In situ benthic flow-through chambers to determine sediment-to-water fluxes of legacy hydrophobic organic contaminants[☆]

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ABSTRACT

Contaminated sediment can release hydrophobic organic contaminants (HOCs) and thereby act as a secondary source of primarily legacy hazardous substances to the water column. There is therefore a need for assessments of the release of HOCs from contaminated sediment for prioritization of management actions. *In situ* assessment of HOC sediment-to-water flux is currently done with (closed) benthic flux chambers, which have a sampling time exceeding one month. During this time, the water inside the chamber is depleted of oxygen and the effect of bioturbation on the sediment-to-water release of HOCs is largely ignored. Here we present a novel benthic flux chamber, which measures sediment-to-water flux of legacy HOCs within days, and includes the effect of bioturbation since ambient oxygen levels inside the chamber are maintained by continuous pumping of water through the chamber. This chamber design allows for sediment-to-water flux measurements under more natural conditions. The chamber design was tested in a contaminated Baltic Sea bay. Measured fluxes were 62–2300 ng m^{-2} d^{-1} for individual polycyclic aromatic hydrocarbons (PAHs), and 5.5–150 ng m^{-2} d^{-1} for polychlorinated biphenyls (PCBs). These fluxes were 3–23 times (PAHs) and 12–74 times (PCBs) higher than fluxes measured with closed benthic chambers deployed in parallel at the same location. We hypothesize that the observed difference in HOC flux between the two chamber designs are partly an effect of bioturbation. This hypothesized effect of bioturbation was in accordance with literature data from experimental studies.

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1. Introduction

Legacy hydrophobic organic contaminants (HOCs) have over time reached aquatic environments through pathways such as direct emissions from point sources, atmospheric deposition or transport via run off from land. On a global scale, sediment acts as a sink for HOCs due to strong association of these hydrophobic substances to settling organic matter (Jönsson et al., 2003; Nizzetto et al., 2010). However, as primary emissions of legacy HOCs (such as polychlorinated biphenyls; PCBs, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans; PCDD/Fs) have been reduced, contaminated sediment may start acting as a secondary source of these regulated chemicals. Release of HOCs from sediment to water occurs via diffusive flux driven by higher chemical activity in the sediment compared to water, and mechanisms such as resuspension of particle-associated HOCs, advective pore water due to gas ebullition and bioirrigation (Meysman et al., 2006; Yuan et al., 2007; Cornelissen et al., 2008a; Armitage et al., 2009). For diffusive and advective processes to be significant, concentrations in the pore water need to be substantially different from the overlying bottom water.

The Baltic Sea was historically polluted by industrial activities along the coastlines, which caused high concentrations of e.g. PCBs, hexachlorobenzene and PCDD/Fs in sediments. Since the mid-1980s when concentrations peaked in coastal sediment, actions

were taken and emissions strongly reduced (Assefa et al., 2014; Sobek et al., 2015). As sediments are still polluted, high chemical activity ratios between sediment and water may cause contaminated sediments to release legacy HOCs to water. For instance, high chemical activity ratios between pore water and bottom water for PCDD/Fs in coastal areas of the Baltic Sea were observed, demonstrating a potential release of PCDD/Fs from sediment to water (Sobek et al., 2014).

Several different methods exist and have been used for the assessment of flux of legacy pollutants from sediment to water, each with its advantages and disadvantages. In the end, the choice of method sets the limit for what is possible to determine, as there is an inherent trade-off between resembling the environment, on the one hand, and defining the boundaries and reducing uncertainties on the other. The diffusive flux of HOCs between sediment and water can indirectly be quantified by using Fick's first law of diffusion based on data on concentrations in bottom water and pore water (Eek et al., 2010; Liu et al., 2013; Lin et al., 2015), as chemical transport takes place along a concentration gradient. The same principle is frequently used in multimedia models describing sediment-water mass transfer of HOCs (Wania et al., 2000, 2006). Direct measurements of sediment-to-water flux have been done in micro- and mesocosm studies, where HOCs were collected by pumping the overlaying water through a filter followed by a polyurethane foam (PUF) sorbent (Fisher et al., 1980; Larsson, 1985; Granberg et al., 2008; Hedman et al., 2009). The flux was thereafter calculated from the mass of substance collected on the sorbent, the area of the sediment surface, and time of incubation.

Benthic chambers offer a method for *in situ* determination of sediment-to-water fluxes of chemicals, and have recently been used to determine sediment-water fluxes of nitrogen and phosphorous in the Baltic Sea (Viktorsson et al., 2013; Ekeroth et al., 2016), where the flux was calculated based on the difference in concentration over time inside the chamber. Benthic chambers have also been used for direct measurements of HOC fluxes from sediment to water (Eek et al., 2010; Cornelissen et al., 2011, 2012). As it is difficult to measure HOC concentration changes over time in water inside the chamber, different systems for sediment-water flux measurements have been developed. *In situ* flux measurements of legacy HOCs have been performed by exposing an infinite sink (semi-permeable membrane device, SPMD, or a silicone polymer) to the water phase inside a closed chamber placed on the sediment bed (Eek et al., 2010; Cornelissen et al., 2011, 2012, 2016) and the HOCs are sorbed as they are diffusing from the seabed. This is a similar principle frequently used in *ex situ* measurements where water exposed to a contaminated sediment surface was pumped through a sorbent (Schaanning et al., 2006; Granberg et al., 2008; Josefsson et al., 2010). One drawback with the closed benthic chamber is that it does not allow for water flow through the chamber, which has the consequence that oxygen is depleted and anoxic conditions prevail during the main part of the deployment that often exceeds one month. Benthic organisms will therefore be severely disturbed and the natural effect of bioturbation on sediment-to-water flux is therefore not reflected in the measured flux.

