder (The Netherlands) were taken from a depth of 0 – 0.5 meter below ground level. The sediment was characterized for particle size distribution (PSD), soil organic matter content (SOM), and concentration of dieldrin. SOM and concentrations of dieldrin were determined for both the complete sediment and the different particle size classes. SOM was determined gravimetrically by combustion of dried samples for 6h at 550 °C.

Particle size fractions were made using Retsch sieves with mesh sizes of 32, 45, 63, 90, and 125 µm. Based on similarity of the SOM content of the individual size fractions we continued with three particle size fractions: <32, 32-125, and 125-2000 µm. These three particle size fractions were thoroughly analyzed using a Beckman Coulter LS 230 laser diffraction particle size analyzer with Polarization Intensity Differential of Scattered Light (PIDS). The Fraunhofer theory of light scattering was used to calculate the particle size distribution. Prior to particle size analysis, sediment samples were dispersed in demineralized water and thoroughly mixed. The injected slurry volume was controlled to obtain a total obscuration level of 10±3% and PIDS obscuration of 50±10% [57].

Pesticide extraction and GC analysis. Samples (1.5 - 3 g dry weight sediment or Tenax) were extracted in a microwave (110 °C for 20 minutes) with a hexane:acetone mixture (30 ml 1:1 v:v). The solution was washed with water (~50 ml) in a separatory funnel to remove the acetone prior to analysis. Pesticides were analyzed on a Trace GC with a CP-Sil 8 CB lowbleed/MS column (50m x 0.25mm x 0.12µm film thickness). Sample injection (1µl) was splitless (5 minutes) at a temperature of 250ºC. Helium was used as carrier gas at a constant flow (1.0 ml·min-1). The temperature program was 40°C for 4 min, increased at a rate of 10°C/min to 270°C, and then isothermal for 13 min. The detector, a Polaris Q, ion trap mass spectrometer (MS) had a constant temperature of 300ºC. Ionization was Electron Impact at 70 eV and detection was full scan. Calibration was multipoint, using external standards.

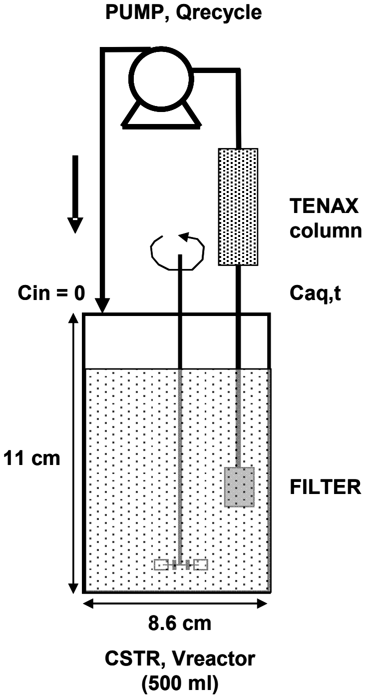

Figure 3-1: schematic of SPEED reactor

Desorption in SPEED reactor. Desorption kinetics were studied at a temperature of 20±1 °C using the SPEED reactor depicted in figure 3-1. A modified 500 ml Schott flask ($V_{reactor}$) combined with a flat-blade turbine impeller (400 RPM) functioned as continuously stirred tank reactor (CSTR). The water phase was pumped through 1 or 2 stainless steel low pressure mobile phase filters (pore size 2 µm, Supelco) and extracted in a glass column containing a packed bed of 3 grams Tenax. After extraction the water phase was recycled into the CSTR. A control column installed behind the extraction column showed that dieldrin was removed completely in the packed bed (c_{in} = 0 µg/l). The pump (Watson Marlow 502S) was installed after the Tenax column to prevent sorption losses of dieldrin. Tubing and connectors were made from PTFE, glass, or steel to minimize losses due to sorption. During experiments the flow rate ($Q_{recycle}$) was kept constant (set flow rate ± 20%) and frequently checked manually by use of a metering glass. When the flow rate decreased more than 20% of the set flow rate the filters were replaced by clean filters. Significant flow rate reduction was observed during our first experiments (HRT 750 min). At predetermined volume intervals the loaded Tenax column was replaced by a clean Tenax column and analyzed for pesticides.

Desorption rates were studied for 4 different HRTs ranging from 10 to 750 minutes. The HRT was calculated as $V_{reactor}$ / $Q_{recycle}$. Experiments were performed in duplicate using separate runs. At the start of each experiment approximately 10 grams (dry weight) of sediment was added to 500 ml 0.01 M $CaCl_2$ solution containing 10 mg NaN_3 to prevent biological activity. In the experiment with set HRT of 10 minutes the amount of sediment sample and the volume of the reactor were reduced by a factor 4 to overcome clogging of the filters. In the experiment with set HRT of 750 minutes approximately 20 grams of sediment (dry weight) was used. The contaminants in the slurry were equilibrated for at least 24 hours before starting the experiment. After each experiment dry matter, organic matter, and dieldrin concentration of the solid fraction were determined.

Aqueous concentrations of dieldrin were calculated using the amount of dieldrin extracted and analyzed, the averaged flow rate and the duration of the extraction step. The initial sediment concentrations of dieldrin were calculated by summation of the extracted amounts of dieldrin per extraction step and the residual dieldrin concentration at the end of the experiment. For recovery control the total concentration of the original sample was analyzed.

Tenax Solid phase extraction (SPE). Desorption rates of samples with different particle size distributions were studied using a modified Tenax SPE method [23, 58]. In short: a mixture of wet sediment (2.0 g dry weight), NaN_3 (20 mg), 40 ml $CaCl_2$ solution (0.01 M), and Tenax (1.5 g) was shaken at a temperature of 20±1 °C in a separatory funnel (150 SPM). Nine extraction steps were performed, each at a predetermined time interval ranging from 1 to 20 hours. After each extraction step the sediment slurry and loaded Tenax beads were separated and fresh Tenax was added. At the end of the experiment the sediment slurry was centrifuged to reduce the water content of the solid sediment fraction. Loaded Tenax beads and the remaining solid sediment fraction were then extracted and analyzed as described before. Experiments were performed in triplicate.

3.3. Results and discussion

Sediment characteristics. Based on the organic matter content of 6 particle size classes (data not shown), three distinctive fractions were identified: <32 µm (OM 14.6%, dieldrin 6.1 $mg\cdot kg^{-1}$), 32–125 µm (OM 6.1%, dieldrin 3.6 $mg\cdot kg^{-1}$), and 125-2000 µm (OM 30.5%, dieldrin 13.3 $mg\cdot kg^{-1}$). The particle size distributions of each fraction, analyzed by laser scattering, are depicted in figure 3-2.

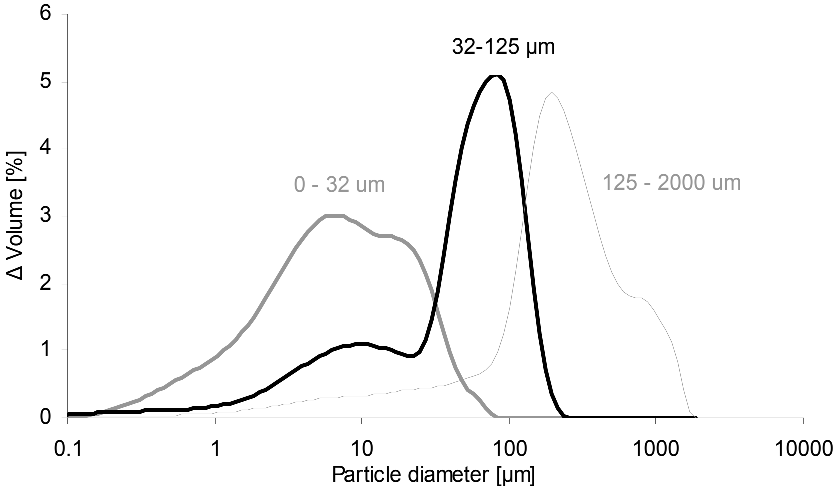

Figure 3-2: particle size distribution of three particle size fractions by laser diffraction. ΔVolume is the amount of volume related to a discrete particle size range.

Sieving did not lead to a sharp cut off at the lower diameter. In each fraction approximately 30% by volume of the particles were smaller than the lower limit of the particle size classes. During fractionating by sieving the small particles could have formed aggregates or were attached to larger particles. The upper limit of all particle size classes was only exceeded by approximately 5% of the particles volume, probably due to non spherical particles. For the SPEED reactor experiments the particle size fraction 32–125 µm was used which had a SOM content of 6.1 % ± 0.9. In this particle size fraction two distinct particle size peaks were observed by laser diffraction analysis, one peak at 10 µm and one peak at 84 µm. The areas of these peaks were integrated and the cumulative volumes were 27% and 73% for the peaks at 10 and 84 µm respectively. We choose this particle size fraction because the fraction 125-2000 µm was heterogeneous regarding SOM content and dieldrin concentration. The particles of the fraction <32 µm are expected to reach instant equilibrium with the aqueous phase, limiting the possibility to study mass transfer kinetics. This fraction also leads to clogging of the filters.

The experimental conditions regarding average flow rates, measured HRT, sample sizes, and initial sediment concentrations of dieldrin (S_0) are presented in table 3-1.

Table 3-1: experimental conditions of SPEED experiments.

set HRT [min]	average flow rate [ml·min-1] [a]	reactor volume [ml]	measured HRT [min]	sample size [g d.m.]	dieldrin S0 [mg·kg-1d.m.]
10	11.4	125	10.96	2.45	3.89
	12.9	125	9.66	1.73	3.36
25	20.15	500	24.81	10.56	4.09
	20.15	500	24.81	11.02	4.17
75	5.31	500	94.16	11.21	3.11
	7.54	500	66.31	10.00	3.42
750	0.68	500	735.29	20.01	3.45
	0.67	500	746.27	20.03	3.04

[a] flow rates were controlled within boundary ± 20% except for set HRT 750 where the flow rate decreased continuously

Normalized concentrations of dieldrin in the aqueous phase and the fraction of dieldrin that is extracted in time are depicted in figure 3-3A. Concentrations were normalized because small variations in total dieldrin concentrations (S_0) obscured the extraction profiles of the various experiments. Differences between duplicates of each experiment were caused by differences in actual flow rates and thus the amount of fresh water that was available during each extraction step. HRT clearly effected the aqueous concentration in time and the desorption rate. A small HRT maintained the highest concentration gradient between dieldrin sorbed to the sediment phase and dieldrin dissolved in the water phase and therefore gives the highest extraction rate. At the smallest HRT (10 min.) half of the dieldrin was extracted within one day of operation whereas less than 10% was extracted in the same time at the largest HRT (750 min.). For comparison also results from a Tenax SPE are included in the graph. The Tenax SPE is in fact equivalent to a SPEED experiment with a very small HRT. The results are nicely in line with the SPEED experiments and provide an upper limit of desorption rate. To study desorption at more realistic, field-like conditions however requires more freedom to change parameters like mixing conditions and water refreshment which can be set and controlled with the SPEED reactor.

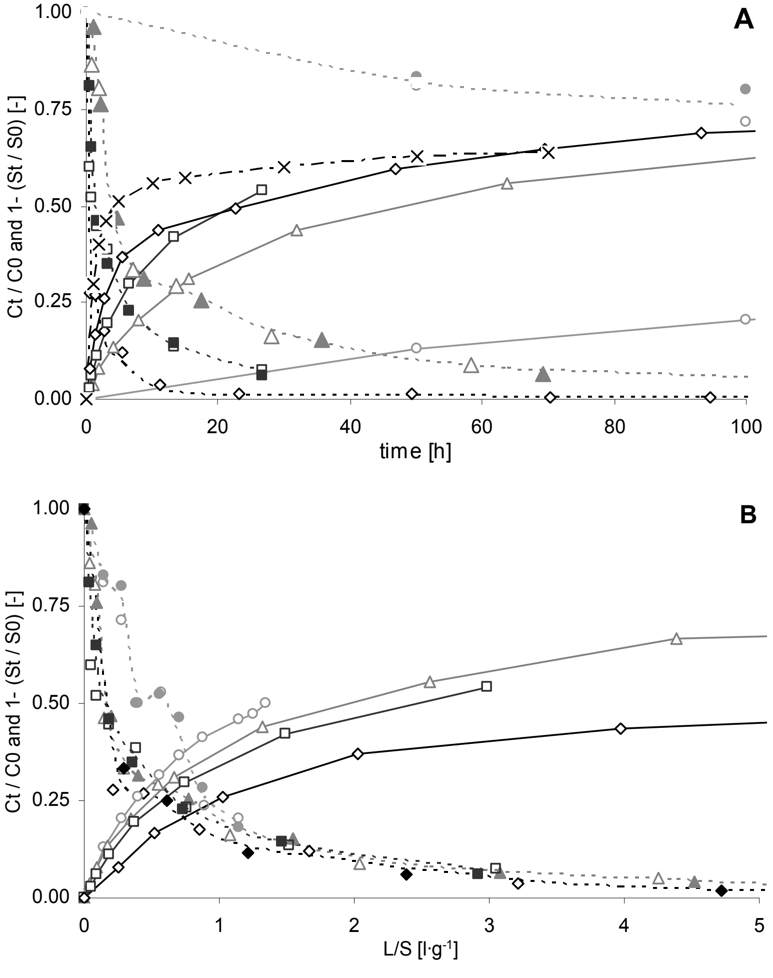

Figure 3-3: Dieldrin concentration in aqueous phase (dotted lines) and fraction extracted (solid lines) as function of time (A) and liquid to solid ratio (B). The set HRTs (duplicates) are: ♦ and ◊ = 10 minutes, ■ and □ = 25 minutes, ▲and △ = 75 minutes, ● and ○ = 750 minutes, and X = Tenax SPE.

Not only time but also the amount of water available for extraction affects the extent of desorption, specially during a flood event. In figure 3-3B the results of the same SPEED experiments are presented, but recalculated as function of liquid to solids ratio (L/S). The decrease of dieldrin concentration for the different experiments are about equal and seem to be independent of HRT. The amount of dieldrin extracted per volume of water (L/S) however decreases at lower HRT. A high HRT provides more time for desorption per volume of water and thus enhances extraction efficiency. No results of Tenax SPE were included as we did not specifically measure the partition constant of dieldrin between Tenax and water (K_{tenax}).

At the start of all experiments the sediment samples and aqueous phase composition were similar. As a result, also the amount of dieldrin on or near the sediment/water interface was equal. As we observed large differences of desorption rates with different HRT we conclude that the concentration gradient plays a major role in desorption and mass transfer is kinetically hindered within the sediment particles.

Tenax SPE. Sediment concentrations of dieldrin (S_t/S_0) are presented in figure 3-4 as function of time for three particle size classes. The slope of each profile in time represents the desorption rate. Desorption rates are higher for smaller particle sizes. The effect of particle size on desorption rate is supportive to the observation that desorption rates are determined by mass transfer rates within the sediment particles. The relation between particle size and desorption of organic contaminants from soils and sediments in literature is contradicting. In a paper often cited to demonstrate the absence of particle size effects on desorption kinetics [59], it was shown that milling had no effect on desorption behavior of contaminants. The presence of organic matter as a thin coating around mineral particles however was overlooked. Therefore not only particle size but also the spatial configuration of organic matter in the soils and sediments affects desorption kinetics.

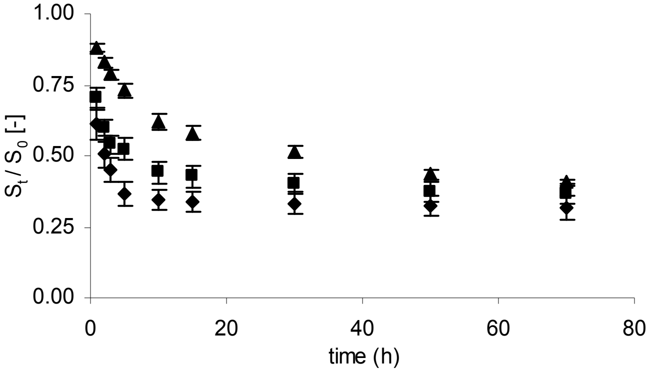

Figure 3-4: normalized sorbed concentration of dieldrin as function of time of three particle size fractions. ♦ 32 µm, ■ 32 – 125 µm, and ▲125-2000 µm. Error bars are standard deviation (n=3).

Flux based approach. From the SPEED experiments and the Tenax SPE we concluded that mass transfer is kinetically hindered within the sediment particles. To assess the type of hindrance, desorption rates of SPEED experiments were explored using the flux calculated by equation 3-1:

$$J_1 = \frac{1}{A_p} \cdot \frac{\Delta M}{\Delta t} \tag{3-1}$$

Where J_1 is the average flux of dieldrin per extraction step ($mg \cdot m^{-2} \cdot s^{-1}$), A_p is the surface area of the particles (m^2), $\Delta M/\Delta t$ is the change of dieldrin mass per extraction step ($mg \cdot s^{-1}$). The surface area of the particles was calculated from the sample size, the density according to a standard value of 2600 $kg \cdot m^{-3}$, and the particle sizes 10 µm (27%) and 84 µm (73%).

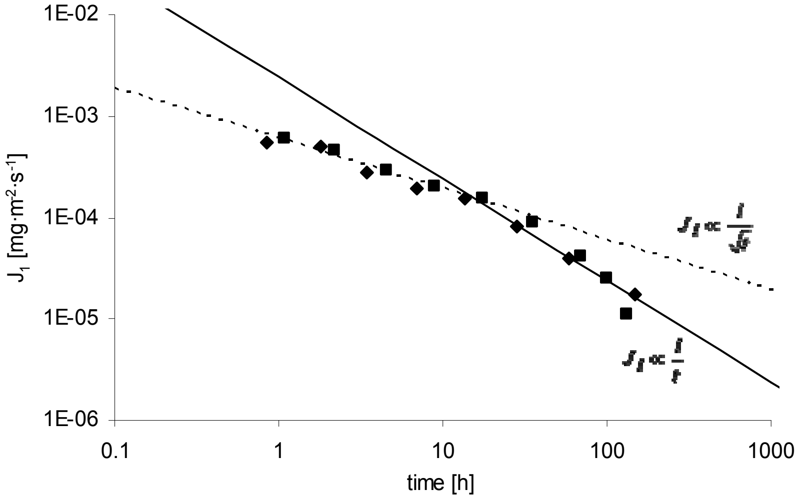

Figure 3-5: dieldrin flux (J1) for HRT = 75 minutes. Lines are model fits for short ($J_1 \propto t^{-0,5}$) and long term ($J_1 \propto t^{-1}$) data.

