

Sediments, Section 1: Sediment quality and impact assessment

Research Article

Desorption of Dieldrin from Field Aged Sediments: Simulating Flood Events

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Abstract

Background, Aim and Scope. With the predicted climate change, it is expected that the chances of flooding may 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. The distribution of POPs between sorbed and aqueous phases and the time needed to obtain equilibrium are required to calculate the exposure to potential receptors. A reactor was designed in which the water flow is controlled and low POP concentrations could be measured by tenax extraction outside the reactor vessel. This reactor design named SPEED (Solid Phase Extraction with External Desorption) was used to study desorption from aged contaminated sediment in relation to sediment particle size.

Materials and Methods. In the newly developed SPEED (Solid Phase Extraction with External Desorption) reactor, the water flow rate was set and controlled, and low aqueous POP concentrations were measured by sorption to Tenax® outside the reaction vessel. The effect of particle size on desorption rate was studied using a widely used Tenax® solid phase extraction method.

Results. The experiments, by specific measurement of the aqueous dieldrin concentration at different HRT, show that desorption of dieldrin in time is faster when short HRTs were applied. However, the mass of dieldrin desorbed per liter refreshed water is higher for longer HRTs. Therefore, the mass transfer of dieldrin within the sediment particles is the rate determining process in contaminant desorption. This observation was confirmed by Tenax® solid phase extractions which were applied for different particle size fractions. Desorption rates of POPs from the sediment fraction with small particles were faster than desorption rates from the sediment fraction with large particles. Organic matter was present as separate particles in the sediment sample. All experiments demonstrated biphasic desorption. The fluxes calculated for both phases are supportive of non-stationary diffusion as the main process of mass transfer.

Discussion. In the literature, the relation between particle size and desorption of organic contaminants from soils and sediments is contradictory. Most often this seems to be due to overlooking the spatial configuration of organic matter in the soils and sediments. In several papers the presence of organic matter as a thin coating around mineral particles has been overlooked. There-

fore, milling had no effect on desorption behavior of contaminants, as the diffusion length will not be affected. In our opinion, both the particle size and spatial configuration of organic matter are rate determining parameters of the desorption process.

Conclusions. 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. Furthermore, the diffusion length will be smaller when sediment particles are suspended and more water is present to decrease the aqueous concentration. We conclude that non-stationary diffusion within organic matter is the main process of mass transfer. The combination of simulated in-situ measurements of desorption from sediments with generic measurable parameters like flow rate and particle size distribution results in a quantitative measurable flux of contaminants, which resembles the in-situ (bio)availability as the result of dynamic processes in the sediment/water system.

Recommendations and Perspectives. The results obtained provided a sound basis for mechanistic modeling of POP mass transfer from sediment to water. The modeling results will be presented in a separate paper. Besides the HRT, also mixing conditions can be changed to assess the desorption from sediment layers. The possibility to combine flow rate and mixing intensity enables the study of the effect of hydraulically different river systems on desorption of contaminants. In a long term perspective we foresee a link with hydrology and sediment transport with desorption in water bodies.

Keywords: Bioavailability; dieldrin; flood events; particle size; persistent organic pollutants; POPs; radial diffusion; sediments

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 [1, 2]. 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 [3,4].

The equilibrium distribution of hydrophobic pollutants between natural soils or sediments and an aqueous phase has been the subject of many studies since the 1960s [5–8]. Sorption equilibria are often described mathematically by linear isotherms that define contaminant concentration in the

sorbed phase as function of the concentration in the aqueous phase [6,7]. This concept has been challenged by experimental isotherm data showing non-linear relations between aqueous and sorbed concentrations, and sorption hysteresis. Di Toro [9] 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 [10–14]. 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 [14]. At present many authors [10–12,15] 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 [16]. 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 or three compartment, 1st order kinetic model where the compartments describe a fast and one or two slow desorbing fractions [17]. Although many types of models are able to fit experimental data, only mechanistic models, like physical/diffusion models, provide insights to understand the mass transfer of POPs in the sediment/water system and make it possible to predict the behavior of a contaminant [18,19]. Application of diffusion models, however, is 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 [20–24], a radial diffusion model with a concentration-dependent diffusion coefficient [25,26], or a statistical distribution of diffusion rates [27] 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.

1 Materials and Methods

Chemicals. Tenax®-TA (20–35 mesh) was purchased at Buchem b.v. (Apeldoorn, The Netherlands), acetone (p.a.), hexane (HPLC grade), NaN₃ (extra pure), and CaCl₂ (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 a PIDS obscuration of 50±10% [28].