Several studies have demonstrated that bioturbating organisms may increase the sediment-water flux of HOCs, with the observed flux being 0.25 (i.e. flux lowered due to bioturbation) to 25 times higher with bioturbation (Granberg et al., 2008; Hedman et al., 2009; Josefsson et al., 2010; Koelmans and Jonker, 2011). The effect of bioturbation on the sediment-water flux of HOCs depends on both benthic species composition and density, as organisms differ in their mode of reworking the sediment and in how deep they can penetrate in to the sediment (Granberg et al., 2008; Hedman et al., 2009; Josefsson et al., 2010; Kristensen et al., 2012). Two

bioturbation processes have been identified. i) moving of sediment particles vertically and horizontally, as organisms move within the sediment, and ii) moving of water within the sediment as organisms flush their burrows, termed bioirrigation (Kristensen et al., 2012). Both processes may increase the sediment-to-water flux of contaminants. Particle mixing may move contaminated sediment particles from deeper layers to the surface and thus enhance the chemical activity ratio between water and surface sediment (Josefsson et al., 2010). Bioirrigation can increase the transport of methyl mercury from pore water to bottom water (Benoit et al., 2009), and may accordingly increase the flux of dissolved HOCs. In areas where particle resuspension due to abiotic processes is negligible, bioturbation may be the most important process controlling the sediment-water flux of HOCs (Reible et al., 1996).

The aim of the present study was to improve the possibilities of measuring environmentally realistic fluxes of legacy HOCs from contaminated sediment to water. We therefore developed an *in situ* benthic flow-through flux chamber for the determination of sediment-to-water flux of HOCs under environmentally realistic, oxic conditions. The flow-through chamber has the advantage that the total effect of bioturbation on the flux may be assessed. Bioturbation may be of particular importance for the flux from sediment to water for legacy HOCs, as they in general occur at higher concentrations at sediment depths that may be reached by benthic biota (Sobek et al., 2015; Assefa et al., 2014). By constantly pumping bottom water through the chamber, the oxygen concentration inside the chamber is kept at ambient levels and the benthic organisms in the chamber remain undisturbed. The flux measurements by the flow-through chamber were compared with i) fluxes measured in parallel with closed *in situ* chambers, and ii) fluxes calculated based on chemical concentration gradients between pore water and bottom water. A dynamic mass balance model was developed and applied to estimate the effects of chamber design on the measured flux.

2. Materials and methods

Details on chemicals and materials, chemical analysis and instrumental set up and QA/QC are available as Supplementary material, Text S1, Text S2, and Text S3.

2.1. Flow-through chamber design

The benthic flow-through flux chamber (Fig. 1) was developed for assessments of sediment-to-water flux of legacy HOCs in areas with a strong concentration gradient between sediment and water. The principle of the chamber is to collect HOCs released from sediment to water on a sorbent at the chamber outlet, by pumping water through the chamber. This is the same principle as commonly used for *ex situ* flux measurements using retrieved sediment cores (Schaanning et al., 2006; Granberg et al., 2008; Josefsson et al., 2010). The experimental setup builds on the assumption that a steady state situation is quickly reached in the chamber where the net flux out of the sediment is equal to the flux out of the chamber, and the net flux from the sediment inside the chamber can therefore be estimated from the chemical mass captured on the infinite sink.

The chamber, made of stainless steel, is cylindrical with a diameter of 0.25 m, an area of 0.049 m^2 and a volume of 3.4 L. Water is pumped by suction from the outlet through the chamber with an approximate flow of 1 L h^{-1} to retain aerobic conditions inside the chamber. First, water passes through a PUF sorbent at the chamber inlet to remove HOCs. At the chamber outlet, a second PUF sorbent captures HOCs released from sediment during deployment. A precombusted (450 °C, overnight) GF/F-filter (nominal pore size
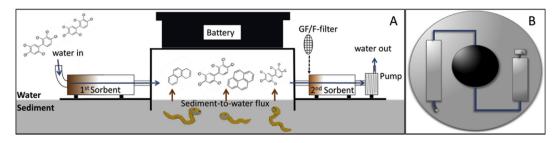
Fig. 1. Schematic figure of the flow-through chamber, side view (A) and top view (B). Blue arrows indicate water flow. Brown arrows indicate net sediment-to-water flux. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

0.7 μm) is placed before the sorbent at the chamber outlet to prevent suspended particles to enter the sorbent. The filter prevents particles from being sampled by the sorbent, as in previous *ex situ* studies on HOC flux from sediment to water (Schaanning et al., 2006; Granberg et al., 2008; Hedman et al., 2008; Josefsson et al., 2012). A minor fraction of DOC-associated HOCs may be collected by the sorbent (for estimation of contribution; see below). To prevent the measured flux to be substantially affected by HOCs from the outside bottom water pumped through the chamber, the water pumped into the chamber was cleaned of HOCs on the incoming sorbent. For contaminants with a strong concentration gradient between sediment pore water and bottom water the effect of a lowered bottom water concentration will be minimal on the measured flux. In situations where pore water concentrations are close to the concentration in the overlying water the cleaning of the water flowing in to the chamber will lead to an overestimation of the flux. This can be corrected for by measuring the concentration in the water outside the chamber (Eek et al., 2010).