In figure 3-5 a representative plot of flux versus time is presented for HRT 75 minutes. Once desorption started, the flux can be described for the first few hours as $J_1 \propto t^{-½}$ and thereafter $J_1 \propto t^{-1}$ which are the slopes of the solid lines drawn in the figure. Theoretically, the flux of a single particle should finally be described by $J_1 \propto e^{-t}$ [60] when non stationary diffusion is the main process of mass transfer. We did not observe this last stage of desorption, possibly because the particle size distribution obscures the clear, theoretical relation between flux and time. The relation $J_1 \propto t^{-1}$ can then be seen as a transition zone and the effect of time on the flux ($t^{-½} \rightarrow t^{-1}$) strengthens the idea that our observations are the result of non stationary diffusion as the main process of mass transfer of dieldrin from the sediment to the aqueous phase. The modeling of SPEED reactor results will be described in a separate paper.

3.4. Conclusions

The SPEED reactor enables to simulate field conditions and flood events by setting the mixing regime and water flow rates, which are universal parameters in every water body like rivers, lakes, and groundwater. Flood events will result in an increase of desorption rate of POPs from sediments to the surrounding water. HRT and particle size determine the concentration gradient and thereby the desorption rate. From the results of the SPEED experiments we concluded that mass transfer of dieldrin within the sediment particles is the rate limiting step. The concentration gradient, which is a function of concentration difference and particle size determines the desorption rate. Similar to Tenax SPE extractions, a rapid and a slow desorbing phase was observed. On a flux based approach, the experimental data are supportive of non stationary diffusion as the main process of mass transfer. Because of the flexibility of the SPEED system, in terms of flow rate adjustment and control as well as the possibility to measure aqueous concentrations directly, it provides a sound basis for mechanistic modeling.

4

Modeling desorption kinetics of a persistent organic pollutant from field aged sediment using a bi-disperse particle size distribution

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4.1. Background, aim and scope

With the predicted climate change it is expected that the chances of river flooding increase. During flood events, sediments will resuspend and, when sediments are polluted, contaminants can be transferred to the surrounding water [61, 62]. Mass transfer of organic compounds like Persistent Organic Pollutants (POPs) from soil and sediment particles to the surrounding aqueous phase is affecting fate and transport of these chemicals in the aqueous environment. Mass transfer, and mass transfer limitation of organic contaminants in polluted sediments and soil has been a key research issue for the last decades and hundreds of articles have been published in this area of research [63]. Roughly a distinction can be made between research focused on equilibrium sorption, and research focused on (de)sorption kinetics. Equilibrium sorption and sorption kinetics are both part of mass transfer phenomena and have a strong relation [34, 35]. An overview of different model concepts presently used to describe desorption kinetics was presented by Saffron et al. [47]. All but one of these models require at least two (mathematical) compartments to fit the experimental data. These compartments can then define a combination of an instantaneous compartment where no mass transfer limitation is assumed with a dynamic compartment where mass transfer is limited [35, 64], two dynamic compartments [17, 19, 25, 51, 65-67], or a continuum of compartments with various parameters [68-70]. Although sometimes excellent fits of experimental and modeled data were demonstrated in the different papers, the physical explanation of the desorption process and its limitations is only briefly elaborated and do not include the effect of particle size distribution.

In diffusion models the driving force of (de)sorption is related to a concentration gradient and a sorption concept. For example Freundlich sorption isotherms [51, 54, 55, 71, 72] or linear sorption isotherm [22, 24, 25, 56, 64, 73-75] were used to model desorption kinetics. In radial diffusion models, particle size effects are generally lumped into a single fit-parameter Da/R2, where Da is a diffusion coefficient and R the radius of the spheres. Particle size effects, or more specifically particle size distribution effects are generally not included. [24] however specifically included measured particle sizes in their diffusion model and concluded that the radial diffusion model was the best model to fit their experimental data using artificial contaminated soils and sediments. They reported that large particles show a slower sorption approach to equilibrium than otherwise similar smaller particles when using the same sorbate. They concluded that sorption kinetics is controlled by intraparticle diffusion.

In this paper we discuss a numerical intra particle diffusion model, similar to the model used by Wu and Gschwend, that simulates desorption of dieldrin from a suspension of contaminated porous sediment particles with a well characterized particle size distribution. The objective of this study was to understand the desorption rate (flux) of dieldrin from a suspension of field aged sediment at different hydraulic retention times (HRT) of the aqueous phase and to elaborate the effect of particle size distribution on mass transfer. For this purpose the SPEED reactor (Solid Phase Extraction with External Desorption) was developed in which it was possible to set and control the HRT and to measure low aqueous concentrations [76].

4.2. Materials and methods

Sediment samples were from Broekpolder (Vlaardingen, The Netherlands) and were taken from a depth of 0 – 0.5 meter. Sediments originate from Rotterdam harbor and were contaminated with dieldrin for more than 40 years. Before the experiments started samples were sieved. The particle size distribution, measured by a laser diffraction method, showed two peaks with a log-normal size distribution around the peaks. One peak was found at a particle diameter of 10 µm and one peak at 84 µm. Detailed information of the sample characteristics were described before [76].

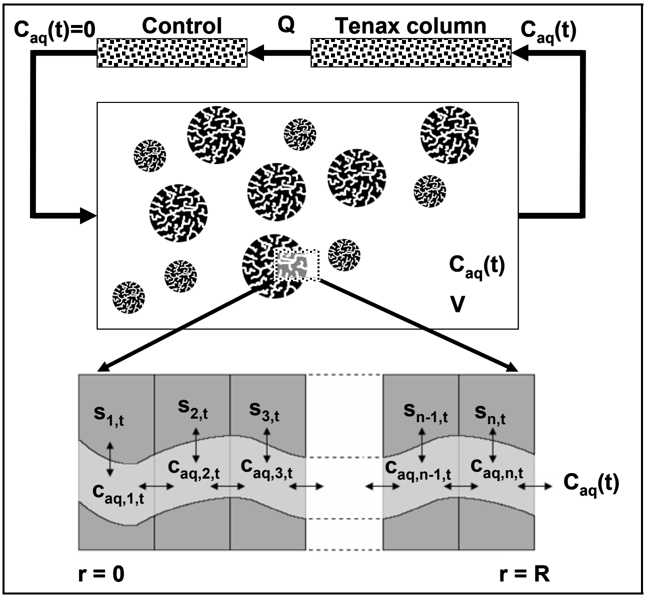

Figure 4-1: conceptual model of mass transfer from organic particles in the SPEED reactor. The offset illustrates a pore in an organic particle. In our modelling approach n = 61. Symbols are elaborated in the text.

Desorption kinetics were measured using the SPEED reactor described before [76]. In short, a Schott bottle (500 cm^3) was used as continuously stirred tank reactor (CSTR). Contaminated sediment and 0.01 M $CaCl_2$ solution were mixed to obtain a homogeneous suspension. From the start of the experiment water is pumped at a set flow rate (Q) from the reactor vessel through stainless steel filters (Supelco, 2µm) to a glass column containing 3 grams of Tenax where the dieldrin is extracted from the aqueous solution. After the Tenax column, the water was directed through a control Tenax column to validate that all dieldrin was indeed extracted and then recycled into the CSTR. At predetermined volume intervals the loaded Tenax column was replaced by a clean column and analyzed for pesticides. All reactor parts were made from HDPE, glass, or stainless steel to minimize sorption of dieldrin. The reactor setup is presented in figure 4-1.

Modeling concept

The model is focused on the concentration of dieldrin in the aqueous phases. We distinct a bulk aqueous phase and an aqueous phase in the pores of organic matter. The dieldrin concentration within the pores is considered to be variable in 1 dimension (1D diffusion). Organic matter was assumed to be present as separate, porous particles that are homogeneously distributed within the sediment sample. Each particle had identical physical/chemical properties except for the particle size. This seems reasonable as the fraction of organic matter and the dieldrin concentration were similar within the sub-samples described in the experimental paper [76]. Inorganic particles were not considered.

Mass balance

The volume of the organic particles in the reactor, V_{om} [cm^3 particles], was calculated with equation (4 -1).

$$V_{om} = \frac{X_{sed} \cdot f_{om}}{\rho_{om}} \qquad (4\text{-}1)$$

Where X_{sed} is the sediment mass [g], f_{om} is the mass fraction organic particles [-], and ρ_{om} is the density of the organic particles [$g \cdot cm^{-3}$ particles]. We assumed a density of 1.20 $g \cdot cm^{-3}$ particles. At any location r within the pores of organic particles we assumed local equilibrium of dieldrin between the immobile phase (organic matter) and the mobile phase (pore water).

The sorption isotherm for this equilibrium is linear:

$$s(r) = K_{om} \cdot c_{aq}(r) \tag{4-2}$$

where s(r) is the dieldrin concentration of the organic matter at location r [$g \cdot cm^{-3}{}_{om}$], K_{om} the sorption coefficient of dieldrin to organic matter [$cm^3{}_{pw} \cdot cm^{-3}{}_{om}$], and $c_{aq}(r)$ the dieldrin concentration in the pore water at location r [$g \cdot cm^{-3}{}_{pw}$]. The sorption coefficient K_{om} was calculated by log(Koc) = 4,46 divided by the density of organic matter resulting in $3.48 \cdot 10^4$ $cm^3{}_{pw} \cdot cm^{-3}{}_{om}$. The concentration of dieldrin in the bulk liquid is assumed to be homogeneously and changes only with time. As dieldrin is reported to be very resistant to (bio)degradation and volatization, the overall amount of dieldrin present in the system remains constant. The mass balance equation of dieldrin in the SPEED reactor will be:

$$\frac{dC_{aq}(t)}{dt} = \frac{1}{V} \cdot \left(J(t) - C_{aq}(t) \cdot Q \right) \tag{4-3}$$

where $C_{aq}(t)$ is the bulk aqueous dieldrin concentration [$g \cdot cm^{-3}$] at time t [s], V is the volume of the bulk aqueous phase in the SPEED reactor [400 cm^3], and Q is the applied flow rate [$cm^3 \cdot s^{-1}$]. The dieldrin mass flow rate J(t) from the organic particles to the bulk aqueous phase [$g \cdot s^{-1}$] is calculated as:

$$J(t) = \frac{dS(t)}{dt} \cdot V_{om} \tag{4-4}$$

Where S(t) is the average dieldrin concentration of the organic particles [$g \cdot cm^3{}_{particle}$]. Analytical solutions of equation (4-3) are given for two boundary conditions: without desorption (J(t) = 0, equation 4-5):

$$\frac{C_{aq}(t)}{C_{aq}(t=0)} = e^{\frac{-Q}{V} \cdot t} \quad \text{and} \quad \frac{S(t)}{S(t=0)} = 1 \tag{4-5}$$

and for instant equilibrium between organic matter and bulk aqueous phase (equation 4-6).

$$\frac{C_{aq}(t)}{C_{aq}(t=0)} = e^{\frac{-Q}{V+V_{om}\cdot K_{om}}\cdot t} \quad \text{and} \quad \frac{S(t)}{S(t=0)} = \frac{C_{aq}(t)}{C_{aq}(t=0)} \qquad (4\text{-}6)$$

Experimental results of a control experiment without any particles confirmed the validity of equation 4-5 down to a dieldrin concentration ($C_{aq}/C_{aq}(t=0)$) ≈ 0.05 (data not shown). The solutions of equation (4-5) and (4-6) are plotted with dashed lines in figure 2-2A and 2-2B as function of dimensionless time $\theta = Q\cdot t / V$ [-].

Particle size distribution (PSD)

The measured PSD of the sediments was presented before [76]. The PSD showed two distinct peaks (k=2). The total number of organic particles, $N_{p,tot}$ [-], is the sum of particles in each defined particle size class $N_{p,i}$ [-]:

$$N_{p,tot} = \sum_{i=1}^{k} N_{p,i} = \sum_{i=1}^{k} \frac{f_{p,i}\cdot V_{om}}{\tfrac{4}{3}\pi\cdot R_i^3} \qquad (4\text{-}7)$$

where k is the number of different particle sizes with radius R_i [cm] and $f_{p,i}$ is the volume fraction as calculated from the PSD. Both diameters represent a narrow PSD as described by Cooney et al. [77]. The volume fraction associated with the peak at 10 μm was 0.27 and for the peak at 84 μm was 0.73. These particle sizes and their corresponding volume fractions were the input of the bi-disperse particle size distribution.

Radial diffusion model

The mass flow rate J(t) of dieldrin from the organic particles to the bulk liquid was modeled assuming that mass transfer of dieldrin is only possible through the pore liquid and that local sorption equilibrium is instantaneous. Furthermore we assumed that because of vigorously mixing of the slurry, mass transfer limitations only occurred within the particles (intra particle diffusion). The local total volumetric dieldrin concentration within an organic particle at location r is defined as:

$$S'(r) = \varepsilon\cdot c_{aq}(r) + (1-\varepsilon)\cdot s(r) \qquad (4\text{-}8)$$

where S'(r) is the local total volumetric dieldrin concentration [g·cm$^{-3}_{\text{particle}}$] and ε is the particle volumetric porosity [cm$^{3}_{\text{pw}}$·cm$^{-3}_{\text{particle}}$]. The particle volumetric porosity was assumed to be 0.4. The change of local total volumetric dieldrin concentration in time as function of the concentration gradient within the particle can then be stated as:

$$\frac{\delta S'(r)}{\delta t} = \varepsilon \cdot \frac{\delta c_{aq}(r)}{\delta t} + (1-\varepsilon) \cdot \frac{\delta s(r)}{\delta t} = \varepsilon \cdot \frac{D_{aq}}{\kappa} \cdot \left(\frac{\delta^2 c_{aq}(r)}{\delta r^2} + \frac{2}{r} \cdot \frac{\delta c_{aq}(r)}{\delta r} \right) \qquad (\text{4-9})$$

where $D_{aq}/\ \kappa$ is the matrix diffusion coefficient of dieldrin in the aqueous phase corrected with tortuosity [cm^2·s^{-1}]. $D_{aq}/\ \kappa$ was optimized by fitting all experimental data. The optimized value (2.0·10^{-7} cm^2·s^{-1}) was then used for all calculations.

Substitution of equations (4-2) and (4-8) into equation (4-9) leads to:

$$\frac{\delta S'(r)}{\delta t} = \frac{\varepsilon \cdot \frac{D_{aq}}{\kappa}}{\varepsilon + (1-\varepsilon) \cdot K_{om}} \cdot \left(\frac{\delta^2 S'(r)}{\delta r^2} + \frac{2}{r} \cdot \frac{\delta S'(r)}{\delta r} \right) \qquad (\text{4-10})$$

Initial and boundary conditions for equation (4-10) are as follow:

$$\frac{S'(r)}{(\varepsilon + (1-\varepsilon) \cdot \rho \cdot K_{om})} = C_{aq}(t=0) \qquad \text{for } 0 < r < R \qquad (\text{IC 1})$$

$$\frac{S'(r=R)}{(\varepsilon + (1-\varepsilon) \cdot \rho \cdot K_{om})} = C_{aq}(t) \qquad (\text{BC 1})$$

$$\left. \frac{\delta S'(r)}{\delta r} \right|_{r=0} = 0 \qquad (\text{BC 2})$$

The mass flux of dieldrin from the organic particles to the bulk liquid will then be:

$$J(t) = \frac{dS(t)}{dt} \cdot V_{om} = \sum_{i=1}^{k} N_{p,i} \cdot \frac{d}{dt} \int_0^{R_i} 4\pi r^2 \cdot S'(r) \cdot dr \qquad (4\text{-}11)$$

We used a numerical integration method similar to the method described by Rügner [55] to approximate the solution of equations (4-3) and (4-11). A Crank Nicolson discretization scheme was used to transform the differential equation into a set of linear equations that can be solved according to LU decomposition. We used 61 space nodes for sufficient resolution of the intra particle concentration of dieldrin [78].

The system of equations was programmed in Matlab®. The values used to model each experiment performed in duplicate are given in table 4-1.

Table 4-1: input parameters for SPEED model calculations.

HRT	Symbol	Parameter	Parameter value	*Parameter dimension*
11 min.	V	volume bulk liquid	125	cm^3
	Q	recycle flow rate	0.190	$cm^3 \cdot s^{-1}$
	X_{sed}	sample mass	2.45	g
	f_{om}	Mass fraction org. particles	0.050	-
	$C_{aq,0}$	initial aqueous concentration	$4.68 \cdot 10^{-9}$	$g \cdot cm^{-3}$
20 min.	Q	recycle flow rate	0.336	$cm^3 \cdot s^{-1}$
	X_{sed}	sample mass	10.56	g
	f_{om}	Mass fraction org. particles	0.059	-
	$C_{aq,0}$	initial aqueous concentration	$4.92 \cdot 10^{-9}$	$g \cdot cm^{-3}$
53 min.	Q	recycle flow rate	0.126	$cm^3 \cdot s^{-1}$
	X_{sed}	sample mass	10.00	g
	f_{om}	Mass fraction org. particles	0.060	-
	$C_{aq,0}$	initial aqueous concentration	$4.12 \cdot 10^{-9}$	$g \cdot cm^{-3}$
430 min.	Q	recycle flow rate	0.015	$cm^3 \cdot s^{-1}$
	X_{sed}	sample mass	10.00	g
	f_{om}	Mass fraction org. particles	0.054	-
	$C_{aq,0}$	initial aqueous concentration	$4.12 \cdot 10^{-9}$	$g \cdot cm^{-3}$

4.3. Results and discussion

Particle size effect on desorption

In figures 4-2A (bulk aqueous phase) and 4-2B (sediment phase), dieldrin concentrations are presented as a function of dimensionless time (θ) for various values of the particle size. Calculations were performed using conditions similar to the experiments performed at HRT ≈ 11 minutes. Lines labeled by a particle diameter were the model results of that single particle diameter.

