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Passive Equilibrium Sampler for in Situ Measurements of Freely Dissolved Concentrations of Hydrophobic Organic Chemicals in Sediments

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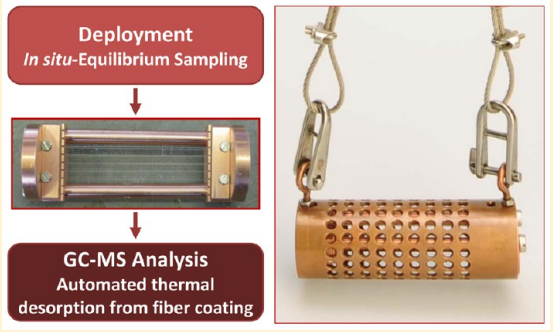
Supporting Information

ABSTRACT: In this study, an equilibrium passive sampling device is introduced that facilitates the in situ measurement of hydrophobic organic chemicals bioavailability in sediments in terms of freely dissolved concentrations. The new field sampler allows SPME fibers and silicone hollow fibers to be immersed and equilibrated in situ, whereas an automated liner exchanger (ALEX) facilitates the quantitative transfer of analytes to the GC without the use of extraction solvents. The sampler was developed for environmental monitoring as follows: (1) It is of very solid construction and can be reused practically ad infinitum. (2) Fibers with varying surface to volume ratios can be exposed in parallel in order to confirm that equilibrium was reached between sampler and sediment. (3) The equilibrium times allow a temporal resolution that is suited for monitoring of both long-term trends and seasonal effects. The automated thermal desorption reduced sample treatment to a minimum and ensured cost- and time-efficient measurements while minimizing potential error sources after the sampling. The sampler is applicable in a multitude of aquatic environments, especially where currents are low and sediments are muddy and well-mixed, e.g. by bioturbation. Examples for such environments are mud flats, harbor basins, river banks, and lakes.



INTRODUCTION

Hydrophobic organic contaminants (HOCs) enter aquatic ecosystems via numerous pathways, such as dumping, direct discharge into the water, aeolian deposits, or bound to suspended particles in river runoff. A substantial part is retained in the sediments. Among these, the toxic and persistent organic pollutants (POPs) are of special ecotoxicological concern. While being widely resistant to biodegradation, hydrophobic POPs can be incorporated into the fatty tissues of living organisms. Further contaminant accumulation may occur in the individual organism, both as a result of continuous exposure to a contaminated environment (bioconcentration due to diffusive uptake through biological membranes), and due to the ingestion of contaminated foodstuff or prey (biomagnification along aquatic food chains). Since humans are also end members of food chains originating from sediment-associated communities, reliable risk assessment of HOC contaminated sediments is required not only for ecological reasons, but also for human health.

When assessing the ecotoxicological risk of contaminated sites, bioavailability of contaminants must be taken into account. To this end, the contaminant's total amount is not a suitable measure since it addresses neither of the two aspects of bioavailability:[1] (i) Accessibility: The quantity of the contaminant in the system which can be made available for an organism (i.e., the fraction which is not "trapped" in the environmental matrix). (ii) Chemical activity: The contaminant's potential for spontaneous physicochemical processes such as partitioning between different compartments in an environmental system, including partitioning into biological tissues (bioaccumulation). Chemical activity (a) is proportional to C_{free}:

$$a = \frac{C_{free}}{S_L} \quad (1)$$

where S_L is the subcooled liquid solubility of the sparingly soluble compound in water. Chemical activities are often expressed as C_{free} (freely dissolved aqueous concentration) in environmental media with high water content.

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Hence, other than mere concentration measurements, in situ chemical activities and C_{free} express the thermodynamic potential of the contaminants to partition into benthic organisms.[1,2] Research over the past decade has shown that measurements of freely dissolved concentrations, rather than their estimations using generic K_D values, can significantly improve the prediction of bioaccumulation.[3] Kraaij et al.[4] predicted, for instance, internal concentrations in *Tubificidae*, a common class of benthic oligochaetes, as product of C_{free} and bioconcentration factors. For C_{free} and chemical activity measurements of environmental contaminants, passive sampling methods have been successfully applied.[5−10]

The major advantages of passive equilibrium sampling over "classical" methods in water analysis are the simple sample preparation and considerably lowered detection limits especially regarding the highly hydrophobic substances that are enriched from water to polymer by 3−7 orders of magnitude.