Batteries to power the pump are placed in a waterproof container on top of the chamber. By a delay function installed on the battery package, the sampling starts 10 h after placement of the chamber on the sediment bed. The 10 h delay allows suspended sediment particles to settle before water is pumped through the sorbent. The stainless steel sorbent holders (1 L inlet and 0.5 L outlet) were packed with 65 g and 45 g of PUF cut into cubes (1.5 cm^3), corresponding to a density of 65 and 90 g PUF L^{-1} in the inlet and outlet, respectively. The higher PUF density in the outlet sorbent holder was used to secure a higher hydraulic conductivity of the inlet compared to the outlet sorbent. This is important to minimize the pressure drop inside the chamber to avoid drawing pore water into the chamber. The small size and cubic shape of the sorbents were used to prevent the occurrence of preferential pathways for the water between the sorbent and the wall of the sorbent holder.

The oxygen demand inside the chamber during deployment was estimated based on a laboratory incubation test with five sediment cores sampled at the study site. The cores were closed with rubber stoppers. Dissolved O$_2$ was measured in the water 1 cm above the sediment surface during six days (at 17 °C) using an Oxical-SL probe. The oxygen demand was determined based on a linear regression of O$_2$ concentration in the water over time. The resulting oxygen demand was 660–2590 μmol O$_2$ m^{-2} h^{-1}, which is 0.8–12 times the previously reported for the Gulf of Finland in the Baltic Sea (462–525 μmol O$_2$ m^{-2} h^{-1}) (Conley et al., 1997) and in the Baltic Proper (214–777 μmol O$_2$ m^{-2} h^{-1}) (Koop et al., 1990). Based on the dissolved oxygen levels in the bottom water at sampling (8 mg L^{-1}), a water flow of 1 L h^{-1} was considered sufficient, as it would supply the chamber with almost three times the amount of O$_2$ consumed by the sediment inside the chamber during three days of deployment.

2.2. Performance test of sorbent and water flow through the chamber

The amount of PUF sorbent needed to remove HOCs from incoming water (1st sorbent) and from water exiting the chamber (2nd sorbent) was determined in an initial study. For this, 2 L of spiked MilliQ water (9 PAHs; 2–6 rings at μg L^{-1} level, and 7 PCBs; 3–7 Cl at ng L^{-1} level) were pumped at a flow of approximately 2 L h^{-1} through a sorbent holder containing varying masses of PUF (95–130 g PUF L^{-1}). Two sizes of sorbent holders were tested, 0.5 L and 1 L. The amounts of PAHs and PCBs in water exiting the sorbent were quantified as described in the Supplementary material. Sorption efficiency criteria were set to avoid breakthrough of the 1st sorbent and thus interference of the flux measurements at the 2nd sorbent, and to enable collection of all PCBs and PAHs that were released from the sediment (on the 2nd sorbent). We judged it necessary to have a 99% removal efficiency of individual HOCs from the incoming water if the concentration was >30 ng L^{-1} and a 90% removal efficiency of individual HOCs if the water concentration was <10 ng L^{-1}. These criteria were based on concentrations in the sediment, estimates of concentration in bottom water (C$_{bw}$) and flux from previous studies (Eek et al., 2010) in combination with the volume of water pumped through the chamber. The hydraulic conductivity of the sorbent was determined with the sorbent holder (1 L) containing two different amounts of PUF (48 and 93 g PUF L^{-1}). The water flow and the hydraulic head was monitored and the conductivity (K) was determined by K= (q*l)/(A*h), where q is the flow [L h^{-1}], l is the length of the sorbent holder [m], A is the cross section area [m^2] of the sample and h is the hydraulic head [m]. In addition, the flow rate through the chamber was assessed in a mesocosm study prior the *in situ* test. For this, a flow-through benthic chamber was placed in a cylindrical tank (i.d.: 0.9 m; h: 0.6 m), with 10 cm of sediment collected at the study site placed at the bottom of the mesocosm to mimic field conditions. The tank was filled with 150 L of water to cover the chamber in- and outlets and the water flow was measured at several time points during 4–5 days, which currently is the maximum duration of the battery. Water flow was measured through both the incoming and outgoing columns.

2.3. Study site, sampling and deployment

The flow-through chambers were tested *in situ* in Ålöfjärden (N58° 40′45; E17° 8′28) in June–July 2015. Ålöfjärden is a contaminated Baltic Sea bay in the direct vicinity of an active steelworks site, located approximately 100 km south of Stockholm. The salinity is 6–8‰ and water depth at the sampling sites was 7.5–9.5 m. The sediment consists of silty loam (see Table S1, Supplementary material), which has a hydraulic conductivity in the range of 10^{-9}-10^{-5} m s^{-1} (Clapp and Hornberger, 1978; Freezer and Cherry, 1979). The concentration of $\sum$PAH$_{15}$ in the sediments of the