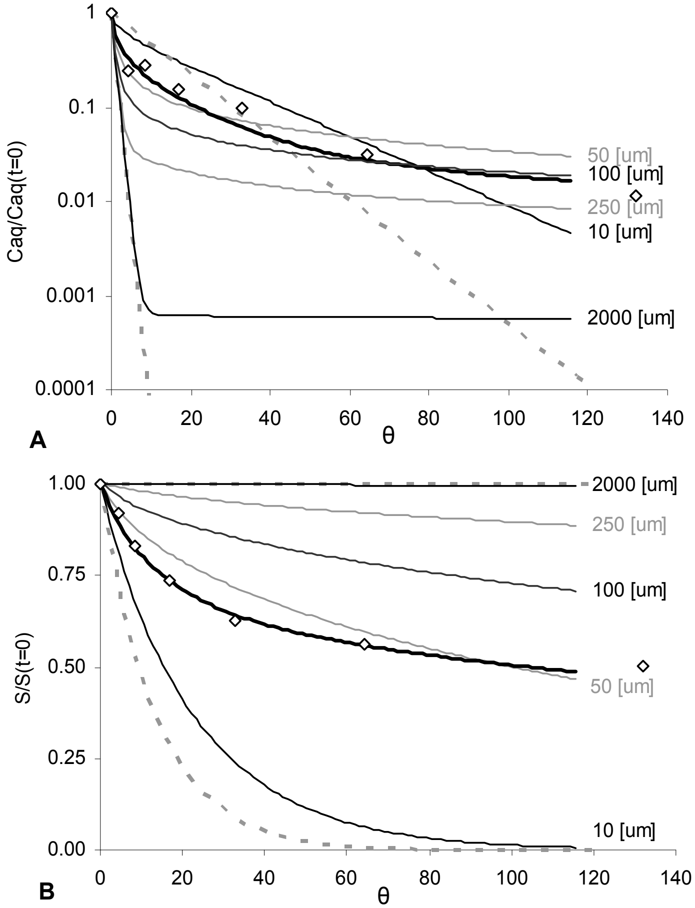

Figure 4-2: calculated (mono-disperse, solid lines) and experimentally measured (◊) normalized dieldrin concentration as function of dimensionless time (θ) in water (A) and sediment (B) for various values of particle diameter. Dashed lines are theoretical limits (eq.2 and 3). The thick solid line through the symbols was calculated using the bi-disperse model with particle diameters of 10 and 84 μm.

As can be seen in figure 4-2B, the dieldrin concentration of the sediment phase decreases faster when particles are smaller, leading to a higher concentration in the bulk aqueous phase (figure 4-2A). Only when particles are almost depleted with dieldrin, the concentration in the aqueous becomes lower compared to the larger particles as can be seen for particles with a diameter of 10 µm. In figure 4-2B we see that the boundary conditions calculated with equations (4-5) and (4-6) are similar to the upper and lower limits of the soil particle size. Small particles with a diameter of 10 µm already show some mass transfer limitations and a reduced desorption rate compared to the boundary condition. The largest particles (2000 µm) demonstrate a very slow release of dieldrin and concentrations are about equal to the boundary condition where desorption is absent. Only at a very low normalized aqueous dieldrin concentration ($C_{aq}/C_{aq}(t=0) \approx 6.1 \cdot 10^{-4}$) desorption starts to become visible. Experimental results (HRT ≈ 11 minutes) and calculated concentrations using a bi-disperse particle size distribution are given as well in figure 4-2. From the start of the experiment the behavior of the bi-disperse model shifts from small particles to larger particles, or in other words from rapid to slow desorption. This phenomenon could not be approached with a single, mono-disperse particle size distribution.

Comparison of modeling results with experimental data

In figure 4-3 we show the normalized concentration of dieldrin in the bulk aqueous phase (4-3A) and the sediment phase (4-3B) as function of desorption time for various values of hydraulic retention time (HRT). Both experimental data [76] and the results of calculations with the bi-disperse particle size distribution are shown. As can be seen in the figure, model results agree with the experimental data. A smaller HRT results in a faster decrease of bulk aqueous concentration in time. This is the result of diffusion limitation of dieldrin from the sediment to the bulk aqueous phase; removed dieldrin from the bulk aqueous phase cannot instantly be replaced by dieldrin from the sediment phase. These lower bulk aqueous dieldrin concentration enlarge the concentration difference between sediment and aqueous phases thereby increasing the desorption rate. Furthermore we can see in figure 4-3A that with increasing HRT also the curve linearity increases. Increasing linearity indicates an approach to the concept of instant equilibrium. A higher HRT provides a longer time period per liter of recycled water and more mass can be transferred from the sorbed phase to the aqueous phase. Model results of the concentration of dieldrin in the sorbed phase (figure 4-3B) tend to overestimate the extent of desorption at longer times. This overestimation might be related to the presence of larger particles in the experimental setup then we accounted for in the model but were found to be present in the measured PSD [76].

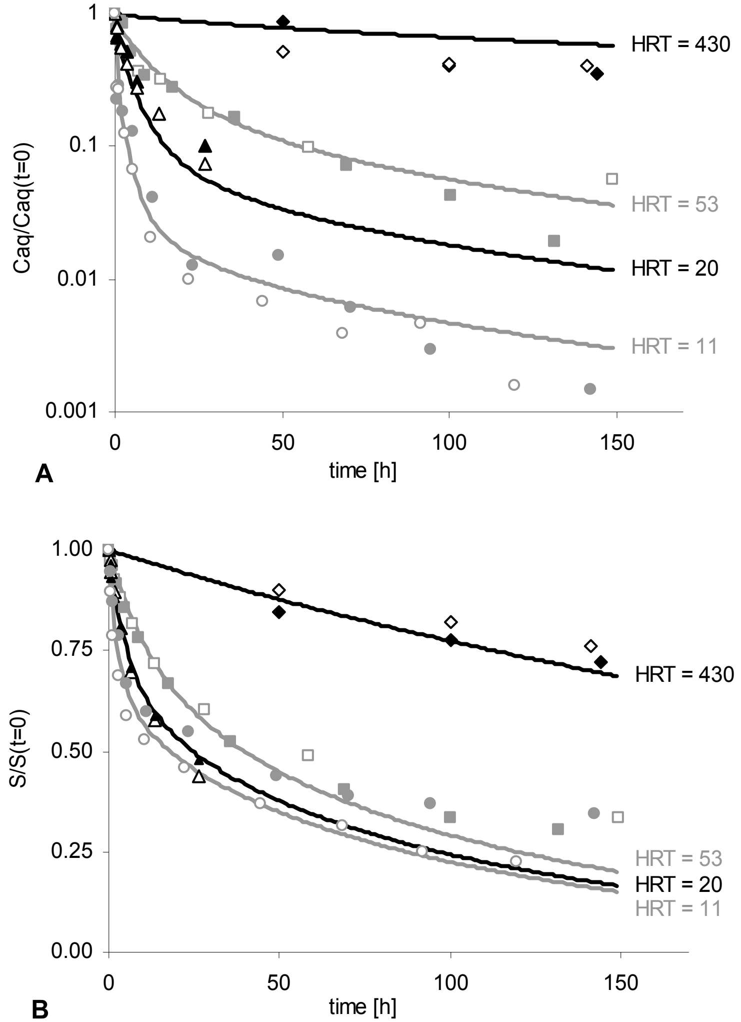

Figure 4-3: calculated (solid lines) and experimentally measured (symbols) normalized dieldrin concentration as function of time in water (A) and sediment (B) for various values of HRT. Experimental results are duplicates and symbols represent: ♦,◊ = 430 minutes, ■, □ = 53 min., ▲, Δ = 20 min. and ●, ○ = 11 min.

The calculated concentration gradients within particles, both small and large, are presented in figure 4-4 for the highest and lowest HRT. Dieldrin concentration at the particle-water interface (right side of the graphs) at a given time are similar for both particle sizes and are, when normalized, equal to the aqueous concentration presented by the graph in figure 4-3A. The concentration gradient of dieldrin within small particles at HRT = 430 is very different from the concentration gradient within large particles. The apparent absence of a concentration gradient at any time in small particles suggests an equilibrium between these particles and the surrounding aqueous phase at any time whereas the presence of such a gradient points at intra particle diffusion limitations. This different behavior is even more pronounced at a low HRT (11 min.).

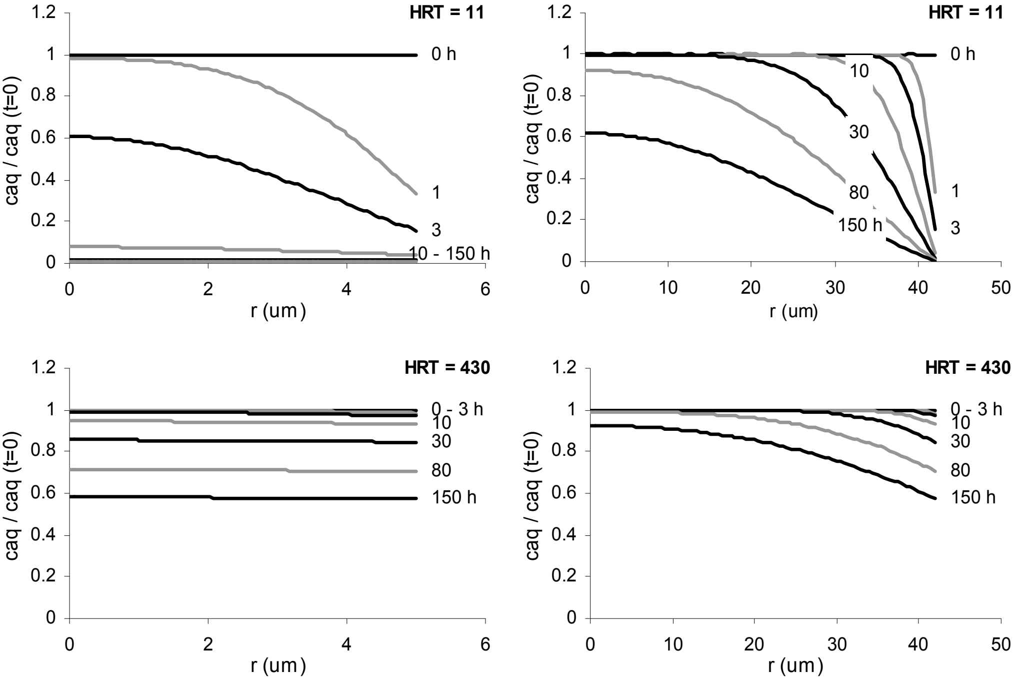

Figure 4-4: normalized concentration of dieldrin within pores of small and large particles after different desorption times as function of the radial position at various values of time for HRT = 430 minutes and 11 minutes.

4.4. Conclusions

Flood events will result in an increase of desorption rate of POPs from sediments to the surrounding water. In this study we demonstrated that intraparticle diffusion is the limiting step in desorption of hydrophobic contaminants from organic particles. The particle size distribution is a key parameter to successfully model experimental data. This might be an explanation why diffusion models using an average particle size and thus a single diffusion parameter sometimes fail to fit experimental data. Furthermore the diffusion length will be smaller when sediment particles are suspended and more water is present to decrease the aqueous concentration. The radial diffusion model combined with particle size distribution facilitates understanding and prediction of contaminant fluxes to potential receptors.

4.5. Recommendations and perspectives

To our opinion, many studies overlooked the importance of particle size distribution and the time required to reach equilibrium. Currently, particle size distribution is often reported by ISSS and NEN protocols; however a more refined method is required to assess the particle size distribution as small differences in particle size have a major effect on mass transfer rate (figure 4-3). We think that the use of particle size distributions is a valuable tool to improve the understanding of the phenomenology related to bioavailability in practice.

5

Dieldrin release from disturbed and undisturbed sediment beds

This chapter will be submitted for publication as:
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5.1. Introduction

Bioavailability of hydrophobic organic contaminants (HOC) in polluted sediments and soils has been a key research issue for the last decades and hundreds of articles have been published in this area of research [63]. The majority of studies focused on sorption and/or desorption of HOC from suspended sediments in close contact with a solid phase extractant like XAD or Tenax. In the field, sediments can indeed be (re)suspended when the flow of the overlaying water mass is turbulent like during flood events or fast flowing rivers. However, in many situations sediments are not suspended but are present as bed sediments. Therefore the results of experiments using suspended sediments seldom apply to these field conditions. Besides research on suspended soils and sediments research was conducted using soil or sediment columns to describe the mass transfer, most of them applying an advective flow through the column. Only a few studies [79-82] looked at sorption of these chemicals into a bed of sediments without an advective solute flow. These studies focused on the concentration profile of target contaminants within the sediment bed. It was concluded that molecular diffusion is the likely transport mechanism. Modeling this HOC transport was done using either an analytical solution of diffusion in a semi-infinite slab [79, 82] or a numerical model incorporating sediment heterogeneity in terms of porosity and fraction organic carbon [79]. In a river system, the role of bed sediments as sink or source of pollutants merely depends on the concentration of pollutants in the sediment fraction and the overlaying aqueous phase [83]. The rate of transport (flux) is affected by diffusion in the pore water, degradation, sorption, sediment deposition and resuspension, and bioturbation [8]. Pollutant fate models incorporate many process descriptions with parameters that are not known a priori.

In this paper we present the results of experimental work on mass transfer from an artificial bed of field aged sediments to the overlaying aqueous phase. We discuss a numerical model that simulates desorption of dieldrin from a thick and a thin bed of porous sediment particles with a well characterized particle size distribution. The model combines mass transfer limitation within sediment particles with mass transfer limitation within the sediment bed. The validated model can then be used to explore engineering options to reduce the aqueous concentration of HOC thereby reducing risks for the aqueous environment.

5.2. Materials and methods

Samples. Sediment samples were from Broekpolder (Vlaardingen, The Netherlands) and originate from the harbor of Rotterdam. The samples were taken from a depth of 0 – 0.5 meter. Sediments were contaminated with dieldrin for more than 40 years. Before experiments started the samples were wet sieved using sieve openings of 32 and 125 µm to obtain a narrow particle size distribution. To limit desorption of dieldrin from the sediment samples during sieving we used as little water as possible. Results obtained by laser scattering particle size distribution analyses showed that particles smaller than 32 µm were still present [84]. The sediment fraction was characterized for soil organic matter content (SOM) and concentration of dieldrin. SOM was determined gravimetrically by combustion of dried samples for 6h at 550 °C.

Chemicals. Tenax-TA (20-35 mesh) was purchased at Buchem b.v. (Apeldoorn, The Netherlands), acetone (p.a.), hexane (HPLC grade), NaN_3 (extra pure), and $CaCl_2$ (dried) were from Merck (Darmstadt, Germany).

Dieldrin extraction and GC analysis. Solid samples (1.5 - 3 g dry weight sediment or Tenax) were extracted in a microwave (110 °C for 20 minutes) with a hexane:acetone mixture (30 ml 1:1 v:v). The solution was washed with water (~50 ml) in a separatory funnel to remove the acetone prior to analysis. Dieldrin was analyzed on a Trace GC with a CP-Sil 8 CB lowbleed/MS column (50m x 0.25mm x 0.12µm film thickness). Sample injection (1µl) was splitless (5 minutes) at a temperature of 250ºC. Helium was used as carrier gas at a constant flow (1.0 ml·min-1). The temperature program was 40°C for 4 min, increased at a rate of 10°C/min to 270°C, and then isothermal for 13 min. The detector, a Polaris Q, ion trap mass spectrometer (MS) had a constant temperature of 300ºC. Ionization was Electron Impact at 70 eV and detection was full scan. Calibration was multipoint, using external standards.

Desorption in SPEED reactor. Desorption kinetics were measured using the SPEED reactor described before [84]. In short, a modified Schott flask was used as reactor ($V = 400\ cm^3$) containing the sediment (X_{sed}), and 0.01 M $CaCl_2$ solution. The aqueous phase is pumped through stainless steel filters to a glass column containing 3 grams of Tenax to extract the dieldrin from the aqueous phase. After the extraction step the water is pumped through a control column filled with Tenax to assure that no detectable dieldrin was present and is then recycled into the reactor (Q). At predetermined volume intervals the loaded Tenax column was replaced by a clean column and the Tenax was extracted and analyzed for dieldrin. The area of the bed/bulk interface is 64 cm^2. When the aqueous dieldrin concentration appeared to be constant in time, the bed sediment and aqueous phases were mixed vigorously for 1 hour using a flat blade impellor at 150 RPM. After mixing the sediment particles were allowed to settle for at least 2 days before pumping was resumed.