According to the type of sampling site and environmental matrix, various formats of equilibrium sampling devices have been used. These included, for example, low-density polyethylene sheets for pelagic sites[11] and thin polyoxymethylene sheets as used in the sampling of Baltic Sea bottom water.[12] Silicone-coated SPME (solid phase micro-extraction) fibers were applied for equilibrium sampling in the laboratory by Mayer et al.,[13] ter Laak et al.,[14] and Witt et al.[15] for soils and sediments.

There are a number of reasons for conducting the equilibrium sampling in situ rather than in the laboratory. Freely dissolved concentrations are under field condition often at steady state, and the result of both phase partitioning and a range of other environmental processes. These processes are normally not reproduced in the laboratory, which then can lead to deviations between laboratory measurements and actual field levels. The poisoning of sediment samples can give additional deviations. Furthermore, laboratory measurements are mostly not able to simulate the natural physicochemical conditions of field sediments, e.g. temperature and salinity.[16,17] Especially for larger rigid apolar compounds such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), the effect of temperature on solubility is significant.[18,19] Cornelissen et al.[12] estimated the temperature effect on low polychlorinated biphenyls (low PCBs) in sediment pore water to decrease chemical activity by a factor of 1.2 per 10 °C. It has been further observed that the presence of inorganic dissolved salts decreases the solubility of nonpolar or weakly polar compounds. For laboratory measurements, sediment samples, e.g. sediment cores, have to be transported to the laboratory. Biocides such as sodium azide or mercury compounds are often added to inhibit biodegradation. For samples collected on a marine research vessel, the sediment is often stored by freezing for several weeks before it arrives at the laboratory.[15] When freezing and thawing the sediment, HOCs that were previously particle-bound and thus not bioavailable might be released.

All these factors may alter freely dissolved concentrations and thus lead to over- or underestimation of the effective concentration. When measuring in situ, these problems are circumvented since the natural environmental conditions are preserved including those factors that potentially can affect either the chemical activity or its measurement.

The objective of the present study was to develop and test the performance of a compact passive sampler that can measure C_{free} for HOCs in sediment pore water in order to achieve more accurate data. The in situ sampling device is based on equilibrium passive sampling in order to assess the in situ chemical activity of HOCs in natural sediments. To achieve this, a prototype sampler was designed and fabricated.

The in situ equilibrium sampling device was designed and developed based on the experience of earlier in situ passive sampling studies by Maruya and co-workers,[20] van der Heijden and Jonker,[21] and Reible and co-workers.[22] The in situ equilibrium sampling device (ESD) should fulfill the same requirements as all ESDs: the polymeric sampling phase (i) should equilibrate with the sediment within a reasonable time and (ii) should not deplete the analytes in the sample by more than, e.g., 5%. The new sampler was designed to allow maximum contact between polymer and sediment, in an attempt to reduce diffusion distances and shorten equilibration times. Furthermore, the sampler was designed to allow the employment of fibers with multiple coating thicknesses in parallel, which were used to confirm equilibrium after sampling.[23]

For method development we focused on two classes of common sediment contaminants: PAHs and PCBs. Three polydimethylsiloxane (PDMS) sampling materials were deployed in parallel with nominal PDMS thicknesses ranging from 10 to 40 μm, aiming at an equilibrium confirmation based on equal analyte concentrations in PDMS materials of varying surface area to volume ratios. It was found necessary to actually measure PDMS coating thicknesses, since they are crucial for the uptake kinetics, the calculation of the polymer volume, and thus the measured analyte concentration in the PDMS. Further, differences in the partitioning properties of the various coatings were determined in the laboratory and later used to assess the equilibrium status in the field.

EXPERIMENTAL SECTION

Fibers. For this study three different polydimethylsiloxane (PDMS) formats were used:

(1) GF10: PDMS-coated glass fibers SPC 210/230 from Fiberguide Industries (Stirling, NJ, USA).
(2) GF30: PDMS-coated glass fibers from Polymicro Technologies Inc. (Phoenix, AZ, USA).
(3) HF40: Silicone tubing "Nagasep Hollow Fiber M-40" from Nagayanagi Co Ltd. (Tokyo, Japan).