bay was in the range of 16 μg g^{-1} DW and the concentration of $\sum$PCB$_7$ was approximately 50 ng g^{-1} DW (Table S2, Supplementary material). To assess the potential for bioturbation, macrofauna densities were determined. Sediment from three Van Veen grabs was sieved (1 mm) and animals were collected for species identification. The densities of common benthic species in this area, such as amphipods (*Monoporeia affinis*), bivalves (*Macoma balitica* and *Mytilus edulis*) and polychaetes (*Marenzelleria* spp) were 0–180, 610–290 and 350–230 (min-max) individuals m^{-2}, respectively. The benthic community composition at the sampling site corresponded to the dominating type in this area of the Baltic Sea, however, the densities were slightly lower than reported by Gogina et al. (2016). An explanation might be natural spatial and temporal variance in abundance (Blomqvist and Bonsdorff, 1986; Boström and Bonsdorff, 1997). Other species such as the bivalves *Cerastobyssum hauniense*, *Cerastoderma glaucum* and *Mya arenaria* were also identified in the sediments at densities ≤10 ind. m^{-2} for the individual species. The species found at the study site represented both organisms dwelling in the top cm of the sediment (e.g. *Monoporeia affinis* and *Macoma baltica),* and organisms that may reach down to 40 cm (e.g. *Marenzelleria* spp.) (ŻMudziński, 1996; Bradshaw et al., 2006).

Three benthic flow-through flux chambers were deployed for 3 days, along a 600 m transect from the inner towards the outer parts of the bay in areas with no direct interference from cargo ship traffic (Fig. S1, Supplementary material). To collect the freely dissolved fraction of PCBs and PAHs in bottom water (C$_{bw}$), 17-μm passive samplers (polyoxymethylene; POM) (Cornelissen et al., 2008b) were deployed at the same sites approximately 0.4 m above the sediment bottom for 4 months (3rd of July to 24th October 2015). Equilibrium for the analyzed PAHs and PCBs should be reached within this sampling duration (Jonker and Koelmans, 2001; Cornelissen et al., 2008a, 2008b). Three closed flux chambers, with identical chamber size and shape as the flow-through chamber but without water being pumped through the chamber, were deployed for 40 days (10th of October to 19th of November 2014) in the middle part of the transect. In the closed chambers, HOCs that diffuse from sediment to water were captured on an SPMD placed within the chamber (Eek et al., 2010). In Eek et al. (2010) the SPMD was demonstrated to serve as an infinite sink during the same deployment time as used in this study. Sediment samples (sediment depth: 0–5 cm, n = 3 per site) were collected with a gravity corer on the 30th June 2015 for determination of pore water and total sediment PCB and PAH concentrations and total organic carbon (TOC) content. The pore water concentrations (C$_{pw}$) were determined in the laboratory using POM (Cornelissen et al., 2008a), by equilibrating sediment (25 g wet weight and 0.2 g POM) for 6 weeks in Erlenmeyer glass flasks together with MilliQ water (250 mL), NaN$_3$ (1 g L^{-1}) and NaCl (6 g L^{-1}) during horizontal shaking (180 rpm). Detailed descriptions of the analytical procedures to analyze PCBs and PAHs are available as Supplementary material, Text S2.

2.4. Measured and calculated flux

Flux is defined as the transport of chemicals from a defined area of one medium to another medium per unit time, e.g. the mass of chemical released per sediment area to water per day (equation (1)). The driving force governing the transport of chemicals is concentration gradients between the two media, where the transport occurs in the direction from high to low chemical activity. In this study, sediment-to-water flux of legacy HOCs was measured with two types of benthic chambers and calculated using a measured concentration gradient between pore water and bottom water. The measured flux, F$_{measured}$, [ng m^{-2} d^{-1}] was determined as:

$$F_{measured} = \frac{mass}{area * time} \tag{1}$$

where mass is the mass of substance [ng] quantified in either the outlet sorbent of the flow-through chamber, or in the infinite sink used in the closed chamber. Area is the chamber area [m^2] and time is the time (d) water was pumped through the chamber (i.e. deployment time minus 10 h) for the flow-through chamber, or total deployment time for the closed chambers. Inside the flow-through chamber the condition for the sediment-water boundary layer (d$_x$) is assumed to be similar to the natural occurring conditions. Inside the closed chamber, however, two boundary layers will be present; one at the sediment-water interface and one at the water-infinite sink interface (Eek et al., 2010). Assuming steady state is reached soon after placement of the closed chamber on the sediment bed, and equal transport through the two boundary layers, the concentration of contaminants in water inside the chamber will increase to half of the concentration in the pore water (see description in Text S7). Hence, when there is a strong gradient between pore water and bottom water (C$_{pw}$ » C$_{bw}$), the chemical gradient (see equation (2)) between the water inside the chamber and the SPMD will be approximately half of what is occurring initially in the chamber (with the naturally occurring boundary layer). The closed chamber flux measurements were therefore multiplied by a factor of two to account for the weaker chemical gradient inside the chamber at steady state. Flux was calculated from the concentration gradient between pore water and bottom water using Fick's first law of diffusion (equation (2)). Fick's law is a mathematically simple model and will describe any diffusive flux as long as its different input parameters are well described.