Assessment of Mass transfer process

The first step in our modeling was to verify that diffusion through the sediment bed was the rate determining process in the SPEED reactor. The dieldrin mass flux from sediment to the aqueous phase was used to understand the occurring mass transfer phenomena. The mass balance equation of dieldrin in the SPEED reactor is:

$$\frac{dC_{aq}(t)}{dt} = \frac{1}{V} \cdot \left(J(t) - C_{aq}(t) \cdot Q\right) \tag{5-1 }$$

where $C_{aq}(t)$ is the bulk aqueous dieldrin concentration [$g \cdot cm^{-3}$] at time t [s], V is the volume of the bulk aqueous phase in the SPEED reactor [400 cm^3], and Q is the applied flow rate [$cm^3 \cdot s^{-1}$]. The dieldrin mass flow rate J(t) from the organic particles to the bulk aqueous phase [$g \cdot s^{-1}$] is calculated as:

$$J(t) = \frac{dS(t)}{dt} \cdot V_{sed} \tag{ 5-2 }$$

where S(t) is the average dieldrin concentration of the sediment bed [$g \cdot cm^3{}_{bed}$] and V_{sed} is the volume of the sediment bed [cm^3]. The mass flux of dieldrin, $\Phi(t)$ [$g \cdot cm^{-2} \cdot s^{-1}$], will then be:

$$\Phi(t) = \frac{J(t)}{A_{bed}} \tag{ 5-3 }$$

where A_{bed} is the area of the bed/bulk interface [cm^2]. In case of a practical constant dieldrin concentration at the sediment/water interface, the mass flux of dieldrin can be calculated using the geometry of a semi-infinite slab [60]. The mass flux is a combination of 1D diffusion and retardation and can be calculated as:

$$\Phi(t) = \sqrt{\frac{D_{eff,bed}}{\pi \cdot t}} \cdot c^* \cdot \left(1 + \frac{K_{om}}{\varepsilon_b} \right) \qquad (5\text{-}4)$$

Where $D_{eff,bed}$ is the effective diffusivity of dieldrin in the sediment bed [$cm^2 \cdot s^{-1}$], c^* is the dieldrin concentration at the sediment/water interface [$g \cdot cm^{-3}$], K_{om} is the sorption coefficient of dieldrin to organic matter [$cm^3{}_{pw} \cdot cm^{-3}{}_{om}$], and ε_b is the sediment bed porosity [-]. K_{om} is the product of K_{oc} and ρ_b, where K_{oc} is the partitioning coefficient of dieldrin to the organic matter [$cm^3 \cdot g$] and ρ_b is the bulk density of the organic matter [$g \cdot cm^{-3}$]. In equation 5-4 all parameters but time are constant. Therefore mass transfer can only be modeled using the semi-infinite slab geometry when experimental results show:

$$\Phi \cdot \sqrt{t} = constant \qquad (5\text{-}5)$$

Modeling concept. For more realistic, complex situations like thin contaminated sediment layers, and variable dieldrin concentration on the sediment/water interface, or during disturbances of the sediment bed, the simple analytical model described in the previous paragraph cannot be used. We therefore extended the numerical model described in chapter 4. In our numerical model we distinguished 2 parallel diffusion steps: radial diffusion and bed diffusion. Radial diffusion is used to model dieldrin mass transfer through pores within organic particles (intra particle diffusion) to the surrounding sediment pores. The number of particles was calculated based on the volume fractions of the particle size distribution, the organic matter content and the amount of sample as was described before [84]. Bed diffusion (or inter particle diffusion) is used to model dieldrin mass transfer through pores of the sediment bed to the bulk aqueous phase. The sediment bed is therefore divided into several (model) layers. Desorption starts when the concentration of dieldrin in the bulk aqueous phase decreases.

Radial diffusion Radial diffusion within particles located in layer z in the sediment bed is modeled using the radial diffusion numerical model. Within this layer the mass flux of dieldrin from the organic particles to the sediment pore liquid, J(z,t), will be:

$$J(z,t) = \frac{dS(z,t)}{dt} \cdot V_{om}(z) = \sum_{i=1}^{k} N_{p,i}(z) \cdot \frac{d}{dt} \int_0^{R_i} 4\pi r^2 \cdot S'(z,r) \cdot dr \qquad (5\text{-}6)$$

where S(z,t) is the average dieldrin concentration of the organic particles [$g\cdot cm^{-3}_{particles}$] in model layer z at time t, $V_{om}(z)$ is the volume of organic particles in the model layer [$cm^{3}_{particles}$], $N_{p,i}(z)$ is the number of particles in layer z using k different particle size classes with radius R_i [cm], r is the location within the organic particle [cm], and S'(z,r) is the local total volumetric dieldrin concentration at location r [$g\cdot cm^{-3}_{particles}$] defined as:

$$S'(z,r) = \varepsilon_p \cdot c_{aq}(z,r) + (1-\varepsilon_p)\cdot s(z,r) \tag{5-7}$$

where ε_p is the porosity of the organic particles [$cm^{3}_{pw}\cdot cm^{-3}_{particles}$], $c_{aq}(z,r)$ is the dieldrin concentration within the pore liquid at location r [$g\cdot cm^{-3}_{pw}$], and s(z,r) is the dieldrin concentration of the organic matter at location r [$g\cdot cm^{-3}_{om}$]. Inside the particle we assume instant, local equilibrium based on a linear partitioning isotherm:

$$s(z,r) = K_{om}\cdot c_{aq}(z,r) \tag{5-8}$$

The change of the local concentration in time is then calculated by the radial diffusion model:

$$\frac{\delta S'(z,r)}{\delta t} = \varepsilon_p \cdot \frac{\delta c_{aq}(z,r)}{\delta t} + (1-\varepsilon_p)\cdot \frac{\delta s(z,r)}{\delta t} = \varepsilon_p \cdot \frac{D_{aq}}{\kappa}\cdot\left(\frac{\delta^2 c_{aq}(z,r)}{\delta r^2} + \frac{2}{r}\cdot\frac{\delta c_{aq}(z,r)}{\delta r}\right) \tag{5-9}$$

where D_{aq}/κ is the matrix diffusion coefficient of dieldrin in the aqueous phase corrected with tortuosity [$cm^{2}\cdot s^{-1}$]. Substitution of equations (5-7) and (5-8) into differential equation (5-9) leads to:

$$\frac{\delta S'(z,r)}{\delta t} = \frac{\varepsilon_p\cdot\dfrac{D_{aq}}{\kappa}}{\varepsilon_p + (1-\varepsilon_p)\cdot K_{om}}\cdot\left(\frac{\delta^2 S'(z,r)}{\delta r^2} + \frac{2}{r}\cdot\frac{\delta S'(z,r)}{\delta r}\right) \tag{5-10}$$

We assume a homogeneous distribution of dieldrin within the particles at t=0. Furthermore the dieldrin concentration at the interface of particles in a sediment layer is equal to the dieldrin concentration in that sediment pore water at that depth ($C_{aq,b}(z,t)$) and no dieldrin flux in the center of the particles. Initial and boundary conditions for equation (5-10) are therefore:

$$\frac{S'(z,r)}{(\varepsilon_p + (1-\varepsilon_p) \cdot \rho_{om} \cdot K_{om})} = C_{aq}(t=0) \qquad \text{for } 0 < r < R \qquad \text{(IC 1)}$$

$$\frac{S'(r=R)}{(\varepsilon_p + (1-\varepsilon_p) \cdot \rho_{om} \cdot K_{om})} = C_{aq,b}(z,t) \qquad \text{(BC 1)}$$

$$\left.\frac{\delta S'(z,r)}{\delta r}\right|_{r=0} = 0 \qquad \text{(BC 2)}$$

To approximate the solution we used a numerical integration method similar to the method described by Rügner [55]. A Crank Nicolson discretization scheme was used to transform the differential equation into a set of linear equations that can be solved according to LU decomposition. We used 61 space nods for sufficient resolution of the intra particle concentration of dieldrin [78].

Bed diffusion. Diffusion through the sediment bed is assumed to proceed solely through the pore water present between the particles. All layers with a modeled thickness of 250 µm were assumed to contain an equal number of particles, $N_{p,i}(z)$, with different diameter but identical physical/chemical properties. Other properties of a sediment layer, like bed porosity, tortuosity, and density were also assumed to be similar. Only the dieldrin concentration of the pore water between the particles, $C_{aq}(z,t)$ is allowed to vary in each layer (multilayer model). The relation between dieldrin in the particles and dieldrin in the sediment pore water is stated in (BC1). For every time step the amount of dieldrin entering or leaving the inter particle pore water is calculated using equation 11 where z=0 identifies the bottom of the sediment and z=Z the interface with the overlaying aqueous phase:

$$\frac{\delta C_{aq}(z,t)}{\delta t} = \varepsilon_{bed} \cdot \frac{D_{aq}}{\kappa_{bed}} \cdot \frac{\delta^2 C_{aq,b}(z,t)}{\delta z^2} + \frac{J(z,t)}{\varepsilon_{bed} \cdot A_{bed} \cdot \delta z} \qquad (5\text{-}11)$$

where ε_{bed} is the sediment bed porosity [$cm^3_{pw} \cdot cm^{-3}_{bed}$], and D_{aq}/κ_{bed} is the matrix diffusion coefficient of dieldrin in the aqueous phase corrected with tortuosity [$cm^2 \cdot s^{-1}$]. We assume a homogeneous distribution of dieldrin within the sediment bed at t=0. Furthermore the dieldrin concentration at the interface of the sediment bed is equal to the dieldrin concentration in the bulk aqueous phase and no dieldrin flux at the bottom of the sediment bed. Initial and boundary conditions will then be:

$$C_{aq}(z,t=0) = C_{aq}(t=0) \quad \text{for } 0 < z < Z \tag{IC 2}$$

$$\left. \frac{\delta C_{aq,b}(z,t)}{\delta z} \right|_{z=0} = 0 \tag{BC 3}$$

$$\left. C_{aq,b}(z,t) \right|_{z=Z} = C_{aq}(t) \tag{BC 4}$$

The system of equations 5-6 – 5-11 with their respective initial and boundary conditions was programmed in Matlab®.

5.3. Results and discussion

Flux calculation to validate diffusion from a semi-infinite plate. Measured concentrations of aqueous dieldrin in time were processed into relative fluxes to visualize the dieldrin mass flux in time for the thick and thin sediment beds (figure 5-1A and 5-1B).

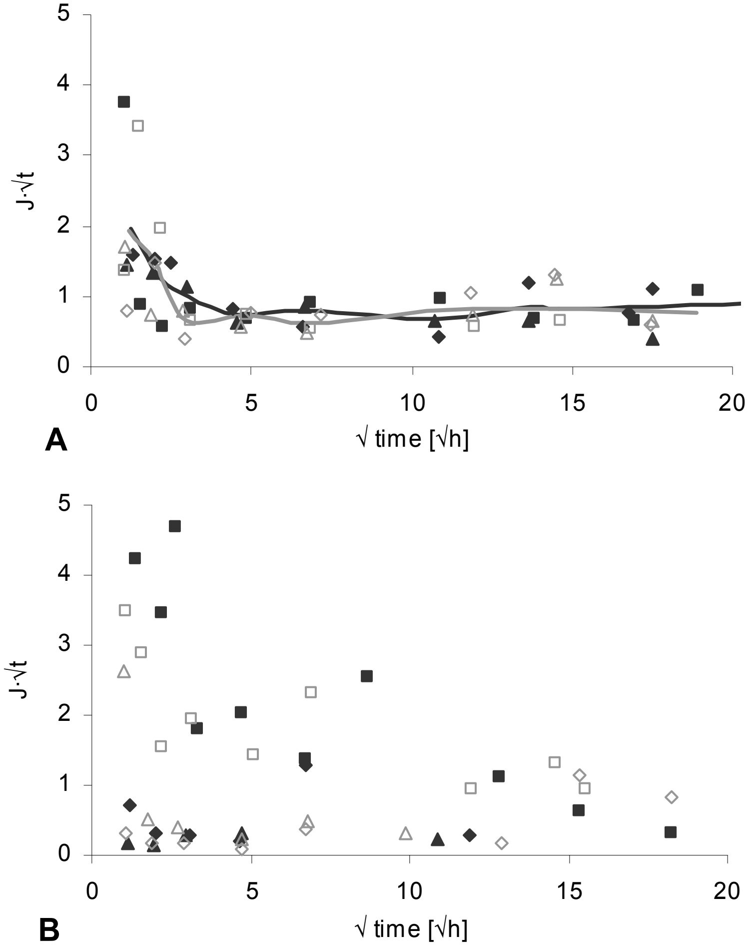

Figure 5-1: dieldrin mass flux of a thick (A) and a thin (B) sediment bed. Data is shown for duplicate experiments (solid markers and empty markers). Different desorption steps (each separated by a mixing event) are indicated as follows: ■,□ = 1st step of desorption, ♦,◊ = 2nd step of desorption, and ▲,Δ = 3rd step of desorption

At the start of every experiment, with a thick or thin sediment bed, a relatively high but decreasing dieldrin flux is seen. Regarding the thick sediment bed, after the initial start of the experiment and after each mixing (next desorption step), it requires approximately 3 volume refreshments, represented in figure 5-1A by √t ≈ 5, before the product index J√t is about constant, similar to the theory of diffusion from a semi-infinite slab. Although some dieldrin was obviously removed from the system (sediment bed and aqueous phase) no indication can be seen that the sediment bed is depleted. After mixing, desorption of the next step is about equal to the 1st step of desorption. The assumption that dieldrin mass transfer from a thick sediment bed can be described by diffusion from a semi-infinite slab was correct.

For sediments in a thin bed however, we observe a different behavior (figure 5-1B). The product index J√t decreases continuously, even after 3 volume refreshments. We therefore conclude that desorption of dieldrin from the thin sediment bed can not be described as diffusion from a semi-infinite plate. After mixing (next desorption step), desorption continued at the same low level as before mixing. The lack of flux enhancement after mixing suggest that no dieldrin was quickly available to increase the mass transfer and the bottom layer of the sediment bed is already starting to be depleted as can be the case with desorption from a finite slab. Analytical models of diffusion from a finite slab however also fail to describe the experimental data as we can see that desorption of dieldrin continued at a low, but not zero flux. Furthermore a relatively high concentration of dieldrin was found to be present in the sediment bed after the experiment was stopped which is in contrast to the model predicting that the sediment should be depleted from dieldrin when the flux continues to decrease. We therefore continued our modeling approach using the radial diffusion model with parallel 1D bed diffusion.

Diffusion from particles in the bed sediment. The numerical model was first tested for two conditions: with only one particle size (84 µm) and with the two particle sizes (10 µm and 84 µm) that dominated the particle size distribution as reported before [84]. Although both conditions gave overall reasonably good matches with experimental data, the fast decrease in the first few hours could only be approximated when small particles were present. Results of model runs using the radial diffusion model with two particle sizes and parallel 1D bed diffusion as well as measured data are displayed in figures 5-2 and 5-3 for the thick bed and the thin bed respectively. We distinct the concentration in the aqueous phase (A) and the solid phase (B). With measurable sediment properties like organic matter content, bed porosity, dieldrin concentration, and sample weight, and controllable system parameters (flow rate), the model provided a good match with the measured concentrations in the aqueous phase and the deduced concentrations in the sediment phase, while keeping other parameters constant for all experiments.

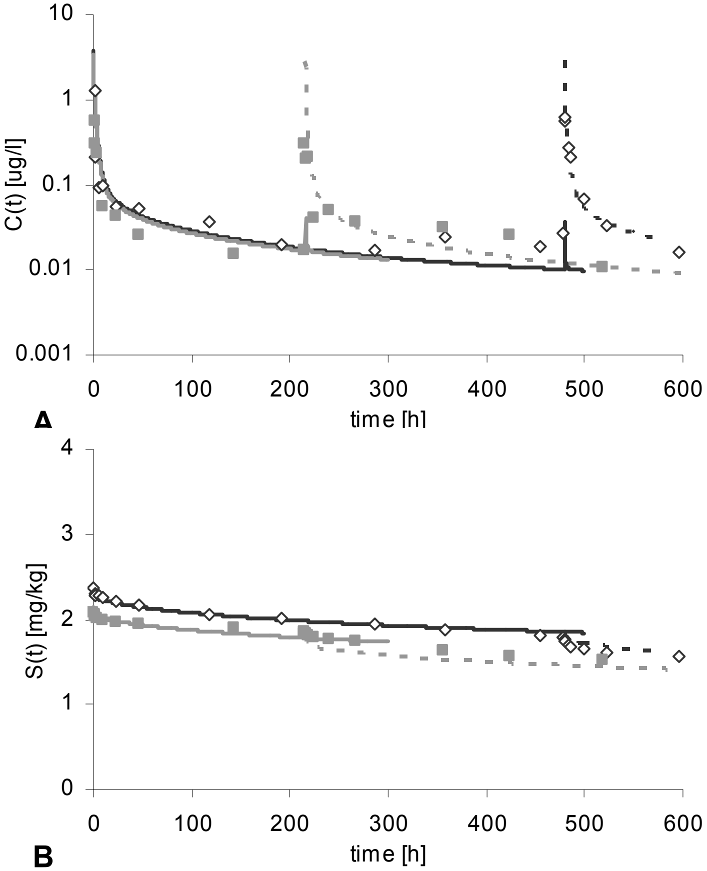

Figure 5-2: model results and measured concentrations in the aqueous phase (A) and sediment phase (B) using a thick bed. Duplicate experiments are depicted with black and grey. Markers are experimental data. Solid and dashed lines are model results for different conceptual models of mixing.

Mixing as a mimic of flooding was simulated in the numerical model with two different conceptual models. These two conceptual models can be considered as the minimum and maximum boundary of mixing and consequently the dieldrin redistribution. The first conceptual model describes mixing only as redistributing the dieldrin mass between pore water from the sediment bed and the bulk aqueous phase resulting in a higher dieldrin concentration in the bulk phase and a lower concentration in the pore water. Dieldrin concentration and the concentration gradient within sediment particles remained as they were before mixing and no additional desorption occurred. The results of this model concept are depicted as the peaks of the solid lines in figures 5-2 and 5-3. The second conceptual model describes mixing as a complete redistribution of the remaining dieldrin mass between the particles, the pore water, and the bulk aqueous phase. This equilibrium situation is similar as the initial situation at start of the experiment. The results of this model concept are depicted as the dashed lines in figures 5-2 and 5-3.

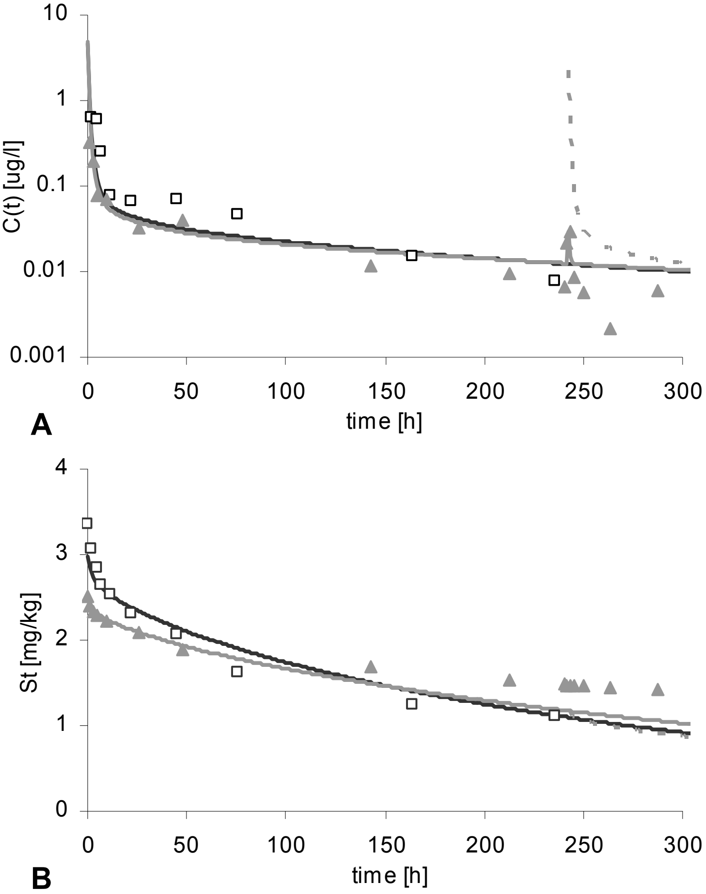

Figure 5-3: model results and measured concentrations in the aqueous phase (A) and sediment phase (B) using a thin bed. Duplicate experiments are depicted with black and grey. Markers are experimental data. Solid and dashed lines are model results for different conceptual models of mixing.