Pesticide extraction and GC analysis. Samples (1.5–3 g dry weight sediment or Tenax) were extracted in a microwave (110°C for 20 min) 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 low-bleed/MS column (50m x 0.25mm x 0.12µm film thickness). Sample injection (1µl) was splitless (5 min) at a temperature of 250°C. 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 300°C. 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 studied at a temperature of 20±1°C using the SPEED reactor depicted in Fig. 1. A modified 500 ml Schott flask (Vreactor)

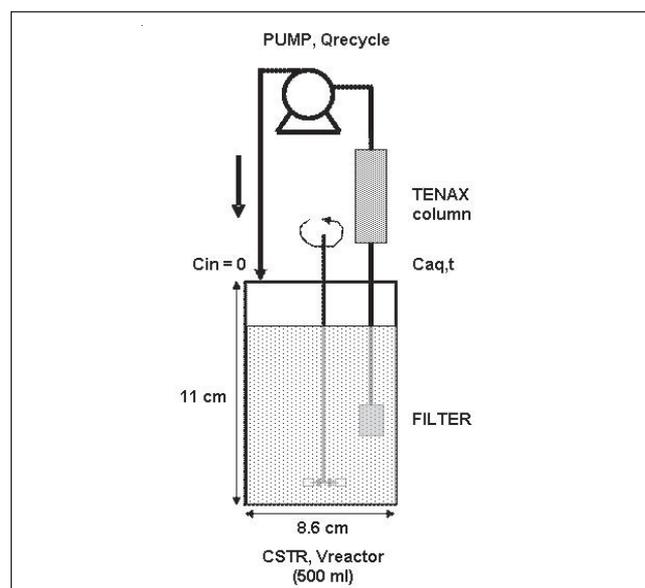


Fig. 1: Schematic of SPEED reactor

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 ($c_{\text{in}} = 0 \mu\text{g/l}$). 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 $\pm 20\%$) 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 min. The HRT was calculated as $V_{\text{reactor}}/Q_{\text{recycle}}$. 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 min 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 min 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 [29, 30]. 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 $20 \pm 1^\circ\text{C}$ 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.

2 Results and Discussion

Sediment characteristics. Based on the organic matter content of 6 particle size classes (data not shown), three distinctive fractions were identified: $<32 \mu\text{m}$ (OM 14.6%, dieldrin $6.1 \text{ mg}\cdot\text{kg}^{-1}$), $32\text{--}125 \mu\text{m}$ (OM 6.1%, dieldrin $3.6 \text{ mg}\cdot\text{kg}^{-1}$), and $125\text{--}2000 \mu\text{m}$ (OM 30.5%, dieldrin $13.3 \text{ mg}\cdot\text{kg}^{-1}$). The particle size distributions of each fraction, analyzed by laser scattering, are depicted in Fig. 2. 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 $32\text{--}125 \mu\text{m}$ was used which had a SOM content of $6.1 \% \pm 0.9$. In this particle size fraction, two distinct particle size peaks were observed by laser diffraction analysis, one peak at $10 \mu\text{m}$ and one peak at $84 \mu\text{m}$. The areas of these peaks were integrated and the cumulative volumes were 27% and 73% for the peaks at $10 \mu\text{m}$ and $84 \mu\text{m}$, respectively. We choose this particle size fraction because the fraction $125\text{--}2000 \mu\text{m}$ was heterogeneous regarding SOM content and dieldrin concentration. The particles of the fraction $<32 \mu\text{m}$ 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.

SPEED reactor experiments. The experimental conditions regarding average flow rates, measured HRT, sample sizes, and initial sediment concentrations of dieldrin (S_0), are presented in Table 1.

Normalized concentrations of dieldrin in the aqueous phase and the fraction of dieldrin that is extracted in time are depicted in Fig. 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

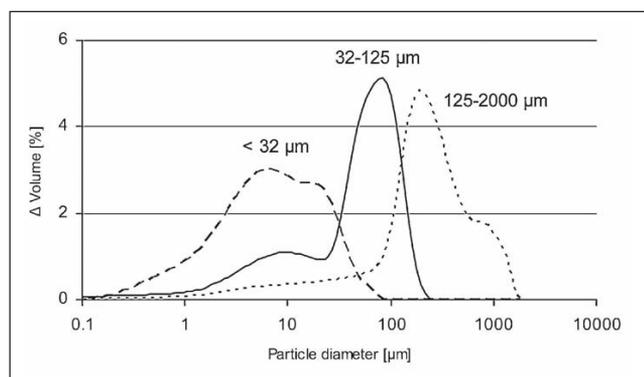


Fig. 2: Particle size distribution of three particle size fractions by laser diffraction. Δ Volume is the amount of volume related to a discrete particle size range

Table 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 S ₀ [mg·kg ⁻¹ d.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 a boundary of $\pm 20\%$, except for set HRT 750 where the flow rate decreased continuously