$$F_{calculated} = B_w \frac{C_{pw} - C_{bw}}{d_x} \tag{2}$$

In equation (2), F$_{calculated}$ is the sediment-to-water flux [ng m^{-2} d^{-1}], B$_w$ the diffusion coefficient [m^2 d^{-1}] and d$_x$ is the thickness [m] of the diffusive boundary layer at the sediment-water interface. C$_{pw}$ and C$_{bw}$ are the freely dissolved concentrations [ng m^{-3}] measured in sediment pore water and in bottom water. The d$_x$ is the water adjacent to the seabed sediment where transport of chemicals between sediment and water is assumed to be restricted to diffusive transport. We assumed an average d$_x$ of 0.0007 m as reported in (Eek et al., 2010), which agrees with other laboratory and field measurements of d$_x$ from similar aquatic systems (0.0001 m–0.002 m) (Santschi et al., 1983; Jørgensen and Revsbech, 1985; Archer et al., 1989; Jørgensen and Des Marais, 1990; Santschi et al., 1991). In case measured C$_{pw}$ or C$_{bw}$ were below limit of detection (LOD), a concentration calculated from the average blank value was used. The diffusion coefficient (B$_w$) was calculated from the molar mass of each substance as previously outlined (Eek et al., 2010) and adjusted to 13 °C (average water temperature during sampling). C$_{bw}$ can change with environmental conditions in the overlying water, while C$_{pw}$ vary less with time than C$_{bw}$, but can vary with sediment depth and is influenced by sorption and desorption between pore water and sediment particles. Above a contaminated sediment where other major sources have been reduced, and with a water exchange rate high enough to dilute the release from the sediment, such as in many coastal Baltic Sea areas, the typical situation for a wide range of legacy HOCs is that C$_{pw}$ » C$_{bw}$. The size of C$_{bw}$ will therefore be of minor importance, whereas C$_{pw}$ will be important for the flux. The bottom water and pore water concentrations were determined from the measured concentration in the POM samplers and the POM-water partition coefficient (K$_{POM}$). K$_{POM}$ –values were from literature (Hawthorne

et al., 2009, 2011). No corrections for effects of temperature and salinity on partitioning of PAHs and PCBs to POM were done as these effects would be minor in the Baltic Sea (Schwarzenbach et al., 2003). The amount of PAHs and PCBs sorbed to dissolved organic carbon (DOC) caught on the 2nd outgoing sorbent in the flow-through chamber was estimated to understand the potential effect of DOC on the measured flux. For this estimate, data on the measured DOC concentration in the bottom water (5 mg L^{-1}), the DOC-water partition coefficient $K_{DOC} = K_{ow}*0.08$ (Burkhard, 2000) and the volume of water pumped through the flow-through chamber during sampling were used as described in the references (Schwarzenbach et al., 2003; Sobek et al., 2004). K_{ow}-values were from literature (Schenker et al., 2005; Ma et al., 2010) except for dibenz[a,h]anthracene for which K_{ow} was estimated from an regression of K_{ow}, from Ma et al. and molecular weight.

2.5. Mass balance model

The presence of the chamber on the seabed and the water flow through the chamber can influence the flux in two important ways: 1) the water flow rate can influence the thickness of the d_x, 2) the water flow rate will also determine the concentration of HOCs in the water inside the chamber during the measurement and therefore also the flux (equation (2)). A one-box mass balance model describing the transport of HOCs in and out of the flow-through chamber was set up in Microsoft Excel 2013 and used to assess the magnitude of potential errors in flux measurements arising from the chambers' impact on bottom water concentrations and thickness of the diffusive boundary layer. The model describes the diffusive water-sediment exchange and advective transport via water out of the chamber. Degradation is assumed to be slow compared to elimination via outflowing water (i.e. assumed to be negligible) and bioturbation is not considered due to large uncertainties in parameters describing this process. The modeled mass balance, input-output, equals the change of chemical mass in the flow-through chamber over change in time ($dM\ dt^{-1}$ = input − output), where M is mass [mol] and t time [h]. Following the methods described by (Mackay, 2001) this can be expressed as:

$$f_w\ Z_w\ V\ dt^{-1} = D_{diff}\ (f_{sed} - f_w) - D_{out}\ f_w \qquad (3)$$

where f_w is the fugacity of the water enclosed by the chamber [Pa], Z_w is the fugacity capacity of water [mol m^{-3} Pa^{-1}] and V is the volume of the chamber [m^3]. D_{diff_w} is the transport parameter (D-value) for diffusion [mol h^{-1} Pa^{-1}], and D_{out} is the D-value for advective transport of chemical out of the flow chamber [mol h^{-1} Pa^{-1}], and f_{sed} is the fugacity of the sediment [Pa]. D-values were taken from the references (Wania et al., 2000, 2006), where D_{diff_w} is a function of the diffusivity of the chemical in water B_w [m^2 h^{-1}], thickness of diffusion boundary layer d_x [m], bottom area of the flow-through chamber [m^2] and fugacity capacity in water Z_w [mol m^{-3} Pa^{-1}] ($D_{diff} = (B_w/d_x)*Area*Z_w$). The estimated flux is hence dependent on the assumed thickness of d_x. D_{out} is the product of the water flow through the chamber G [m^3 h^{-1}] and Z_w ($D_{out} = G * Z_w$).