The multiple coating thickness approach should ideally be conducted with samplers that are coated with one PDMS material, but with various coating thicknesses. This is easily accomplished with PDMS-coated jars or vials, where coatings can be made by addition of a PDMS prepolymer solution in a volatile solvent and the subsequent solvent evaporation on a laboratory roller.[1] Unfortunately, for fiber-based sampling materials, it was not so easy to obtain fibers with varying coating thickness of one PDMS material. Potential differences in the partitioning properties of the applied fibers are thus crucial, but expected to be minor to moderate based on a recent study by Difilippo et al.[17] They performed a two-tailed t test for comparing K_{PDMS} values for equal compounds measured with different PDMS sources. The authors demonstrated that the majority (92%) of the results were not statistically different ($p \leq 0.10$). The authors concluded that PDMS source did not significantly impact measured K_{PDMS}. Differences in partitioning properties were, in the current study, experimentally determined on the basis of PDMS to PDMS partition coefficients that were determined as concentration ratios

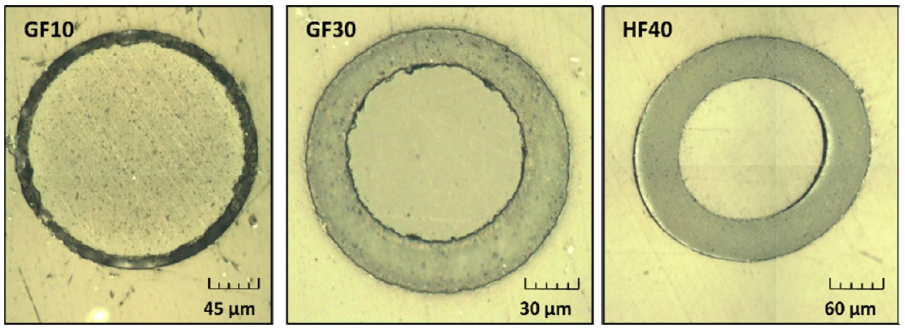

Figure 1. Photographic images of the fiber coatings measured with laser scanning confocal technology (OLS3000 LEXT Microscope); submicrometer imaging with 0.12 μm resolution.

Table 1. Important Fiber Parameters and Fiber Geometry Calculated for 1 cm Fiber Length

name	coating thickness[a] s (μm)	inner radius r (μm)	outer radius[b] R (μm)	PDMS-volume V (μL cm^{-1})	surface area A (cm^2)	A/V ratio (cm^2 cm^{-3})	V_{sed}/V_{fiber} ratio (cm^3 cm^{-3})
GF10	12.7	103.6	116.3	0.0877	0.0731	832.9	9118.2
GF30	26.7	53.6	80.3	0.1123	0.0505	449.2	7122.8
HF40	48.1	85.3	133.4	0.3305	0.0838	253.6	2420.7

[a]Mean values for 12 replicates are given. [b]$R = r + s$); GF: fiber with glass core and PDMS coating; HF40: PDMS tube/hollow fiber.

between the applied PDMS materials in the initial laboratory experiments.

Differences between nominal and actual coating thicknesses would directly affect the calculated PDMS volumes and thus analyte concentrations, when based on nominal thicknesses as it is common for Solid Phase Microextraction with PDMS coated fibers. Therefore, actual coating thicknesses were measured with laser scanning confocal technology (Figure 1). Three fiber samples per subgroup were embedded in an epoxy resin (EpoThin, Buehler GmbH, Düsseldorf, Germany) and cured for 8 h. Samples were ground and further polished with an oxide suspension. Inner and outer diameter as well as coating thickness was determined by means of optical microscopy (Olympus LEXT OLS 3000, Hamburg, Germany) with 20× and 50× magnification. Data are calculated as mean ± standard deviation (Table S1). Results show that the coating thickness differs markedly from the specification of the manufacturer in all cases. Important fiber parameters and the fiber geometry of the 3 different formats are given in Table 1.

Sample Preparation and Analyses. Fibers were cut into 10-cm pieces and washed twice in methanol and twice in ultrapure water by sonication before use. All solvents (ultrapure grade) were checked for impurities.