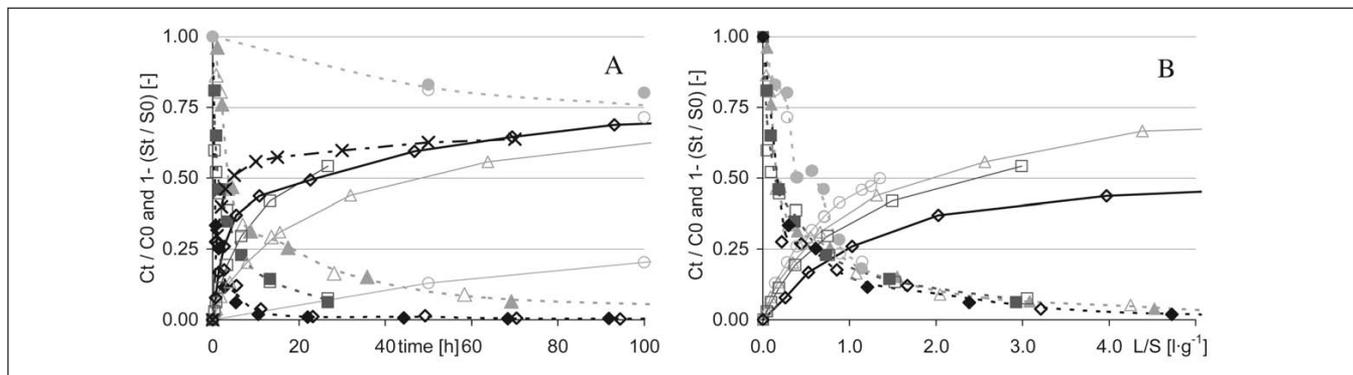


Fig. 3: Dieldrin concentration in aqueous phase (dotted lines) and fraction extracted (solid lines) as function of time (A) and liquid to solid ratio (B). The set HRTs (duplicates) are: \blacklozenge and \diamond = 10 min, \blacksquare and \square = 25 min, \blacktriangle and \triangle = 75 min, $\%$ and $\%$ = 750 min, and X = Tenax SPE

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[®] solid phase extraction are included in the graph. The Tenax[®] solid phase extraction 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.

Not only time but also the amount of water available for extraction affects the extent of desorption, especially during a flood event. In Fig. 3B, the results of the same SPEED experiments are presented, but recalculated as a 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[®] solid phase extraction 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[®] solid phase extraction. Sediment concentrations of dieldrin (S_t/S_0) are presented in Fig. 4 as a 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 de-

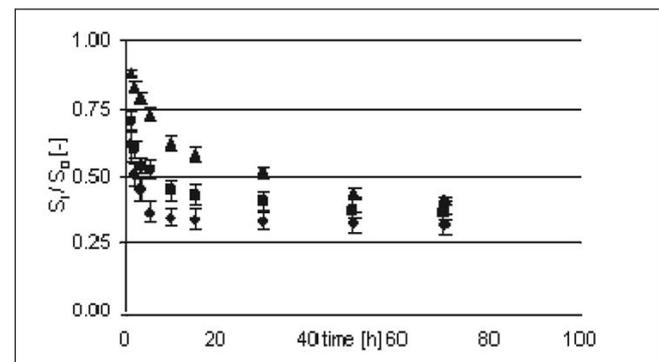


Fig. 4: Normalized sorbed concentration of dieldrin as a function of time of three particle size fractions. \blacklozenge 32 μm , \blacksquare 125 μm , and \blacktriangle 125–2000 μm . Error bars are the standard deviation ($n=3$)

sorption 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 contradictory. In a paper often cited to demonstrate the absence of particle size effects on desorption kinetics [31], 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.

Flux based approach. From the SPEED experiments and the Tenax[®] solid phase extractions, 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 Eq. 1:

$$J_I = \frac{I}{A_p} \cdot \frac{\Delta M}{\Delta t} \quad (1)$$

Where J_I is the average flux of dieldrin per extraction step ($\text{mg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), A_p is the surface area of the particles (m^2), $\Delta M/\Delta t$ is the change of dieldrin mass per extraction step ($\text{mg}\cdot\text{s}^{-1}$). The surface area of the particles was calculated from the sample size, the density according to a standard value of $2600 \text{ kg}\cdot\text{m}^{-3}$, and the particle sizes $10 \mu\text{m}$ (27%) and $84 \mu\text{m}$ (73%). In Fig. 5, a representative plot of flux versus time is presented for HRT 75 min. Once desorption started, the flux can be described for the first few hours as $J_I \propto t^{-1/2}$ and, thereafter, as $J_I \propto t^{-1}$ which are the slopes of the solid lines drawn in the figure. Theoretically, the flux of a single particle should finally be described by $J_I \propto e^{-t}$ [32] 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 $J_I \propto t^{-1}$ can then be seen as a transition zone and the effect of time on the flux ($t^{-1/2} \rightarrow t^{-1}$) 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.