For the thick bed we can see that the first conceptual model failed to approach the measured concentrations. The dieldrin mass present in the sediments pore water was too low to increase the aqueous concentration to the level we measured in the experiments. Additional desorption by redistribution dieldrin as assumed in the second concept described the increase of dieldrin concentration in the aqueous phase much better, suggesting that only a small fraction of the particles in the sediment bed were indeed participating in the desorption process. The majority of particles remained unaffected. As the dieldrin flux from the bed sediments into the bulk liquid is small, the dieldrin remains available, posing a long term threat for spreading due to mixing through flood events or other reasons.

For the thin bed we can see that the first concept successfully simulates the experimental data. The measured dieldrin concentration after mixing was similar to the modeled concentration and no additional dieldrin desorption was required. In the experiment, sediment particles at the bottom of the sediment bed were probably starting to desorb, resulting in an absence of easily available dieldrin that can raise the aqueous concentration in the bulk water. Another aspect worth mentioning is the lower dieldrin concentration in the thin sediment bed after 300 hours compared to the thick bed, both experimentally measured and as outcome of the model runs. The faster decrease of dieldrin concentration in the sediment is the result of a limited replenishment of dieldrin from the lower sediment layers as both pore water concentration and sediment concentration are decreasing down to the bottom of the sediment bed.

The increasing difference in time of modeled and experimentally deduced dieldrin concentration of sediment in the thin bed (figure 5-3b) can be explained by the presence of larger particles. The importance of dieldrin desorption from larger particles increases as desorption continues after the pore water concentration at the bottom of the sediments decrease. Dieldrin can then only be transferred from particles. The sediment bed will become more like a suspension of particles as was described in chapter 4.

Sensitivity analysis and exploring engineering options for risk reduction. We performed a sensitivity analyses of the main model parameters: fraction organic matter, recycle flow rate, and bed porosity. This sensitivity analyses helps first of all to explore the relative importance of different model input on the outcome of the model as well as the stability of the model itself. Additionally, given the validity of the model, the analyses identifies the main parameters that can be adjusted to reduce risks of spreading HOC into the environment. Knowing these parameters and how they affect desorption rates enables us to select effective engineering options. The results of the sensitivity analyses are summarized in figure 5-4 for aqueous dieldrin concentration (top) and for sediment dieldrin concentration (lower).

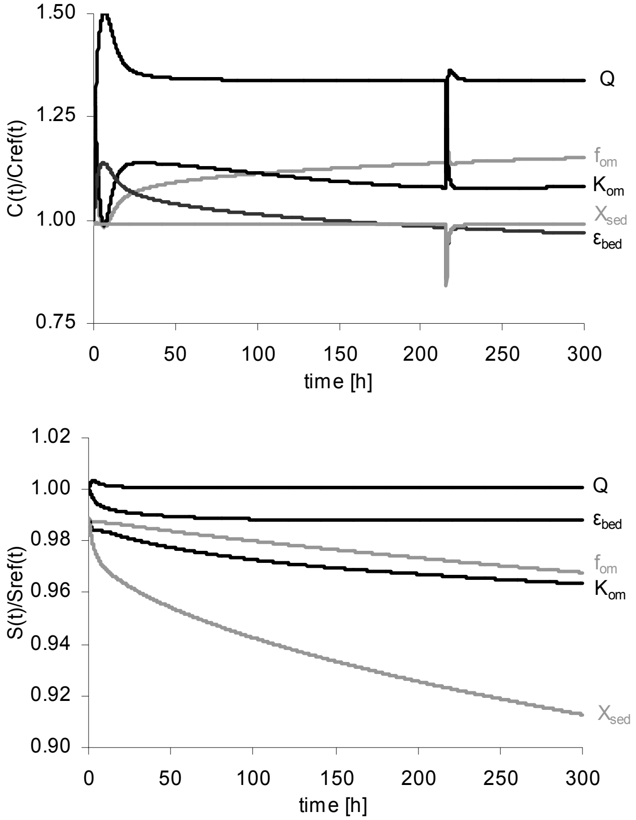

Figure 5-4: aqueous (a) and sediment (b) dieldrin concentration in proportion to a standard run for five parameters with a value of 75% of the standard parameter value except ε_{sed} (87.5% of ref. value).

In figure 5-4a we see that the value of flow rate (Q) has the largest impact on the dieldrin concentration of the bulk aqueous phase. A decrease of Q to 75% of the reference value results in an increase of ~30% of the aqueous concentration. On the other hand, a decrease of Q has a minor effect on the sediment concentration as can be seen in figure 5-4b; the increase of aqueous concentration is compensated with the decreased flow rate. The second largest impact was seen for K_{om} (up to 100h) and f_{om} (after 100h). The increase of aqueous concentration was however smaller than the applied step of -25%. For the sediment concentration, the largest impact was the amount of sediments (X_{sed}). A smaller amount of sediment lead to a faster decrease of dieldrin concentration, at least when the same flow rate was applied.

Engineering options to reduce risks for the aqueous environment should focus on a reduction of the aqueous concentration of HOC. Increasing the flow rate enhances dilution of the aqueous phase and has the largest effect to decrease aqueous concentrations locally. However, for persistent pollutants this will only result in a movement of contaminants from the sediments into the river and from there into the food chain. More sustainable will be the addition of organic matter with a high affinity to the contaminants (e.g. activated carbon). Adding organic matter will have positive effects on aqueous contaminant concentration both under “normal” conditions and during extreme situations like flooding. It should be noted that preferably large particles should be used as small particles will again approach equilibrium conditions quickly. Finally reducing the bed porosity by for example compaction will reduce aqueous contaminant concentrations on the long run.

In conclusion the physical models that we used in this study compared well to our experimental results, both for undisturbed and disturbed sediment beds. Therefore these models are valuable tools to design engineering options for risk reduction.

6

Usefulness of contaminant release models in risk assessment of polluted sediments

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6.1. Introduction

Sediments contaminated with organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) may cause serious environmental problems. To solve these problems a lot of research into remediation processes has been carried out during the last fifteen years. However, with exception of a very few, most remediation processes fail to be cost effective. This is one of the main reasons that is currently the management approach to solve the problem of contaminated sediments is moving from complete removal of pollutants to an approach that primarily based on risk assessment. One of the most important factors in this risk assessment is the potential of in situ release of pollutants from sediment layers. In risk assessment of sediment layers, but also in case of calamities, such as flooding where the sediment particles are transported with the flood as separate particles, it is of crucial importance to be able to predict the release of PAHs from these separate particles during transport. Mechanistic (and empirical) models can be very helpful to that aim. However, the development of mechanistic and empirical models for this release is rather limited. Further, the type, completeness, quality and the usefulness of these mechanistic models for practical application in remediation and in risk assessment vary strongly. Also the physical background used as basis for these models varies strongly [16, 85, 86].

The aim of this paper is to present mechanistic models that can be used in risk assessment approaches of polluted sediments. In that respect models are derived for the release of pollutants from single particles and from stagnant sediment layers. Also models are derived for assessment of the effectiveness of a protecting layer consisting of granular absorbing material to prevent release of pollutants from the sediment layer to the surface water. The emphasis in the derivation of these models is on its simplicity and the possibility to perform calculations with these models using input parameters that can easily be measured experimentally.

6.2. Characterization of polluted sediment particles

Polluted sediment is characterized by a very heterogeneous structure. The size and shape of the sediment particles and the composition of the particles vary strongly. According to conceptual models presented in literature three major sorption domains for the pollutants in the sediment particles can be distinguished: amorphous organic matter, condensed organic matter and micro-pores of mineral material [14].

Pollutants in the sediment particles such as PAHs can be present in several modifications: dissolved in the water phase inside the particles, absorbed into the organic matter, adsorbed to the pore walls in the sediment particles or present as a pure component. Models for transport of pollutants in or out single sediment particles described in literature and based on experimental results, show that two physical phenomena can be considered as important: the transport of the pollutant in the sediment particle and the affinity of the pollutant to the sediment material. The affinity can be characterized by an equilibrium constant K, defined as the ratio of the concentration of the pollutant in the water phase and the equilibrium concentration in the sediment particle or solid phase of the sediment particle. A high value of K means that the pollutant has a high affinity to the sediment particle. Transport of a pollutant in a sediment particle can very often be described by a diffusion process characterized by an (overall) effective diffusion coefficient D_p [82, 87]. This effective diffusion coefficient depends on the composition of the sediment particle and the interaction between the pollutant and the various components or phases present in the sediment particle. Three main types of particles will here be distinguished:

1. Homogeneous particles characterized by an effective diffusivity D_p.
2. Particles, containing water filled pores and in which the major part of the pollutants is present in the solid phase separating the pores. Assuming that equilibrium between water and solid phase in the particles and transport of pollutants out of the particles occurs via diffusion through the water phase only than it can be derived that the effective diffusivity is given by:

   $$D_p = \frac{D}{\left(1 + (1 - \varepsilon_p) \cdot K / \varepsilon_p\right) \cdot f_t}$$

   where ε_p is the volume fraction water in the particles and f_t the tortuosity factor of the pores in the particle and D in the diffusivity of the pollutant in the water phase.
3. Particles, containing water filled pores and in which the major part of the pollutants is adsorbed to the pore walls. It is assumed that the equilibrium between the concentration of pollutants in the water phase and the concentration of pollutants at the pore walls is characterized by an equilibrium constant and that transport of pollutants out of the particles occurs via diffusion through the water phase only. Then it can be derived that the effective diffusivity is given by:

   $$D_p = \frac{D}{(1 + K \cdot a_s / \varepsilon_p) \cdot f_t}$$

   where a_S is the specific surface area of the pore walls.

In the next paragraph the diffusion transport in particles will be characterized by D_p

6.3. Diffusion of pollutant from a single spherical particle

Consider a homogeneously polluted, spherical sediment particle present in a water phase of infinite volume. It is assumed that transport in the particle takes place by diffusion. The general equation for this transport is given by:

$$\frac{\partial C_p}{\partial t} = \frac{D_p}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial C_p}{\partial r} \qquad (6\text{-}1)$$

where C_p is the concentration of the pollutant in the particle, t is the time, D_p is the effective diffusivity of the pollutant in the particle and r the coordinate in the direction of transport. It is assumed that D_p is constant.

At the solid liquid interface the flux of pollutant into the water phase N_p is given by:

$$N_p = kC_i \qquad (6\text{-}2)$$

where k is the mass transfer coefficient in the water phase and C_i the concentration of the pollutant in the water phase at the interface. The mass transfer coefficient k depends on the flow conditions around the particle, which are characterized by the Reynolds number (Re):

$$Re = \rho V_p R_p / \eta \qquad (6\text{-}3)$$

where ρ is the density of the water phase, V_p the relative velocity between the particle and water phase, η the dynamic viscosity of the water phase, and R_p the particle radius. The value of k can be calculated from the following relationship:

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3} \qquad (6\text{-}4)$$

In this equation, Sh represents the Sherwood number, which is defined by $Sh=2kR_p/D$ and Sc represents the Schmidt number, which is defined by $Sc=\eta/\rho D$. D is the diffusivity of the pollutant in water. If Re < 1, which is the case for small particles and also for large particles if the relative velocity is small, then equation (6-4) can be simplified by:

$$Sh = 2kR_p / D = 2 \qquad (6\text{-}5)$$

The initial and boundary conditions of equation (6-1) are given by

$$C_p = C_{po} \qquad for\ t = 0\ and\ 0 \le r \le R_p \qquad (6\text{-}6)$$

$$-D_p \frac{\partial C_p}{\partial r} = kC_i \qquad for\ t > 0\ and\ r = R_p \qquad (6\text{-}7)$$

$$-D_p \frac{\partial C_p}{\partial r} = 0 \qquad for\ t > 0\ and\ r = 0 \tag{6-8}$$

The concentration Ci is in equilibrium with the concentration of the pollutant in the sediment particle at the solid/liquid interface. It is assumed that this equilibrium can be expressed by the equation:

$$KC_i = C_p \qquad for\ r = R_p \tag{6-9}$$

K is the equilibrium constant. With the initial and boundary conditions equation (6-1) can be solved analytically. From the solution it follows that E_p, defined as the ratio of the average concentration of the pollutant in the particle at time t and the initial concentration of the pollutant in the particle, is a function of two dimensionless parameters only, the Fourier number Fo_p and the Biot number Bi, defined respectively as:

$Fo_p = D_p t/R_p^2$ and $Bi = kR_p/KD_p$

The Biot number represents the ratio of the resistance for mass transfer inside the sediment particle, R_p/D_p, and the resistance for mass transfer in the surrounding water phase K/k. If Bi>20 then the mass transfer rate is mainly determined by the resistance for mass transfer inside the sediment particle. If Bi<0.1 then the mass transfer rate is primarily determined by the resistance for mass transfer in the surrounding water phase. Then the concentration of the pollutant in the particle is at each time t homogeneous. The exact solution of equation (6-1) is given by [60]. Graphically the solution of equation (6-1) is given in figure 6-1.

In general it can be concluded that for Bi>20 the value of E_p is determined by the Fourier number only and not by the flow conditions around the particle in the water phase. E_p can then be approximated with a high accuracy by:

$$\begin{aligned} E_p &= 1 - 6\sqrt{\frac{Fo_p}{\pi}} + 3Fo_p \quad for\ (Fo_p < 0.157) \\ E_p &= \frac{6}{\pi^2} exp\left(-\pi^2 Fo_p\right) \quad for\ (Fo_p \geq 0.157) \end{aligned} \tag{6-10}$$

For Bi <0.1 the value of E_p is dependent on both Fo_p and Bi. Then the concentration in the sediment particle can at each time be considered as almost homogeneously. In that case the decrease in the average concentration of the pollutant in the sediment particle, $\overline{C}_p$, is given by the differential equation:

$$\frac{4\pi}{3} R_p^3 \frac{d\overline{C}_p}{dt} = -4\pi \cdot R_p^2 \cdot kC_i \qquad (6\text{-}11)$$

Substitution of equation (6-9) in equation (6-11) results in:

$$\frac{4\pi}{3} R_p^3 \frac{d\overline{C}_p}{dt} = -4\pi \cdot R_p^2 \cdot kC_p / K \qquad (6\text{-}12)$$

Using the definitions of Fo_p and Bi the solution of equation (6-12) is given by:

$$E_p = exp(-3Fo_p \cdot Bi) \qquad (6\text{-}13)$$

Using figure 6-1 or the above mentioned equations it is possible to calculate the value of E_p as a function of time and therefore the release of a pollutant from the sediment particle as a function of time. To this end data for R_p, D_p, K and k are required.

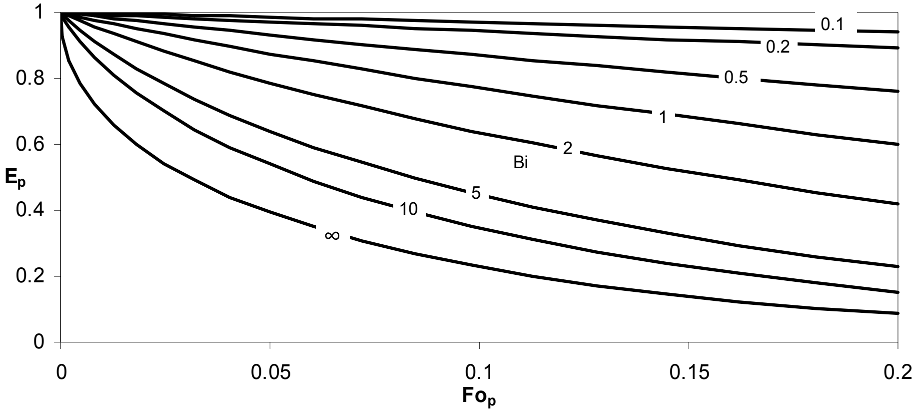

Figure 6-1: relative concentration in particle E_p as a function of Fo_p and Bi

6.4. Release of pollutants from a sediment layer

In Figure 6-2 a schematic representation of a polluted sediment layer with thickness L_s and covered with a protecting layer of thickness L_a is shown. First the sediment layer without protecting layer will be considered. The porosity of the layer is ε_s. The average radius of the sediment particles in the layer is R_p. It is assumed that the effective diffusivity of the pollutant in the sediment particles is D_p. Initially the concentration of the pollutant in the water phase between the particles is assumed to be zero. The sediment particles are considered as the main source for pollution. Further it is assumed that transport of pollutant in the layer occurs by diffusion through the water phase between the sediment particles only and that the tortuosity of the water filled pores between the sediment particles is f_s. There is no resistance for mass transport at the interface of sediment layer and water layer.