The model was used to estimate effects of the chamber design on the measured flux; that is how enclosing a small volume of water and pumping water through the chamber may impact the net sediment-water flux and hence the measured flux (based on the mass of HOCs captured on the sorbent). To do this, we calculated the ratio between modeled mass of HOCs on the sorbent per m^2 sediment by the end of the sampling period divided by sampling duration in hours, and the modeled net flux from the sediment per m^2 and hour at the very beginning of the sampling period. The modeled net flux is described by equation (2). The ratio between

the two calculated fluxes is referred to as 'theoretical experiment error'. A theoretical experiment error of 1 indicates that the flux out of the chamber is predicted to be identical to the net flux out of the sediment during the entire sampling period. A theoretical experiment error <1 indicates that the flux out to the sorbent is smaller than the flux out of the sediment at the beginning of the experiment, meaning that the chamber design inherently underestimates the sediment-to-water flux. A theoretical experiment error >1 indicates that the chamber design inherently increases sediment-to-water flux. A sensitivity analysis was performed to quantify how the theoretical experiment error would change due to changes (one by one) in a) concentration gradient between pore water and bottom water, b) d_x, and c) water flow through the chamber. Default values and tested range of each of the parameters are given in Table S4 and Table S5.

3. Results and discussion

3.1. Performance of the flow-through chamber

The performance test of the PUF sorbent demonstrated that 95−124 g PUF sorbent captured 99.9% or more of the amount of individual 3−6 ring PAHs in the incoming water (900−1400 ng). With 48−65 g PUF, more than 99% of the amount was captured, with the exception of phenanthrene and benzo(*b*)fluoranthene, of which 96.5 and 98.5% were captured (with 48 g PUF). For PCBs, only congeners #52 and #138 were detected in water that passed through 48 g and 124 g PUF, respectively. The detected congeners demonstrated that the sorbent captured 99.7% or more of the amount of the individual PCB congeners. This means that any of the tested PUF amounts can sorb at least 1000−1500 ng of individual PAHs and 20 ng of individual PCBs, and thus meets the required sorption efficiency criteria. Initial tests of flow rates through the sorbents demonstrated that a) a flow rate of ~1 L h^{-1} could be maintained for at least four days, and b) the flow rates through the 1st and 2nd sorbent were not systematically different (Fig. S3, Supplementary material). The similar flow rates through the two sorbents ensure that water exiting the chamber through the 2nd sorbent was not drawn out of the sediment. Also, the hydraulic conductivity of the PUF sorbent was 10^{-2} m s^{-1}, which is about 3−7 orders of magnitude higher than the hydraulic conductivity through the sediment. This implies that the preferred pathway for water into the chamber is through the inlet sorbent. Suspended solids may clog the filter after prolonged sampling and change the conductivity of the outgoing PUF. Situations with high amounts of suspended solids may therefore be less suitable for the flow-through chamber.

3.2. In situ performance of the flow-through flux chambers

The sediment to bottom water flux of PAHs and PCBs determined by the flow-through chambers ranged from 62 to 2300 ng m^{-2} d^{-1} for individual PAHs and between 5.5 and 150 ng m^{-2} d^{-1} for the measured PCB congeners. The order of magnitude higher fluxes of PAHs reflect a combination of higher sediment concentrations and lower organic carbon normalized partition coefficients (K_{oc}) for most PAHs (Table 1, Fig. S5, Supplementary material). The relative standard deviation (RSD) for the flow-through flux chamber measurements was 3−20% (min-max) for PCBs (3−7 Cl), which agrees with the RSD of 15−50% for measurements of dissolved seawater concentrations of PCBs (3−8 Cl) in the Baltic Sea, also using PUF sorbents (Sobek et al., 2003). The RSD of the flux measurements for PAHs ranged between 17 and 96% (min-max). The flow-through chamber fluxes were 0.1−54 (PAHs) and 22−360 (PCBs) times higher than the calculated fluxes. It is

Table 1
In situ flux measurements and calculated flux [ng m^{-2} d^{-1}] for PAHs and PCBs. Standard deviation of triplicate measurements. Ratios for flow-through chamber measurements vs closed chamber measurements or calculated flux. Log K$_{ow}$ are from the references (Schenker et al., 2005; Ma et al., 2010). na indicates where calculation of ratio was not applicable.

Flux	log K$_{ow}$	Flow-through [ng m^{-2} d^{-1}]	Closed [ng m^{-2} d^{-1}]	Calculated[a] [ng m^{-2} d^{-1}]	Flow-through/Closed	Flow-through/Calculated
Naphthalene	3.40	< LOD	600 ± 89	< LOD	na	na
Acenaphthene	3.95	< LOD	68 ± 28	560 ± 380	na	na
Fluorene	4.11	< LOD	81 ± 22	440 ± 250	na	na
Phenanthrene	4.47	880 ± 300	280 ± 68	2900 ± 1100	3.1	0.3
Anthracene	4.57	110 ± 46	41 ± 22	1200 ± na	2.6	0.1
Fluoranthene	4.97	1500 ± 530	180 ± 110	5300 ± 2000	8.2	0.3
Pyrene	5.01	2300 ± 390	98 ± 54	3000 ± 1300	23.0	0.8
Benzo(*a*)anthracene	5.83	290 ± 140	40 ± 24	150 ± 58	7.4	1.9
Chrysene	5.67	360 ± 94	75 ± 42	210 ± 69	4.8	1.7
Benzo(*b*)fluoranthene	5.86	420 ± 180	29 ± 20	64 ± 18	15.0	6.6
Benzo(k)fluoranthene	5.86	170 ± 100	17 ± 7.3	28 ± 9.9	10.0	6.0
Benzo(*a*)pyrene	6.05	410 ± 390	18 ± 7.4	24 ± 7.6	23.0	17
Indeno(1.2.3-cd)pyrene	6.57	260 ± 170	18 ± 8	5.5 ± 1.4	15.0	48
Dibenz(a,h)anthracene[b]	6.61	62 ± 29	7.1 ± 1.1	1.7 ± 0.39	8.7	37
Benzo(g,h,i)perylene	6.63	280 ± 180	15 ± 6.2	5.3 ± 1.3	19.0	54
PCB 28	5.92	150 ± 7.3	2.1 ± 1.3	4.1 ± 1.2	74	38
PCB 52	6.26	55 ± 7.1	1.7 ± 0.52	2.5 ± 1.3	32.0	22
PCB 101	6.76	44 ± 1.4	1.2 ± 1	1.1 ± 0.42	37.0	40
PCB 118	7.08	12 ± 0.77	< LOD	0.11 ± 0.047	na	110
PCB 153	7.31	25 ± 1.2	1 ± 0.68	0.14 ± 0.036	25.0	180
PCB 138	7.3	24 ± 1.3	1 ± 0.67	0.21 ± 0.057	23.0	110
PCB 180	7.66	5.5 ± 1	0.45 ± 0.28	0.015 ± 0.0082	12.0	360