For GC/MS method development and for the external standard quantification of the SPME devices, external standard solutions from Dr. Ehrenstorfer (Augsburg, Germany) were used: PAH-Mix 9 containing the 16 U.S. EPA-PAHs (acenaphthene, acenaphthylene, anthracene, benzo[a]-anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo-[g,h,i]perylene, benzo[k]fluoranthene, chrysene, dibenz[a,h]-anthracene, fluoranthene, fluorene, indeno[1,2,3-c,d]pyrene, naphthalene, phenanthrene, pyrene) and PCB-Mix 3 (PCBs 28, 52, 101, 118, 138, 153, 180).

After sampling, C_{PDMS} was calculated to determine the polymer to polymer concentration ratios (C_{PDMS1}:C_{PDMS2}) for the different fiber materials. C_{free} of the PAH experiments was calculated from its concentration in the fiber coating (C_{PDMS}), with K_{PDMS} being the PDMS-to-water partition coefficient as measured by Witt et al.[15] for PAHs:

$$C_{free} = \frac{C_{PDMS}}{K_{PDMS}} \quad (2)$$

In method development, two sediments originating from the port of Hamburg/Germany were used:

(1) Hamburg Harbor (Moldauhafen) sediment for the tank experiments
(2) Sediment from the METHA treatment plant for dredged harbor sediments for the kinetic experiments, kindly provided by the Hamburg Port Authority

These muddy, fine-grained, and carbon-rich sediments were known to be heavily contaminated by HOCs. Both sediments were collected in November 2010, intensively mechanically homogenized, and subsequently stored in the dark at 10 °C.

Nondepletion Criteria. Driven by diffusion, analytes partition into a suitable sampling phase, e.g. polymer phases for passive sampling of HOCs, until a thermodynamic equilibrium is reached, i.e. analyte activities in environmental system and the passive sampler are equal. Equilibrium concentrations in the sampling phase are measured and eventually linked to the analyte's chemical activity. For valid measurements it is important that the transfer into the sampling phase does not deplete the sample as this would lead to an underestimation of C_{free} and chemical activity of the sample.[24,13] To test if the PDMS used for passive sampling depleted the HOC levels in the sediment by more than 5%, eq 3 was applied, where V_{PDMS} is the volume of PDMS (μL), K_{PDMS} is the compound-specific PDMS to water partition coefficient, K_{OC} is the compound-specific organic carbon to water partition coefficient, and m_{OC} is the mass of the OC in the sediment (g).

$$V_{PDMS}K_{PDMS} \ll m_{OC}K_{OC} \quad (3)$$

The compound-specific K_{OC} values were calculated from organic carbon normalized sediment concentrations (measurement of sediment concentration: see SI text S1) and the freely dissolved pore water concentration:

$$K_{OC} = \frac{c_{OC}}{c_{free}} \quad (4)$$

The TOC content of the METHA sediment was 4.5% and that for Moldauhafen was 5.9% (for sediment analyses and TOC measurements, see SI text S1).

Time to Equilibrium. For the in situ sampler it is important to prove that equilibrium is reached within a reasonable time. Two different approaches were applied to verify that equilibrium had been established:

(1) Equilibration times for target substances under static conditions were determined in a time-series experiment.
(2) PDMS with multiple coating thicknesses and area to volume ratios were applied (see Table 1 for fiber properties).

Time series experiments were performed with the three different fiber materials. For each experiment three equal aluminum tanks were filled with homogenized wet METHA sediment (each with 160 g). SPME fibers of the different fiber types (n = 52; fiber length: 4 cm; Table S2) were added into the different tanks. The fibers were manually separated from each other. The sediment sample was sized to ensure nondepletive extraction throughout the experiment (Table S4) according to eq 3. The jars were kept in the dark at a controlled temperature of 4 ± 1 °C throughout the experiment.