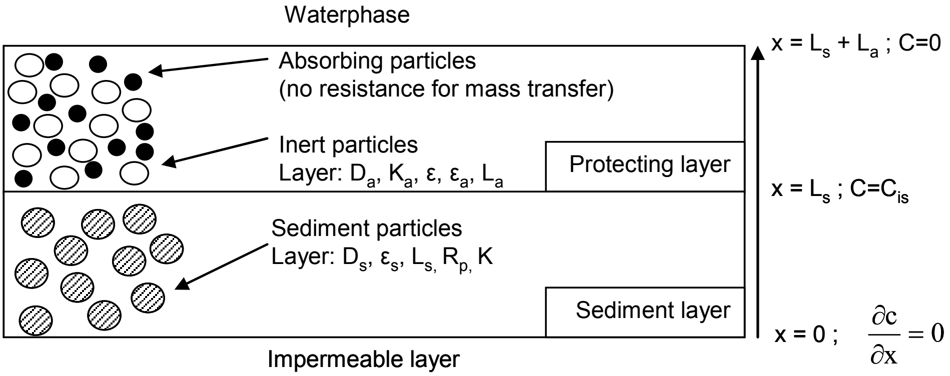

Figure 6-2: sediment layer covered by a protecting layer

Two extreme situations will now be considered: resistance for mass transfer inside the sediment particles can be neglected or resistance for mass transfer in the sediment layer between the sediment particles can be neglected.

If the resistance for mass transfer in the sediment particle can be neglected then transport of pollutant in the sediment layer can be described by the following diffusion equation:

$$\varepsilon_s \frac{\partial C}{\partial t} + (1-\varepsilon_s)\frac{\partial C_p}{dt} = \varepsilon_s \frac{D}{f_s}\frac{\partial^2 C}{\partial x^2} \qquad (6\text{-}14)$$

Equilibrium between the concentration of pollutant in the particles, C_p and the concentration of pollutant in the water phase, C, is assumed to be given by the equation:

$$C_p = KC \qquad (6\text{-}15)$$

Combination of equation (6-15) with equation (6-14) results in:

$$\frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial x^2} \qquad (6\text{-}16)$$

where the effective diffusivity D_s is defined as:

$$D_s = \frac{\varepsilon_s D}{(\varepsilon_s + (1-\varepsilon_s)K)f_s} \qquad (6\text{-}17)$$

The initial and boundary conditions for equation (6-16) are:

$$\begin{matrix} C = 0 \\ C_p = C_{po} \end{matrix} \qquad for\ t = 0\ and\ 0 = x = L_s \tag{6-18}$$

$$\frac{\partial C}{\partial x} = 0 \qquad for\ t \geq 0\ and\ x = 0 \tag{6-19}$$

$$C = 0 \qquad for\ t \geq 0\ and\ x = L_s \tag{6-20}$$

The ratio between the total amount of pollutant in the sediment layer per m^2 cross section area at time t and the total amount of pollutant present in the sediment layer per m^2 cross section area at t=0, E_s, is only a function of the Fourier number of the sediment layer, Fo_s, defined as $Fo_s = D_s t / L^2 s$ and is given by Crank [60]. The solution of equation (6-16) with the initial and boundary conditions can be approximated with a high accuracy by:

$$\begin{matrix} E_s = 1 - 2\sqrt{\dfrac{Fo_s}{\pi}} & (Fo_s < 0.213) \\ E_s = \dfrac{8}{\pi^2} exp(-\pi^2 Fo_s / 4) & (Fo_s \geq 0.213) \end{matrix} \tag{6-21}$$

In figure 6-3 the value of E_s is given as function of Fo_s. If the resistance for mass transfer in the layer between the sediment particles can be neglected then the relative release of pollutant from the sediment layer is equal to the relative release of pollutant from a single sediment particle. The relative release of pollutant from such a particle, with a concentration at the particle liquid interface which is approximately zero (no resistance for mass transport in the liquid phase) is given by equation (6-10).

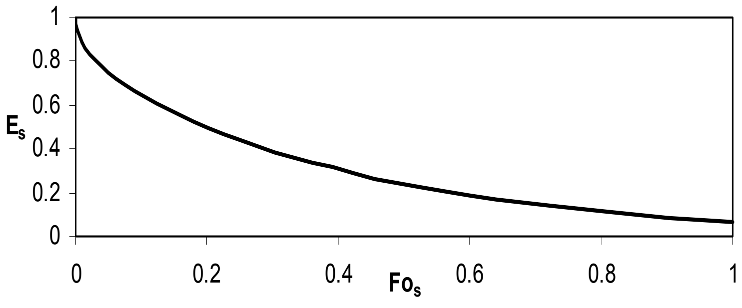

Figure 6-3: relative amount of pollutant in sediment layer E_s as a function of Fo_s

Whether resistance for mass transfer in the sediment particles determines the release of pollutants from the sediment layer or resistance for mass transfer between the sediment particles in the layer determines the release of pollutants depends on the ratio of the Fourier of the sediment particles Fo_p and the Fourier number of the layer Fo_s. Using the same time interval the ratio of Fo_p and Fo_s can be calculated. If $Fo_p/Fo_s >> 1$ then no effect of resistance for mass transfer in the particles on the release of the pollutant exists. Resistance for mass transfer in the layer is in fact governing the release of pollutant from the sediment layer to the water phase above the layer. If $Fo_p/Fo_s << 1$ then the resistance for mass transfer in the sediment particles is in fact governing the release of pollutant from the sediment layer to the water phase above the layer.

6.5. Transport of pollutants from a sediment layer covered by a protecting layer

Figure 6-2 shows also the situation that the polluted sediment layer is covered by a layer of a mixture of inert particles and absorbing particles. The absorbing layer reduces the release of pollutants from the sediment layer to the surface water by two mechanisms: formation of a resistance to mass transport of the pollutant to the water phase and formation of sinks for the pollutants entering the absorbing layer. It is assumed that the thickness of the sediment layer is L_s and the thickness of the granular layer at the top of the sediment layer is L_a. At the bottom of the sediment layer there is no release of pollutants from the sediment layer. It is further assumed that the concentration of pollutants at the top of the sediment layer in the water phase between the sediment particles is constant and equal to C_{is} and the concentration in the water phase at the top of the layer of absorbing material is equal to zero. Furthermore it is assumed that there is no resistance to mass transfer in the absorbing particles. In that case the layer has a maximum reducing effect on the release of pollutant from the sediment layer to the water phase.

Transport of pollutants in the granular absorbing layer takes place by molecular diffusion through the water filled pores between the particles. This diffusion process can be described by:

$$\varepsilon \frac{\partial C}{\partial t} + \varepsilon_a \frac{\partial C_a}{\partial t} = \varepsilon \frac{D}{f_a} \frac{\partial^2 C}{\partial x^2} \tag{6-22}$$

where x is the coordinate in the direction of transport, ε is the porosity of the absorbing layer, ε_a is the volume fraction of absorbing particles in this layer, D is the molecular diffusivity of the pollutants in the water phase between the absorbent particles and f_a is the tortuosity of the pores in the protecting layer. C_a is the concentration of the pollutant in the absorbing particles. It is further assumed that there is locally always equilibrium between the concentration of the pollutant in the liquid phase, C, and the concentration in the absorbent, Ca, and that this equilibrium can be described by:

$$C_a = K_a C \tag{6-23}$$

where K_a is the equilibrium constant. Substitution of equation (6-23) in equation (6-22) results in:

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2} \tag{6-24}$$

D_a is the effective diffusivity of the pollutant in the water phase of the granular layer, defined as:

$$D_a = \frac{\varepsilon D}{(\varepsilon + \varepsilon_a K_a) f_a} \tag{6-25}$$

The initial and boundary conditions of equation (6-25) are:

$$C=0 \quad \text{for } t = 0 \text{ and } L_s \le x \le L_a + L_s \tag{6-26}$$

$$C=0 \quad \text{for } t \ge 0 \text{ and } x = L_a + L_s \tag{6-27}$$

$$C=C_{is} \quad \text{for } t \ge 0 \text{ and } x = L_s \tag{6-28}$$

From equations (6-24 – 6-28) it can be calculated that the total amount of pollutant that passed 1 m^2 surface area of the granular layer and reached the water phase above the granular layer in time t, Q_t, is given by [60]:

$$Q_t = C_{is} L_a \left[Fo_a - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} e^{-n^2 \pi^2 Fo_a} \right] \tag{6-29}$$

or

$$Q_t = 2 C_{is} L_a \sum_{n=1}^{\infty} \left(2 \sqrt{\frac{Fo_a}{\pi}} e^{-\frac{(2n-1)^2}{4Fo_a}} - (2n-1) \operatorname{erfc}\left(\frac{2n-1}{2\sqrt{Fo_a}} \right) \right) \tag{6-30}$$

where Fo_a is the Fourier number of the absorbing layer, defined as:

$$Fo_a = D_a t/L_a^2 \tag{6-31}$$

The flux per second and per m^2 at the interface of granular layer into the water phase is:

$$N_a = \frac{dQ_t}{dt} \tag{6-32}$$

From equation (6-29), (6-30) and (6-32) the flux can be approximated with high accuracy by:

$$N_a = N_{am}\frac{2e^{-\frac{1}{4Fo_a}}}{\sqrt{\pi Fo_a}} \qquad (Fo_a < 0.237)$$

$$N_a = N_{am}\left(1 - 2e^{-\pi^2 Fo_a}\right) \qquad (Fo_a > 0.237) \tag{6-33}$$

N_{am} is defined as the maximum flux through the absorbing layer and is given by:

$$N_{am} = D_a C_{is}/L_a \tag{6-34}$$

There are several possibilities to calculate the protecting efficiency of the absorbing layer. One possibility is to define the breakthrough time as the time during which the flux N_a is lower than a certain fraction of the maximum flux, for example $N_a = 0.01N_{am}$. This breakthrough time t can be calculated as a function of ε, ε_a, K_a, L_a, f_a, D. Assume, for example, that $\varepsilon = 0.5$, $\varepsilon_a = 0.1$, $f_a = 2$, and $D = 10^{-5}$cm^2/s. In Figure 6-4a this breakthrough time (years) is given as a function of L_a and K_a. In Figure 6-4b this breakthrough time is given as a function of K_a and ε_a for a layer thickness $L_a = 50$ cm.

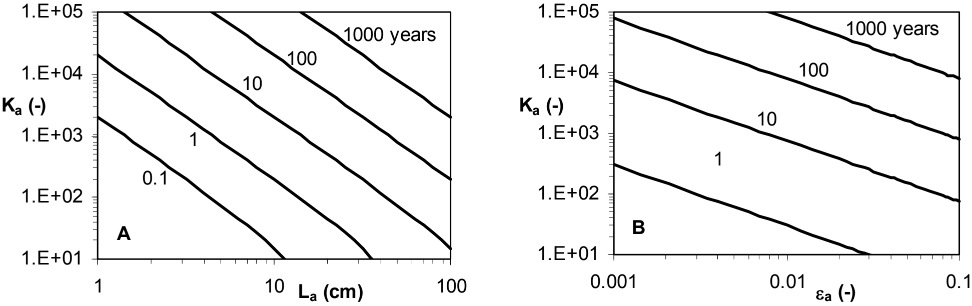

Figure 6-4: breakthrough time t as a function of Ka and La (A) and as a function of Ka and εa (B)

If the accepted breakthrough time is given and the value of K_a is known then the required layer thickness L_a can be calculated. In this respect it has to be noted that the ratio of the accepted flux N_a and the maximum flux N_{am} is also an independent external factor that can be changed. This also holds for the volume fraction of the absorbing material ε_a.

If there is a resistance for mass transfer in the sediment particles then C_{is} will be lower than in the situation that C_{is} is in equilibrium with the average concentration in the sediment particles. In that case the efficiency of the absorbing layer is higher and the operational life time of the layer is longer.

6.6. Discussion and conclusions

The observation from literature that transport of pollutants such as PAHs in sediment particles very often can be described as a diffusion process characterized by an effective diffusion coefficient and that the binding of pollutants to sediment material very often can be characterized by an equilibrium coefficient makes it possible to derive simple mathematical tools to estimate the release of pollutants from individual sediment particles. This release is governed by two dimensionless parameters, the Fourier number of the particles and the Biot number of the particles. Several methods can be used to measure the characteristic aspects of sediment particles such as size, size distribution, concentration of pollutants, effective diffusivity and equilibrium constant. The transport rate of a pollutant out of a sediment layer in case of a diffusion process can also be calculated in a simple way if the characteristic aspects of the sediment layer are known. This transport is characterized by the Fourier number of the sediment layer or the Fourier number of the separate sediment particles. In this way the environmental risks of a sediment layer can be estimated. Simple mathematical equations can also be derived for the efficiency of a protecting granular layer, partly consisting of granular strongly absorbing particles. These equations are also based on the Fourier number of the protecting layer, characterized by the layer thickness, effective diffusivity and absorption behavior of the pollutant.

The mathematical tools presented here are simple and do no correspond completely with reality. However, they can be used for calculating a first estimate. They can also be used for calculation of the effects of changes in assumptions or changes in process conditions. Together with experimental results and practical experience obtained elsewhere they provide a tool that can easily be applied if basic characteristics of polluted sediment particles, sediment layer and protecting layer are know. These basic characteristics can in general easily be measured. Further improvement of these tools is possible, for example taking into account particle size distribution. More precise calculation of the release of pollutants from sediment particles and sediment layers and the effect of protecting layers is of course possible but requires the measurement of numerous data and complicated time consuming calculations. In this respect it has also to be taken into account that sediment particles are seldom spherical, distribution of pollutants over all particles is in general not homogeneously and transport of pollutants in particles and layers does not always occur by diffusion. It is therefore doubtful whether estimates that can be made with more sophisticated and complicated mathematical tools might be substantially superior compared to the estimates obtained by these simplified mathematical tools.

7

Role of availability and biodegradability to determine emission control options for polluted sediments

This chapter is published in a modified form as:

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7.1. Introduction

In industrialized areas like Rotterdam harbor (NL) and the Bitterfeld region (Ger) but also in agricultural areas, soils and sediments received a high load of organic components. Among these components were PAHs and chlorinated pesticides like drins and DDT. Since the 1970's the direct flow of these materials to the water system is reduced due to a growing application of wastewater treatment and international restrictions in the use of persistent pesticides. These developments diminished the direct input of pesticides and possible harmful byproducts, however environmental quality is enduringly affected by the low environmental quality of the soil and sediment in these systems until the contaminants are contained from the surrounding environment or removed. Availability of organic contaminants plays a key role in selecting appropriate emission control options. The part of contaminants that is able to be released from the sediment to the aqueous phase in a limited time is in this paper defined as the available fraction. The availability concept can be used to assess risks in an ecotoxicological sense, e.g. [88, 89], but can also be used to predict final concentrations of organic contaminants after remediation actions, e.g. [65, 90, 91]. This study focuses on emission control of biodegradable PAHs and the persistent chlorinated pesticide DDT. Risks of these contaminants for potential receptors are strongly dependent on the availability of contaminants. Emission control of pollutants is then only necessary when the release rate and availability are too high.

Availability and Biodegradability of organic contaminants

Since the start of environmental legislation a system of target and risk values is constructed for pollutants in soils, sediments, and ground and surface water. Environmental samples are exhaustively extracted, analyzed and compared with appropriate target and risk values. This approach leads to an overestimation of risk, as part of the organic pollutants is strongly bound in geosorbents and not directly available for biota. This phenomenon is observed and studied within different fields of research e.g. ecotoxicology and environmental technology.

Since the late 1980s the phenomena of reduced availability of organic contaminants in different matrices is put under attention by several research groups, e.g. [20, 25, 30]. In contrast to the generally applied equilibrium partitioning theory, where concentrations in soils and sediments are linearly related to the aqueous concentration and sorption/desorption are assumed to take place instantaneous, these researchers found non linear sorption isotherms and non instantaneous sorption/desorption (hysteresis). Although the responsible processes for this reduced availability remain unresolved, several aspects seem to be generally valid.

- Contaminants present in low amounts (e.g. µg/kg) are strongly bound to the sorbents.
- Desorption rate is not constant. A short period of rapid desorption is followed by a long period of slow desorption.
- Prolonged contact between contaminants and sorbents reduces the fraction that can rapidly be desorbed.

For modelling purposes different approaches are used to describe this reduced availability for an assumed equilibrium condition. Equilibrium sorption can be described by Freundlich isotherms (equation 7-1) [20, 92] or a combination of Langmuir or Freundlich isotherms with a linear partitioning isotherm (equation 7-2) [92].

$$C_{s,i,e} = K_{f,i} \cdot C_{w,i,e}{}^{n_i} \qquad (7\text{-}1)$$

$$C_{s,i,e} = K_{p,i} \cdot C_{w,i,e} + K_{f,i} \cdot C_{w,i,e}{}^{n_i} \qquad (7\text{-}2)$$

Where $C_{s,i,e}$ and $C_{w,i,e}$ are equilibrium concentrations of compound i in sediment [$mg \cdot kg^{-1}$] and water [$mg \cdot l^{-1}$] respectively, $K_{f,i}$ and $K_{p,i}$ are the Freundlich [$mg^{1-n} \cdot l^{n} \cdot kg^{-1}$] and linear [$l \cdot kg^{-1}$] partitioning coefficient for compound i, and ni is the Freundlich exponential power [-] which is an indication of non-linearity of the sorption isotherm. In case that $n<1$ the equilibrium concentration of compound i in the sediment is nearly proportional to the concentration in the aqueous phase at low concentrations. At higher aqueous concentrations the equilibrium sediment concentration is lower compared to a linear isotherm.

For desorption kinetics a two compartment model, equation 7-3) is now widely used to fit experimental data [65]:

$$S_{t,i} = F_{rap,i} \cdot S_{0,i} \cdot e^{-k_{rap,i} \cdot t} + F_{slow,i} \cdot S_{0,i} \cdot e^{-k_{slow,i} \cdot t} \qquad (7\text{-}3)$$

Where $S_{t,i}$ [$mg \cdot kg^{-1}$] is the amount of compound i still present in or on the soil, $S_{0,i}$ [$mg \cdot kg^{-1}$] is the original concentration of compound i in the soil, $F_{rap,i}$ and $F_{slow,i}$ [-] are the fractions of compound i sorbed in or on the rapid and slow desorbing domain, $k_{rap,i}$ and $k_{slow,i}$ [h^{-1}] are rate constants for rapid and slow desorption and t is desorption time [h].

Several methods were developed to measure the availability or maximum release rate of pollutants in different environmental matrices. A method now widely used is the Tenax

Solid Phase Extraction (SPE) originally developed by Pignatello [30] and modified by Cornelissen [65]. With this method information on the maximum release rate and the amount of contaminants that can rapidly be released can be obtained and used to select effective management options regarding to risks of the present situation and risk reduction by mitigative measures.