[a] From Fick's first law of diffusion and measured freely dissolved concentrations in pore water and bottom water. For concentrations < LOD, the levels in field blank were used.
[b] Log K$_{ow}$ for dibenz(a,h)anthracene was derived from a linear regression for other PAHs between log K$_{ow}$ and molecular weight.

difficult to directly compare calculated and measured fluxes as they account for different processes. The flux determined with the flow-through chamber also includes HOCs sorbed to both DOC and colloidal organic carbon, whereas the calculated flux exclusively accounts for flux of truly dissolved HOCs. An estimate of the influence of DOC on the measured flux demonstrated that it increased the observed flux with a factor of 1.3–9.2 for PCBs and a factor of up to 2.6 for PAHs, except for PCB 138, PCB 180 and dibenz(a,h)anthracene which were affected by a factor 21, 19 and 3.4, respectively (Table S3, Supplementary material).

3.3. Comparison of flux determined from flow-through and closed chambers

The flux generated from the flow-through chambers was compared to flux determined by the closed chambers. Flux determined with the closed chambers ranged from 7.1 to 280 ng m^{-2} d^{-1} for PAHs and from 0.45 to 2.1 ng m^{-2} d^{-1} for PCBs (Table 1). Hence, for individual substances, the flux determined with the oxygenated flow-through chamber that was designed to include effects of bioturbation, was a factor 3–23 (min-max) and 12–74 (min-max) higher for PAHs and PCBs, respectively (Table 1, and Fig. S2, Supplementary material). The difference between fluxes determined by the flow-through chamber and closed chamber agrees with previous observations of effects of bioturbation on sediment-to-water flux, both from laboratory experiments on collected sediment cores and from a modeling study (Table 2). However, some of the differences between the flux determined by the two chambers may also be caused by chamber design (see below).

A reduced sediment-to-water mass transfer resistance in the flow-through chamber could at least partly contribute to the observed differences between the flow-through and closed chamber flux measurements. Inside the closed chamber, at steady state, the concentration is half of the concentration in the pore water, which however was corrected for. The moving water in the flow-through chamber may reduce the thickness of the d$_x$ (Jørgensen

and Des Marais, 1990), which thus will affect the measured flux. Accordingly, Eek et al. (2010) reported a d$_x$ that was almost 2 times thicker inside compared to outside the closed chamber due to restriction of water movement inside the chamber. At natural conditions, the thickness of the d$_x$ is constantly changing (Glud et al., 2007) due to water turbulence and bioturbation. The flow-through chamber may therefore somewhat better reflect natural conditions than the static closed chambers.

3.4. Model estimates of the effect of chamber design on measured flux

The mass balance model describes the flux in and out of the chamber across the sediment-water interface (diffusive flux) and out of the chamber via outflowing water. The flux out of the chamber depends on the concentration in the enclosed water and the water outflow rate. A high outflow means that steady state (i.e. input = output) is quickly reached, however the water concentration in the chamber is then lowered and this changes the concentration gradient that drives the diffusive flux (flux increases). A low outflow means that it takes longer time to reach steady state and hence the mass on the sorbent cannot be used to estimate the diffusive flux (because the chemical inflow and outflow in the chamber are not equal during sampling). If the combination of water outflow rate and water concentration in the chamber results in a flux identical to the initial net sediment-to-water flux into the chamber, steady state is instantly achieved without a change in concentration in the chamber water and the theoretical experiment error will be low. Using the default model input values (Table S4, Supplementary material), the theoretical experiment error was 0.9–1.1 (i.e. ± 10% under/overestimation of flux) for most PAHs and 1.1–1.2 (10–20% overestimation of flux) for most PCBs. Hence, the inherent error on measured flux due to the experimental setup should be no more than 10–20% for these contaminants and measured concentration gradients. This error is within the uncertainty range caused by sampling and chemical analysis, and

Table 2
Increase in sediment-to-water flux of HOCs due to bioturbation reported in the literature and from this study.