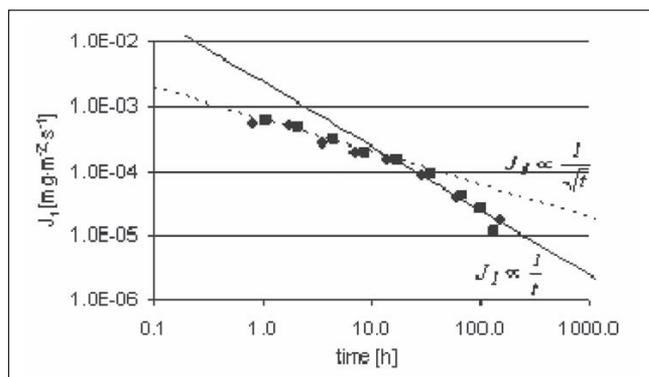


Fig. 5: Dieldrin flux (J_I) for HRT = 75 min. Lines are model fits for short ($J_I \propto t^{-1/2}$) and long-term ($J_I \propto t^{-1}$) data

3 Conclusions

The SPEED reactor enables one to simulate field conditions and flood events by setting the mixing regime and water flow rates, to mimic water refreshment and mixing conditions of distinct water bodies like rivers, lakes, and groundwater. Flood events will result in an increase of desorption rate of POPs from sediments to the surrounding water because of vigorous mixing and by providing a large volume of relatively clean 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. The combination of simulated in-situ measurements of desorption from sediments with generic measurable parameters like flow rate and particle size distribution results in a quantitative measurable flux of contaminants which resembles the in-situ (bio)availability as the result of dynamic processes in the sediment/water system.

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Abstract

Background, Aims and Scope. Effect-directed analysis (EDA) is a powerful tool for the identification of key toxicants in complex environmental samples. In most cases, EDA is based on total extraction of organic contaminants, which may lead to an erroneous prioritisation with regard to hazard and risk. Bioaccessibility-directed extraction aims to discriminate between contaminants that take part in partitioning between sediment and biota in a relevant time frame and those that are enclosed in structures that do not allow rapid desorption. Standard protocols of targeted extraction of the rapidly desorbing, and thus bio-accessible, fraction using TENAX® are based only on small amounts of sediment. In order to obtain sufficient extract for subsequent biotesting, fractionation and structure elucidation, a large volume extraction technique needs to be developed applying one selected extraction time and excluding toxic procedural blanks.

Methods. Desorption behaviour of sediment contaminants was determined by combining consecutive extraction of sediment using TENAX® with a three-compartment desorption model. Time needed to remove the rapidly desorbing fraction, t_{rap} , was calculated to select a fixed extraction time for single extraction procedures. Up-scaling by about a factor of 125 provided a large volume extraction technique for EDA. Reproducibility and comparability to the small volume approach were analysed. TENAX®

blanks and sediment extracts were tested for toxicity using *Scenedesmus vacuolatus* and *Artemia salina* as test organisms.

Results and Discussion. Desorption kinetics showed that 12 to 30% of sediment-associated pollutants were available for rapid desorption, while 70 to 90% of PAHs found in the sediment belong to the slowly and very slowly desorbing pool with very limited bioavailability. t_{rap} is compound dependent and covers a range of 2 to 18 h. A fixed extraction time of 24 h was selected as a time at which even the rapidly desorbing fraction of big hydrophobic compounds should be fully desorbed. High reproducibility of the large volume approach and good agreement with the small consecutive approach were found. Significant toxicity of procedural TENAX® blanks was found with *Scenedesmus vacuolatus*, which is in agreement with chemical analysis and could be reduced by pre-cleaning of TENAX® with Accelerated Solvent Extraction (ASE). Toxicity of blanks prior to ASE-clean up was about three orders of magnitude below the toxicity of sediment extracts.

Conclusions. For consideration of bioaccessibility in EDA, a large volume TENAX® extraction method was presented. Although several other solid phases can be used to extract the bioaccessible fraction, TENAX® has unique properties for depletive extraction of the rapidly desorbing fraction from large amounts of sediment. Toxicity and chemical blanks due to production residues are shortcomings of the method that can be overcome by accurate pre-cleaning, e.g. with ASE.

Recommendations and Perspectives. Higher purity of TENAX® guaranteed by the manufacturers would significantly enhance the applicability of the method. Using TENAX® instead of total extraction may improve key toxicant prioritisation by considering exposure and effect rather than effect only.

Keywords: Bioaccessibility; desorption; Effect-Directed Analysis (EDA); polycyclic aromatic hydrocarbons (PAH); sediment; TENAX®