Besides availability, also the degradability of contaminants is an important characteristic to determine optimal emission control measures leading to the required risk reduction. For example PAHs are known to be biodegradable under aerobic conditions whilst drins and DDT remain persistent for complete mineralisation even under ideal experimental conditions. The relation between availability and biodegradability is schematically presented in Figure 7-1.

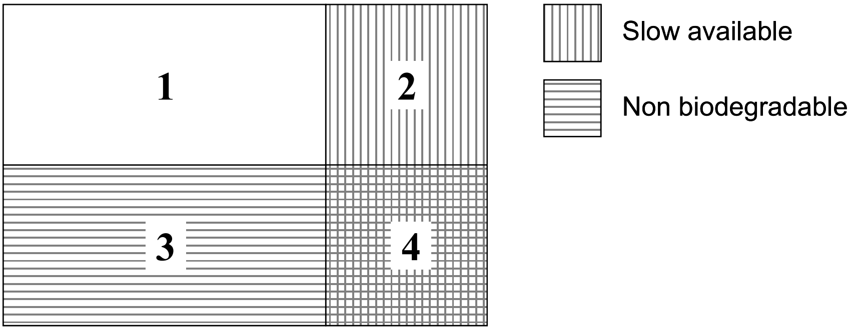


Figure 7-1: relation of availability and biodegradability [32]

Biodegradable contaminants (e.g. 2-4 ringed PAH) are positioned in groups I and II whereas persistent pollutants (e.g. DDT, drins, 5+ ring PAH) are positioned in groups III and IV. We hypothesize that from a risk based perspective groups 1 and 3 are of major interest because of their availability to species possibly resulting in negative and uptake in the food chain. However as contaminants in group I are biodegradable, risks can decrease in time in case that the environmental conditions are favourable for degradation.

Groups II and IV pose a lower risk compared to groups I and III as contaminants are not easily released and therefore less available to species. From a remediation perspective knowledge about the availability of degradable contaminants (groups I and II) is of importance as the availability will determine the residual concentration of contaminants after biological treatment or (monitored) natural attenuation [91].

Emission control options for polluted sediments

Strategies for emission control of contaminated sediments can focus on the source of contaminants, on the pathway between the source of contaminants and the receptor of interest, and on the receptor itself [93]. When concentrations of pollutants are (very) high, emission control at the source of the contaminant is preferred. Depending on the availability and degradability of the contaminants, ex-situ or in-situ remediation options can apply. Source remediation options are different for PAH and DDT because of differences in biodegradability. Biodegradable contaminants like PAH can be removed using biological methods (e.g. landfarming or Enhanced Natural Attenuation (ENA)) whereas persistent contaminants like DDT can only be removed using thermal and/or physical chemical separation methods.

When concentrations of pollutants are relatively low but mobility and availability are high, emission control in the path of contaminant transport is preferred. Emission reduction measures in the path of contaminant transport mainly focus on retardation of contaminants in the sediments.

7.2. Materials and methods

A sediment sample was taken from an orchard in the province of Zeeland (NL) and homogenized and sieved (2 mm) before use. To obtain total contaminant concentrations the sample was exhaustively extracted by acetone/hexane in triplicate.

Combined DDD, DDE, DDT, and PAH analysis.

The contaminants DDD, DDE, DDT, and PAH were extracted from soil samples and Tenax beads in a microwave (Milestone Ethos E, 20 minutes at 110 ºC) using 30 ml of acetone and hexane (1:1 Vol). After extraction acetone was removed by shaking the extract with demineralised water and collecting the hexane fraction. Contaminants were analyzed using a Trace GC with an EP-Sil 8 CB lowbleed/MS column (50m x 0.25mm x 0.12μm film thickness). Sample injection (1μl) was splitless (5 minutes) at a temperature of 250ºC. Helium was used as carrier gas at a constant flow (1.0 $\text{ml}\cdot\text{min}^{-1}$). The temperature program was 40°C for 4 min, increased at a rate of 10°C/min to 270°C, and then isothermal for 13 min. The detector, a Polaris Q, ion trap mass spectrometer (MS) had a constant temperature of 300ºC. Ionization was Electron Impact at 70 eV and detection was full scan. Calibration was multipoint, using external standards. Mass spectra were compared to the data of the NIST library (National institute for standards and technology, 1998).

Availability of DDD, DDE, DDT, and PAH in soil.

Tenax SPE was adopted from Cornelissen [65]. Samples were extracted in duplicate at a temperature of 20ºC. Samples (~2 g dry matter) were weighted into 50 ml separatory funnels together with 40 ml 0.01M $CaCl_2$ solution and 20 mg of NaN_3. After equilibration overnight 1.5 gram Tenax beads were added and funnels were horizontally shaken at 150 strokes per minute (spm). At selected times Tenax beads were replaced and the loaded Tenax was extracted as described in the analysis part. At the end of the experiment the remaining samples were extracted after removal of the supernatant by centrifugation for 10 minutes at 3000 rpm. The results of the extraction were fitted into the two-compartment model (equation 7-3) using the least sum of squares method.

7.3. Results and discussion

Availability of DDD, DDE, DDT, and PAH

Despite the age of pollution approximately 40% of PAH and 50% of DDE and DDT present in the original soil sample desorbed rapidly. Data of the Tenax SPE is presented in figures 7-2 and 7-3 for the two most abundant PAH congeners naphthalene and pyrene respectively. Data points are the measured results (duplicate) and the line is the model fit using the two compartment model.

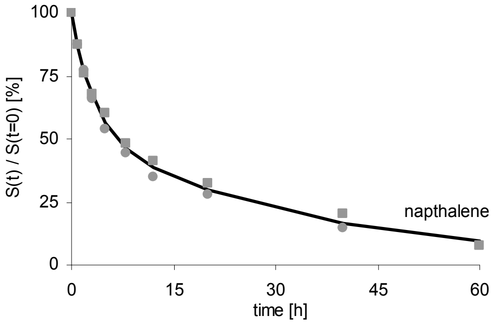


Figure 7-2: desorption naphthalene vs time

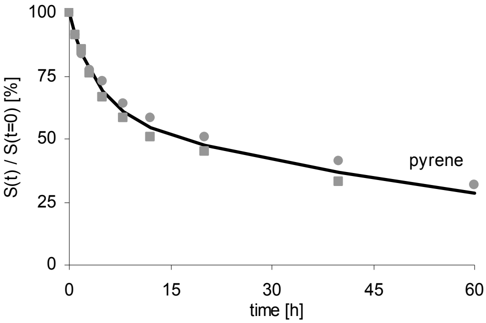
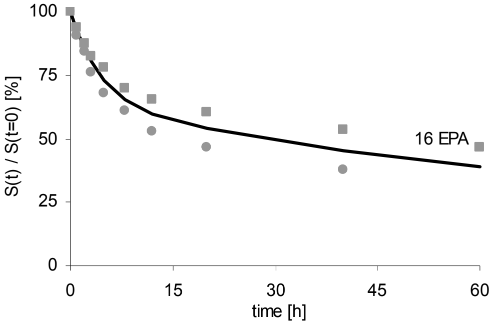


Figure 7-3: desorption pyrene vs time

Data of the Tenax SPE is presented in figures 7-4 and 7-5 for the 16 EPA PAH and the sum of DDE and DDT respectively.



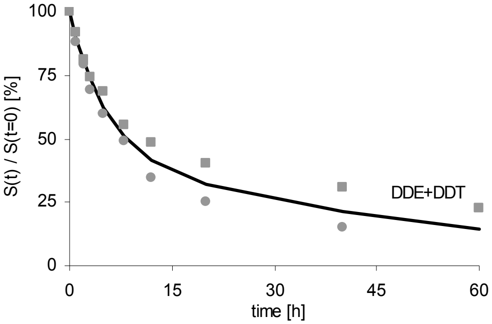


Figure 7-4: desorption 16 EPA PAH vs time

Figure 7-5: desorption DDE and DDT vs time

The initial concentrations of the two most abundant PAH (naphtalene and pyrene), 16 EPA PAH and the sum of DDE and DDT, as well as the parameters obtained from the model fit are summarized in table 7-1.

Table 7-1: results of Tenax SPE extraction of orchard sample

	S_0 [mg/kg	F_{rap} [%]	k_{rap} [h^{-1}]	F_{slow} [%]	k_{slow} [h^{-1}]	$S_{t=\infty}$ [mg/kg d.m.]
Naphtalene	1.91 ± 0.3	48	0.297	52	0.029	1
Pyrene	0.96 ± 0.02	39	0.243	61	0.013	0.58
PAH 16 EPA	6.08 ± 1.04	37	0.223	63	0.008	3.94
DDE+DDT	0.34 ± 0.01	54	0.198	46	0.020	0.16

From the data in table 7-1 we can calculate that 2.25 mg/kg d.m. of PAH and 0.18 mg/kg d.m. of DDE+DDT are rapidly available. Regarding the individual congeners it is clear that physical chemical properties of the contaminants have an influence on the behaviour of these compounds in the sediment. In contrast to the general conscience that PAH and DDT are attached strongly to the sediment matter, we demonstrate that a part of these contaminant can rapidly be released to the aqueous phase. These sediments can therefore act as a secondary source of contamination to the surface water or ground water. The fraction of DDE and DDT that can be release rapidly is higher than the rapid desorbing fraction of PAH. This might be related to the different properties of PAH and DDT but can also be the result of partial degradation of PAH in the field or to the origin of PAH in the sediment matter.

Emission control options for polluted sediments

The sediments studied in this paper were removed from the creek for nautical reasons and water quantity control reasons. However alternative emission control and remediation options can be distinguished for polluted sediments [94, 95]:

1. Direct disposal of sediments on the surrounding land. Allowed when concentrations of contaminants are low
2. Application as construction material. Allowed when concentrations of contaminants are low and leaching of these contaminants is limited.
3. Storage in temporal confined disposal sites. Useful to reduce the water content of the sediments. Some biological degradation of degradable organic compounds might occur because of the presence of oxygen during ripening.
4. Landfarming. Useful to enhance natural attenuation of biodegradable contaminants.
5. Particle size separation. This option is useful when contaminants are present in a specific particle size fraction. Reduction in polluted sediment volume can then be obtained
6. Cold immobilisation. This option reduces the availability and thus mobility of pollutants
7. Thermal immobilisation. This option reduces the availability and thus mobility of pollutants
8. Storage in confined disposal sites.

Depending on the biodegradability and availability of the contaminants in the polluted sediment the most suitable emission control and remediation option can be selected.

PAHs

For biodegradable organic contaminants, such as some PAHs, options 1 - 5 and 8 can be applied, depending on the concentration and availability as depicted in figure 7-6.

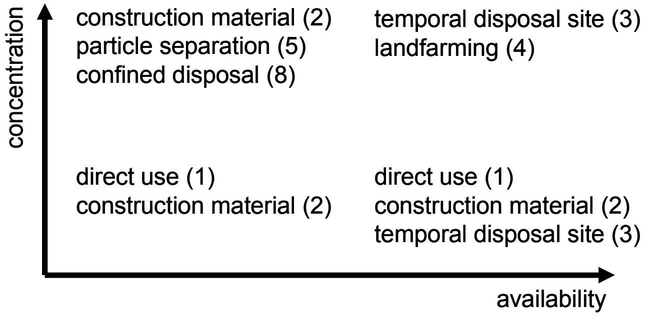


Figure 7-6: emission control options for PAH in relation to concentration and availability

Low concentration and low availability

Sediments containing PAH at a concentration below a selected risk value can directly be used (option 1) or applied as construction material (option 2). Risks for biota and spreading are limited because of the low concentration and low availability. Contaminants are likely to persist in the sediments and biological remediation options will not be effective to remediate the sediments completely.

Low concentration and high availability

Sediments containing PAH at a concentration below a selected risk value but with high availability can directly be used (option 1) or applied as construction material (option 2). Risk for biota is limited because of the low concentration. Contaminants are likely to degrade and biological remediation options can be effective to remediate the sediments completely (option 3).

High concentration and low availability

Sediments containing PAH at a concentration above a selected risk value but with a low availability can be applied as construction material (option 2), can be reduced in volume by particle separation (option 5), or can be disposed in a confined disposal site (option 8). Risks for biota are considered to be limited as these PAH are strongly bound to the sediment matrix. Ecotoxicological studies, like [88], have demonstrated the relation between the fraction of rapidly desorbing contaminants and concentration of these contaminants in animals. The slow desorbing contaminants did not affect the concentration of these compounds in animals. Furthermore it seems reasonable that biodegradable contaminants, once released to the aqueous phase, are biodegraded; reducing possible risks even more. Contaminants are likely to persist in the sediments and biological remediation options will not be effective to remediate the sediments completely.

High concentration and high availability

Sediments containing PAH at a concentration above a selected risk value and with a high availability can be treated using biological remediation options (options 3 and 4). Remaining PAH after treatment are expected to be strongly bound to the sediment matrix and risks for biota are considered to be limited. Contaminants are likely to degrade and biological remediation options can be effective to reduce risks by lowering the concentration.

This study showed that the sediment contained approximately 6 mg 16 EPA PAH per kg dry matter of which approximately 40% is rapidly available; leading to a residual concentration of 4 mg/kg d.m.. Based on PAH this sediment is classified to the group of low concentration and low availability. Risks for biota and spreading are limited and can be further reduced by ripening as oxygen will be present to degrade the available PAH. However PAH are expected to persist in the sediments as part of the PAH remains unavailable for degradation.

DDT

For non-biodegradable organic contaminants, such as DDT, options 1, 2, 5, 7, and 8 can be applied; depending on concentration as depicted in figure 7-7.

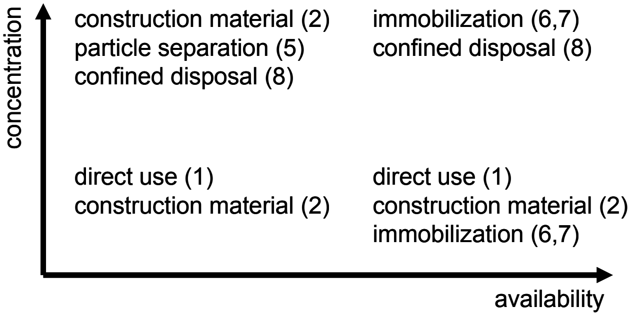


Figure 7-7: emission control options for DDT in relation to concentration and availability

Low concentration and low availability

Sediments containing DDT at a concentration below a selected risk value can directly be disposed (option 1) or applied as construction material (option 2). Risks for biota and spreading are limited because of the low concentration and low availability. Contaminants are likely to persist and biological remediation options will not be effective to remediate the sediments.

Low concentration and high availability

Sediments containing DDT at a concentration below a selected risk value but showing a high availability can be immobilized (option 6 and 7) before use (option 1) or be applied as construction material (option 2). Risk for biota is limited because of the low concentration but leaching can pose a risk. Contaminants are likely to persist and biological remediation options will not be effective to remediate the sediments.

High concentration and low availability

Sediments containing DDT at a concentration above a selected risk value but with a low availability can be applied as construction material (option 2), can be reduced in volume by particle separation (option 5), or can be disposed in a confined disposal site (option 8). Risks for biota are considered to be limited as the DDT is strongly bound to the sediment matrix. Contaminants are likely to persist and biological remediation options will not be effective to remediate the sediments.

High concentration and high availability

Sediments containing DDT at a concentration above a selected risk value and with a high availability can be immobilized (option 6 and 7) or can be disposed in a confined disposal site (option 8). Risks are high for biota and spreading in the environment as DDT persists and can be transported over vast distances. Direct exposure to the surrounding environment should be minimised. In situ confinement might be possible by installing hydraulic barriers or immobilisation barriers (e.g. activated carbon).

This study showed that the sediment contained approximately 0.34 mg DDE and DDT per gram of dry sediment of which approximately 50 % is available and might thus be available for uptake in the food-web and available for transport downstream. Based on DDT this sediment is classified to the group of low concentration and high availability. Risks for biota are limited because of the low concentration but leaching can pose a long term threat.

In this particular case it was decided to dredge the sediments and dispose the sediments on the lands surrounding the creek. These accepting lands were historically contaminated with DDT, and the concentration of both PAH and DDT is higher than the concentration in the sediments. Because of the relatively low concentration of PAH and DDT no special precautions were taken to immobilize the contaminants. The decision scheme presented in this paper is considered to be very useful when concentrations of contaminants are higher.

7.4. Conclusions

Availability and biodegradability are key-parameters to select appropriate emission control options. Different classes of contamination can be distinguished based on concentration, availability, and biodegradability of contaminants. Biological remediation such as natural attenuation and enhanced natural attenuation is effective when concentration and availability of the contaminants are high and micro-organisms are capable to degrade these contaminants. When availability is low, risks are expected to be limited both to biota and spreading in the surrounding environment. However when contaminants are non biodegradable but highly available a long term hazard can be expected and action is required to reduce the direct contact of biota to these sediments and to reduce the mobility of the contaminants.

Acknowledgements

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8

Summary, general discussion and conclusions

8.1. What was the purpose of the research and what did we do

With the predicted climate change it is expected that the chances of flooding increase. During flood events, sediments will resuspend and when these sediments are polluted, contaminants can be transferred to the surrounding water. But also under normal flowing regimes, when sediments are settled and form a sediment bed, transfer of contaminants to the overlaying water is possible. Release of contaminants from sediment particles to water is essential regarding fate and transport of these chemicals within the aqueous environment, especially when these contaminants are persistent towards (bio)degradation like Persistent Organic Pollutants (POP). Despite its importance, many aspects relevant to the mass transfer process of pollutants are not clear. Although our experimental work focused on sediment contaminated with dieldrin, one component from the POP group, the theoretical framework can be applied to soils and sediments contaminated with other Hydrophobic Organic Contaminants (HOC).