Uptake profiles into the PDMS phase were generated by fitting a first-order one-compartment model (eq 5). This model is not necessarily a precise reflection of the uptake process into the fiber. However, it is expected sufficient to fit the experimental data in order to estimate the approximate time to reach 90% of equilibrium concentration in PDMS:

$$c_{PDMS}(t) = c_{PDMS,\infty}(1 - e^{-kt}) \quad (5)$$

Using the rate constant k, the extraction time t needed to reach near equilibrium conditions, e.g. 90% of the equilibrium concentration $c_{PDMS,\infty}$ in the PDMS can be estimated (eq 6).

$$t_{90\%} = \frac{\ln(10)}{k} \quad (6)$$

Passive uptake into coatings of different thickness is employed to confirm equilibrium without studying up-take kinetics while also providing the measurements needed for the calculation of mean concentration and standard deviation. Once equilibrium is achieved, the concentration ratios between the different PDMS coatings are constant. This approach allows not only validation of equilibrium, but extends to disclosing other potential artifacts such as sample depletion and polymer surface adsorption.[23]

Sampler Design. A new sampling device was developed based on the requirements for in situ equilibrium sampling in sediments. It should be compact enough to allow manual deployment, ensure a good sediment contact while protecting the sampling material, and also allow various types of sampling materials to be deployed. The sampling device is composed of two separable units: the fiber assembly and, around that, a protective housing (Figure 2). The housing was attached to a stainless steel rope with 2 stainless steel lashing cleats for retrieval of the sampler. Copper was chosen as base material in order to inhibit biofouling of both the device itself and the silicone-coated fibers.

The device's fiber-holding fixture is capable of accommodating several passive samplers of different PDMS thickness and different formats in parallel, i.e. fibers of different thickness of PDMS and PDMS tubing. This allows for replication and internal validation of the measurements as proposed by Reichenberg et al.[23]

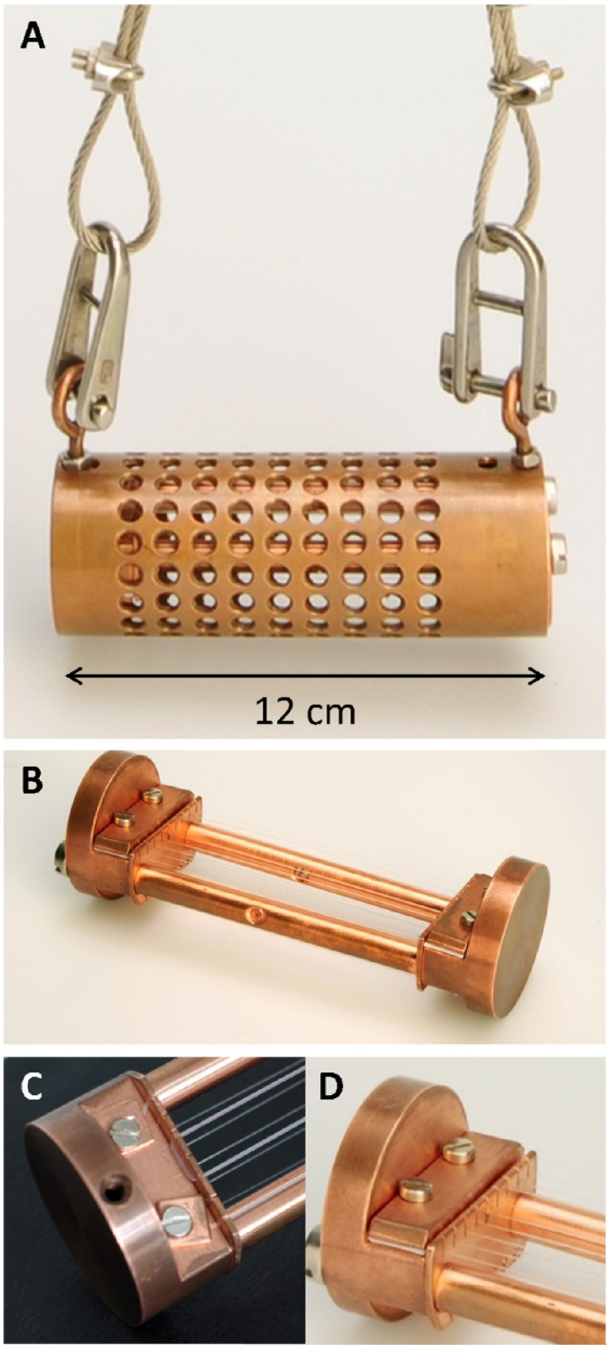

Figure 2. In-situ sampler. Full assembly (A), interior unit (B), holding fixture for hollow fibers (C) and glass fibers (D).