Substance	Increase due to bioturbation Ratio of flux in bioturbated vs non-bioturbated systems	Type of study	Reference
HCB, HCH, DDx, PCBs	1—5	laboratory	Granberg et al. (Granberg et al., 2008)
PCB 32	3	laboratory	Hedman et al. (Hedman et al., 2009)
PCBs	4—13	laboratory	Josefsson et al. (Josefsson et al., 2010)
PCBs	1—25	laboratory	Koelmans et al. (Koelmans and Jonker, 2011)
Clorobenzenes and trifluoralin	4—6	laboratory	Karickhoff and Morris (Karickhoff and Morris, 1985)
Trichlorophenyl and PCBs	60—190	model	Thibodeaux et al. (Thibodeaux et al., 2001)
Sum PAH	9 (3—23, min-max)	field (in situ)[a]	This study
Sum PCB	42 (12—74, min-max)	field (in situ)[a]	This study

[a] Refers to the difference between flux measured by flow-through chamber and closed chamber, and may partly be due to other factors as well. Only PAH and PCB congeners above LOD for both chambers were used to determine the ratio between bioturbated and non-bioturbated systems. Min-max were determined for individual congeners.

substantially lower than the observed difference between measured flux with flow-through and closed chambers. Fluorene and PCB 180 had higher theoretical experiment errors (60% and 360%), due to their weaker measured concentration gradients between sediment pore water and bottom water (3 and 2, respectively, see below). Fluorene and PCB 180 were therefore excluded from the discussion below.

The model was used to estimate effect of chemical gradient, d_x and water flow through the chamber on the theoretical experiment error. The magnitude of the error arising from the experiment setup is dependent on the concentration gradient between sediment pore water and bottom water for most HOCs. Using a concentration gradient of 10, which was also measured for several of the chemicals in this study (Fig. S6), resulted in a calculated theoretical experiment error of 1.0—1.1 (i.e. flux was overestimated by 10% at the most) when default model parameter values were applied. A concentration gradient of 5 resulted in a theoretical experiment error of 1.3 and 1.4 (i.e. experiment overestimated flux of 30—40%) at most, for PAHs and for PCBs, whereas a concentration gradient of 2 increased the theoretical experiment error to 130—150% for PAHs and 150—170% for PCBs. The applicability of the flow-through chambers is hence limited to areas and chemicals with concentration gradients of about 10 and above. The theoretical experiment error for chemicals with a weak gradient would be reduced by lowering the water flow out of the chamber. The effect of d_x on the theoretical experiment error was quantified by using the range of d_x reported in the literature (0.0001—0.002 m; Table S6, Supplementary material, model default value was 0.001 m). This evaluation demonstrated that a d_x of 0.0001 m results in a theoretical experiment error of 0.5—0.7 for PAHs and 0.6—0.8 for PCBs (i.e. flux underestimated by 20—50% by flow-through chamber). Thus, in this situation, the net diffusive flux is greater than the advective transport out of the chamber and the concentration in the chamber will increase until the inflow and outflow matches. This will decrease the concentration gradient and hence the diffusive flux during the experiment. A thicker d_x (0.002 m) resulted in slower diffusive loss and a theoretical experiment error of 1.0—1.3 for PAHs and 1.1—1.4 for PCBs (i.e. flux overestimated by less than 40%). Thus, theoretical experiment error in this study is likely within a factor of 2, depending on the actual value of d_x in the chamber. The water flow through the chamber affects how fast chemicals are transported out of the chamber. A water flow through the chamber 10 times lower than the actual flow through the chamber would result in an underestimation of flux by 40—60%, while a 10 times faster water flow would lead to overestimations by approximately 30% at the most. Note that these numbers are valid only for the concentration gradients observed in this study (activity ratios of 4—34, Table S2), and at lower concentration gradients, the impact of flow on the error will be larger. A fast flow through the chamber results in small errors due to experiment design when the concentration

gradient is large, according to the model (Fig. S6 and Table S5, supporting material). However, a fast flow also impacts the thickness of the diffusive boundary layer, a process not included in the model. It is therefore necessary to keep the flow fast enough to quickly reach steady state, but without impacting the d_x or causing resuspension of the sediment.

In general, the theoretical experiment error is considerably smaller than the observed difference between the measured flux with the flow-through chamber and the closed chamber (PAH: factor 3—23 and PCB: factor 12—74; Table 2, Table S4, Fig. S2 in the Supplementary material). Hence, we hypothesize that a major part of the observed difference between flow-through and closed chambers may be attributed to bioturbation for five of the PCBs (PCB 28, PCB 52, PCB 101, PCB 138 and PCB 153) and for 11 of the PAHs (phenanthrene, anthracene, fluoranthene, pyrene, benzo(a) anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a) pyrene, indeno(1.2.3-cd)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perylene.

4. Conclusion

Field measurements of environmental fate of organic pollutants are associated with a number of uncertainties and limitations, as are also model estimates and extrapolations from laboratory experiments. The results from this study demonstrate that the flow-through chamber may be useful for a more environmentally realistic in situ assessment of HOC fluxes from sediment to water by including effects of bioturbation on the flux. The benthic flow-through chamber design offers a time efficient (within days) method for measurements of sediment-to-water flux of legacy HOCs with high concentration gradients between sediment and water (i.e. $C_{pw}/C_{bw} > 10$), and enables future research and assessments of environmental risk posed by sediments acting as secondary sources of pollutants. Remediation actions to manage contaminated sediments come with a very high cost and prioritizing of the sites at highest risk is therefore necessary. Measurements of fluxes of legacy HOCs from sediment to water could help prioritizing among these sites.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://

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Disclosure

The authors declare no competing financial interest.

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