In this thesis we explore the mechanism of contaminant release from a field aged sediment towards the surrounding aqueous phase. The transfer of contaminants from the sediment to the aqueous phase is the first step in a sequence of processes. In case that this first step is the rate limiting process we speak of mass transfer limitation or reduced (bio)availability. Once in the aqueous phase, contaminants are available for resorption to relative clean sediment matter, (bio)degradation, volatization to air, and uptake by organisms. In chapter 2 we explored the relation between the release of different isomers of HexaChloroCyclohexane (HCH) from the sediment and the sequential (bio)degradation. Although HCH is strictly speaking no POP, it has, besides being biodegradable, other properties similar to compounds from the POP list. We found that (bio)availability indeed plays a role in the biodegradation of some HCH isomers although not solemnly. Environmental conditions (e.g. pH and Eh) and the presence of the right micro-organisms are at least as important for biodegradation as the potential of a contaminant to be transferred to the aqueous phase where biodegradation is assumed to take place. After 45 days of biodegradation not only a part of the available but also a part of the non available HCH was removed and degraded. This suggests that redistribution of HCH over the different fractions takes place. Mass transfer of HCH between the proposed fractions and the aqueous phase therefore plays a relevant role.

Contaminant mass transfer was studied in more detail with the SPEED reactor (Solid Phase Extraction with External Desorption) we developed. In this reactor, macro parameters like mixing intensity of the sediment/water system and flow (or dilution rate) of the aqueous phase can be controlled and low concentrations of dieldrin in the aqueous phase can be quantified. Experimental results of dieldrin release from a suspension of sediment particles obtained with the SPEED reactor are described in chapter 3. Dieldrin initially associated with the sediment particles can only reach the solid phase extractant through the aqueous phase. No direct contact between sediment particles and solid phase extractant is possible. Therefore dieldrin release from the sediment to the aqueous phase can be studied at various experimental conditions, like dilution rate or flow and mixing intensity. Dieldrin release from the sediments was assessed for three different situations, one situation simulating a flood event and two situations simulating less turbulent flow conditions. The flood event was mimicked by applying a high mixing intensity, resulting in a suspension of sediment particles. For the less turbulent flow conditions mixing of sediment particles was absent and sediment particles were present as a sediment bed. In line with the variable discharge rates in rivers, we performed experiments with different flow rates. We found that release of dieldrin in time is faster when higher flow rates were applied. However, the concentration of dieldrin in the aqueous phase was higher at lower flow rates. A larger time period that is available for desorption at lower flow rates, known as the hydraulic retention time, lead to an extended approach to equilibrium. Additional experiments with solid phase extraction showed that desorption rates of dieldrin from the sediment particles were faster for small particles compared to large particles. These observations suggest that the release of dieldrin is governed by mass transfer limitations within sediment particles.

Mass transfer within sediment particles suspended in water is mathematically described by a bi-disperse radial diffusion model in chapter 4. Starting from a situation where contaminants in the aqueous phase are in equilibrium with the suspended sediment particles, the bulk aqueous phase simply starts to be diluted when flow commences. This dilution leads to a decrease of aqueous dieldrin concentration that is partly compensated by an initially rapid release of dieldrin from the sediment particles. This rapid release slows down when more dieldrin is removed. A simple radial diffusion model with an average particle diameter can not describe the desorption behavior we observed during experiments with real, field contaminated sediments. The observed rapid release is underestimated by the simple diffusion model and the observed slow release is overestimated. When the experimentally measured bi-disperse particle size distribution is included in the model, the experimentally measured desorption results can be successfully modeled. Rapid release is mainly the result of the presence of small particles (10 μm) whereas slow release of dieldrin is mainly controlled by larger particles (84 μm).

In sorption experiments, where limited time is available to reach equilibrium, mass transfer limitations may influence the shape of isotherms. Physical properties of the sediment, other than the affinity towards a sorbate, might bias the results. Compared to complex and time consuming experiments targeted to find specific high affinity sorption sites like black carbon as rationale of the (very) slow release of hydrophobic organic contaminants, our findings suggest that a very simple and rapid particle size distribution analysis can largely predict the release rates of contaminants from numerous sediment particles to the surrounding water. Even more, contaminant release can be studied, and modeled, for various cases occurring in the field, like the release from sediment beds under normal and under disturbed situations. On a sub-particle scale, fundamental knowledge regarding molecular sorption and equilibrium conditions between contaminants and a variety of (geo)sorbents is however essential as these determine the equilibrium distribution of contaminants between different phases and thereby the driving force of diffusion within the sediment particles when equilibrium is not present.

In Chapter 5 experimental results of dieldrin release from sediment beds in the SPEED reactor are presented. We demonstrate that dieldrin release from thick sediment beds behave similar as was predicted by an analytical diffusion equation using the geometry of a semi-infinite slab when initially the contaminants in the sediment and the aqueous phase are in equilibrium. However, at the time when the dieldrin flux from the underlying interstitial pore water (vertical direction) is smaller than the dieldrin flux from the particles to the interstitial pore water (horizontal direction), a semi-infinite slab does not fulfill the required geometry. Diffusion from individual particles, like in a suspension, then describes the overall release of dieldrin better than diffusion from the semi-infinite slab.

We conclude that in dynamic environments with some mixing, like rivers, harbors, and the marine environment, the size of sediment particles is a key parameter that determines the release rate of dieldrin and other hydrophobic organic contaminants from the sediment to the aqueous phase. Besides sediment properties like particle size distribution, contaminant concentration, and organic matter content, it depends on properties of the receiving system, e.g. interaction/mixing, dilution, whether the release of contaminants will lead to risks.

8.2. What is the contribution of this research to risk assessment of contaminated sediments?

Risk assessment of contaminated sediments comprises two fundaments: exposure assessment and effects assessment. Exposure assessments generally involves estimating contaminant emission from a source of contamination, the pathways from a source to the receptor of interest and sink terms like biodegradation in order to obtain concentrations or doses to which humans, populations of other species, or environmental compartments are or may be exposed. It also describes the nature and size of populations or compartments exposed to a contaminant, and the magnitude and duration of their exposure. Effects assessment or, more precisely, dose-response assessment, is the estimation of the relationship between the dose or level of exposure to a contaminant, and the incidence and severity of an effect [96]. Exposure assessment and effects assessment are thus linked by the dose of contaminant. Estimating the dose is a major difficulty in risk assessment, especially in a multiphase system like the sediment/aquatic system. Sediment quality standards are mainly derived from data on dose-response relationships from single-species tests with aquatic organisms. Extrapolation of these data to sediment or soil concentrations is performed on the basis of the equilibrium partitioning model [46, 97, 98]. Implicitly it is assumed that equilibrium between compartments like sediment and water is reached immediately. However, as Sijm et al. state: “Often there is no direct link between the extent of bioaccumulation or toxicity, and the concentration of a contaminant in the environment. It is the aspect of bioavailability that determines whether a contaminant is actually taken up and able to exert toxicity” [99].

In the aquatic system the free concentration of contaminants in water is generally assumed to be the key parameter regarding aquatic toxicity [89, 98, 100]. Although this concept is theoretically elegant and explicitly excludes the bioavailability issue, the practice is troublesome as the free concentration is not only difficult to measure but also depends on system properties like temperature, the presence of sorbents, dilution of the aqueous phase, mixing intensity and temporal variations of these properties. The main disadvantage of current exposure assessments is the static nature of the models that are currently used for this purpose [97]. When only parameters like contaminant concentration in a single phase, bioavailable fraction and isotherms are used, only some equilibrium situation can be assessed. Applying dynamic processes, like mass transfer and (bio)degradation and integrating these processes over time (exposure time) will help to develop more realistic risk assessment tools. Contaminant fluxes (mass transfer per time) rather then contaminant concentrations enable us to include exposure times and system specific properties like dilution. This research provides a structure to use fluxes and it provides additional data and insights of the mechanistic processes that can be used in risk assessment studies. Using this flux based approach we can distinct different aqueous systems: open (e.g. rivers) vs closed (e.g. ponds) systems, but also sediment beds with and without advective water flow through the sediments. Contaminant fluxes are also related to mixing intensity as we demonstrate in chapter 5.

The operational difference between open and closed systems is that closed systems have no input or output of contaminants, water, and sediments. In the case that also no degradation of the contaminants can occur, time is available for redistribution of contaminants over all phases until (dynamic) equilibrium is reached. In the field these closed systems can be found as hydrological isolated ponds or lakes and in the subsoil if groundwater flow is absent. In these systems, mixing and disturbances of the sediment bed will not have an effect on the concentration of contaminants in the aqueous phase once equilibrium is reached. In open systems, where input or output of contaminants, water, and sediment particles is expected or where physical conditions allow degradation of the contaminants, equilibrium will not be reached and aqueous concentrations depend therefore on mass transfer between the different phases. Identifying the rate limiting step (flux) is crucial to understand the potential risk of these systems, especially considering the impact of external factors like flooding and dredging. In chapters 3 and 4, where we describe the release of dieldrin from a sediment suspension, the rate limiting step is diffusion of dieldrin within the sediment particles. As the contaminant flux is limited by the intraparticle diffusion, increasing the flow rate leads to a decrease of dieldrin concentration in the aqueous phase. Decreasing the particle size by grinding, erosion or degradation of organic material will enhance the mass flux of contaminants from the particles to the aqueous phase. In chapter 5, where we explore the release of dieldrin from a sediment bed, the rate limiting step is initially the mass transfer of dieldrin within the sediment bed itself. When contaminant release proceeds, the rate limiting step shifts towards diffusion of dieldrin within sediment particles. As long as diffusion within the sediment bed is the rate limiting step, disturbances of the sediment bed by mixing or by applying an advective flow through the sediment bed will lead to an increase of contaminant release.

Flux based risk assessment is also beneficial to estimate long range transfer of persistent and non persistent contaminants in river systems, from the source of contamination to the harbor and further towards the marine system or through the atmosphere [1]. Persistent contaminants are found present on a global scale, even where the chemicals were never applied [101]. Current transport models of hydrophobic organic pollutants in a river system usually focus on the transport of the polluted sediments themselves. This might lead to an underestimation of the total mass transport of these contaminants in the waterbody. Convective transport of free dissolved pollutants might play an important role in overall transport of contaminants. Limitations in the detection and analysis of (very) low concentrations of freely dissolved organic pollutants in water might contribute to the possible underestimation of contaminant mass transport in aquatic systems. Although concentrations of pollutants in the aqueous phase might be very low the overall mass transport can be substantial as large volumes of water can be in contact with (polluted) sediments, especially in the case of flooding when sediment particles and water form a suspension. When the release of, especially persistent, contaminants can be quantified, for point sources as well as for diffuse contaminations, better understanding of the impact of long range transport can be obtained and strategies towards effective emission control can be applied.

8.3. What is its contribution to mitigation measures for contaminated sediment?

The main purpose of any mitigation measures should be the protection of any actual or potential receptor of interest. Results obtained during the risk assessment, both exposure and effects, can be used to select appropriate measures to control the emission of contaminants towards the receptor. Strategies for emission control of contaminated sediments can therefore focus on the source of contaminants, on the pathway between the source of contaminants and the receptor of interest, and on the receptor itself. It merely depends on the receptor of interest what the most effective strategy will be regarding financial, ecological, environmental, and technological aspects. As is presented in chapter 6, when risks are immediate, measures at the source can be interesting. However, when contaminants originate from diffuse sources reducing or eliminating the pathway towards the receptors is probably more effective.

Measures at the source of contamination imply contaminant mass reduction. This contaminant mass reduction can be reached by in situ bioremediation, contaminant removal through excavation or dredging, and physical/chemical reactions. Measures in the pathway between source and receptor require reduction or elimination of the contaminant flux. This reduction can be the result of a complete physical isolation of the source of contaminants, hydrological isolation measures, transport retardation, and contaminant break down within the pathway. Measures at the receptor are more political driven and include the change of function of a receptor, for example terminating drinking water production when risks of water contamination are to be expected or prohibit recreational activities like swimming and scuba diving. The choice of an effective risk reduction strategy should at least consider the different mass fluxes, from sediments to the aqueous phase, and the fate of contaminants once present in the aqueous phase, including the (bio)degradability of the contaminant. Similar to risk assessment, identifying the rate determining process will greatly enhance the understanding of the system and enables problem owners to select an optimal risk reduction strategy.

In closed systems, all contaminants will eventually reach a dynamic equilibrium. In equilibrium, net fluxes between different phases are zero and only the concentration of contaminants in different phases is relevant. Risks can be present locally, e.g. within the closed system. Depots and isolated sites are examples of closed systems. When actual risks in any of the phases are too high for the allocated function, preferential risk reduction measures are contaminant mass reduction (in-situ/ex-situ) and opening the system. Opening the system essentially dilutes the contaminant. Examples are the addition of a new physical phase that will bind the contaminants (e.g. activated carbon) and the introduction of an aqueous flow through the system. Dilution will decrease contaminant concentrations in all phases that were initially present. However, in the added physical or aqueous phase the concentration of contaminants will increase. How rapid the new equilibrium will be reached or what the concentration in the aqueous phase will be, depends on the mass flux between initially present contaminated phases and the newly introduced phase.

In open systems, or systems that have been opened, equilibrium will not be reached, only a steady state might be approached. The work presented in this thesis helps to quantify contaminant mass fluxes and estimates expected doses of contaminants in the aqueous phase before and after mitigation measures. Complete removal of contaminants will certainly reduce contaminant release from the source but is economically, and probably ecologically and technologically, rarely feasible. Taking measures within the pathway is a good alternative. Considering the transfer of contaminants from a sediment bed towards the aqueous phase, preventing the resuspension of sediment particles will reduce the release of contaminants during flooding or erosion. Capping the contaminated sediments is then an effective option. When an advective flow passes the contaminated sediments, hydrological measures, like compacting the sediment bed will reduce the contact between water and contaminated sediments thereby reducing the mass flux out of the sediment bed. Mass flux reduction can further be enhanced by increasing the affinity of the contaminant by addition of a new physical phase that will bind contaminants. These options will especially be beneficial when contaminants are expected to be persistent at the source or in the pathway (e.g. river). On the other hand, risk reduction of degradable contaminants can be obtained by increasing the mass flux from sediments to the aqueous phases as long as toxic thresholds are not exceeded. An alternative to prevent the advective flow going through the contaminated sediments is to reroute relative clean water around the contaminated sediment. This can be done for example by creating more permeable short cuts within the sediment or by discharging the water flow from below the sediments.

Selecting effective emission control strategies thus requires knowledge of the mass fluxes between the various phases present in the aquatic system, and the identification of the receptors of interest.

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Nederlandse samenvatting

Door de voorspelde klimaatverandering is de kans groot dat we vaker te maken krijgen met overstromingen, zowel door rivieren als door zee. Tijdens overstromingen zullen sedimenten die normaal op de bodem van het waterlichaam liggen, of in de uiterwaarden, worden opgewerveld en als suspensie worden meegenomen door het water. Als deze sedimenten verontreinigd zijn, kunnen de verontreinigende stoffen uit de sedimentdeeltjes vrijkomen en in het water worden opgelost. Ook onder normale, rustiger stromingscondities kunnen verontreinigingen vrijkomen, zij het minder snel dan tijdens overstromingen. Het vrijkomen van verontreinigingen uit sedimenten is de eerste stap in een serie van mogelijke processen, zoals afbraak of opname in de voedselketen. De snelheid waarmee de verontreinigende stoffen vrijkomen is onderzocht met een reactor die wij speciaal voor dit doel hebben ontwikkeld. In deze reactor –de SPEED reactor– kunnen mengintensiteit en stromingssnelheid of verdunningssnelheid worden ingesteld zodat verschillende stromingscondities kunnen worden nagebootst. Ook is het met deze reactor mogelijk om zeer lage concentraties van verontreinigingen in het water te meten. In dit proefschrift is voornamelijk gewerkt met dieldrin, een persistente organische stof die in het verleden gebruikt is als insectenverdelger.

In de experimenten die zijn uitgevoerd is gebleken dat de snelheid waarmee dieldrin vrijkomt uit een suspensie van sediment deeltjes bepaald wordt door de diffusiesnelheid in de sedimentdeeltjes. Vergelijkbaar met de diffusiewetten van Fick zijn het concentratieverschil in de sedimentdeeltjes en de diffusieafstand (deeltjesgrootte) de snelheidsbepalende parameters. Bij een hoge verdunningssnelheid van het water wordt de dieldrin concentratie in het water lager en komt per tijdseenheid meer dieldrin vrij dan bij een lage verdunningssnelheid. Aanvullende experimenten laten zien dat de snelheid ook groter is als kleinere sedimentdeeltjes aanwezig zijn. Met een diffusiemodel, waarbij rekening is gehouden met de deeltjesgrootteverdeling, was het mogelijk om het concentratieverloop van de experimenten goed na te bootsen. Het vrijkomen van dieldrin uit een sediment bed is lastiger te beschrijven omdat dan ook rekening moet worden gehouden met een diffusieweerstand in de ruimtes tussen de sediment deeltjes. Het blijkt dat deze weerstand over het algemeen belangrijker is voor het vrijkomen van dieldrin uit het sediment dan de diffusieweerstand in de individuele sediment deeltjes. Alleen als dieldrin in de ruimte tussen de deeltjes bijna is verdwenen, is de diffusie uit de individuele sediment deeltjes het snelheid bepalende proces.

Wij concluderen dat in watersystemen waarin enige vorm van menging plaatsvindt, zoals in rivieren, in havens en op zee, de deeltjesgrootte een belangrijke rol speelt in de snelheid waarmee dit soort verontreinigingen vrijkomen. De eigenschappen van het sediment (deeltjesgrootteverdeling, concentratie van verontreinigende stoffen en het gehalte aan organische stof) maar ook de eigenschappen van het ontvangende watersysteem (mengintensiteit, stromingssnelheid) bepalen uiteindelijk of dit vrijkomen van verontreinigingen leidt tot daadwerkelijke risico's voor aanwezige receptoren.

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Martijn

About the author (curiculum vitae)

Martijn Pieter Jaap Smit was born on Sunday February 24th 1974 in Enschede (the Netherlands). After graduation at "Scholengemeenschap Zuid" in Enschede he started his study milieuhygiene at Wageningen University in 1992. In 1999 he received his master degree with the specialization environmental technology. Until the start of his PhD in 2002 he worked for several private companies as consultant in the field of soil research and remediation. Since January 2007 Martijn works as consultant for TTE (The Three Engineers) in Deventer where his focus is on sustainability, energy, and the relation with complex soil processes.

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