Nine fibers are mounted on a frame (fiber length: 95 mm) where they are fixed by a PTFE-armored clamp. The hollow fiber can be doubled-back to a total fiber length of 1000 mm on a second frame.

The rigid cylindrical housing is made from a perforated copper pipe (inner diameter: 40 mm; wall thickness: 2 mm; diameter of holes: 5 mm) through which fine-grained sediment particles can pass and come into direct contact with the SPME fibers while larger objects, e.g. mussel shells, are kept outside.

Performance Testing. For method validation, equilibrium concentrations of 9 PAHs in SPME fibers of 10-μm fiber coating (GF10) exposed to the sediment by the new sampling device were compared with concentrations from ex situ SPME measurement in the laboratory as described by Witt.[15]

Laboratory Method (ex Situ SPME). The ex situ method (matrix SPME) is described in detail by Witt et al. 2009.[15] Briefly, 4 g (wet weight) of sediment and approximately 2 mL of ultrapure water were filled into 9-mL test tubes closed with PTFE-lined septum caps, and thoroughly mixed by shaking. Three precleaned SPME fibers with 10-μm fiber coating (GF10) were inserted approximately 9 cm deep into each vial through a syringe needle that pierced the septum. After retrieval of the needle, fibers were held in place by the septum. Agitated on an overhead shaker, the SPME sampling in sediment slurries was done in the dark. Experimental parameters such as temperature and exposure time were adjusted as needed to meet the conditions of the corresponding experiment with the in situ sampling device.

Tank Experiment. In a first approach, a tank experiment was performed to compare the ex situ SPME (see Laboratory Method) with the in situ sampling device under laboratory conditions. Therefore a glass tank was filled with 2 L of wet sediment from Hamburg Harbor (Moldau Harbor) which was carefully overlaid with additional water from the sampling site. The sampling device was placed on the sediment surface. Due to its own weight, the device sank into the sediment until it was completely covered. Nine GF10 fibers were placed in parallel in the in situ sampling device. Fibers were exposed at laboratory temperature (20 °C) for 21 days to achieve equilibrium for all PAHs. The experiments were carried out in the dark to prevent photodegradation of PAHs.

Field Experiment. In a second experiment the ex situ SPME in the laboratory was compared with in situ deployment in the field. Glass fibers with 10- and 30-μm fiber coating were used during this experiment. Two freshwater sampling sites were chosen to evaluate the operational reliability and the sampling efficiency of the device under field conditions:

(i) A rather pristine town canal (Entenfleet) in the suburbs of Hamburg/Germany, sampled in winter. A corresponding ex situ SPME experiment was carried out at the same water temperature of 4 °C in the darkness in the laboratory.
(ii) Elbe River sediments near Geesthacht/Germany were sampled in early summer.

In both cases, the sampler was deployed and fixed to a mooring platform. Samples were recovered after 21 days. Sampler position and sediment filling level were visually checked by divers both at deployment and recovery.

Temperature plays an important role for in situ sampling. The in situ temperature during the sampling campaign in winter was significantly different from those used for the calculation of K_{PDMS} in the laboratory. Therefore, K_{PDMS} values of Witt et al.[15] were temperature corrected using the van't Hoff equation[18] and the ΔH_{PDMS} values calculated from Muijs and Jonker.[25]

Fiber Handling and Sample Analysis. When removed from the sediment, fiber samples were rinsed with ultrapure water and wiped dry with a lint-free tissue. Until analysis, fibers were wrapped in cleaned aluminum foil and stored at −20 °C.

The GERSTEL automated liner exchange (ALEX) technology was originally developed for exchanging injector liners in the Cooled Injection System (CIS). In the present study we applied the ALEX for another purpose. After in situ sampling, PDMS coated fibers and silicone hollow fibers were placed in individual GC liners and the ALEX was then used for the automated introduction (GERSTEL Multi Purpose Sampler (MPS)) and thermal desorption (CIS) of the fibers. GC auto sampler trays can hold up to 98 liners which enable the contamination-free storage of the fibers until analysis. Prior to use, the liners (deactivated CIS glass liners with notch, Gerstel GmbH, Muehlheim/Germany) had been prepared by placing a plug of deactivated glass wool right above the notch which is intended to hold the fiber in position during thermodesorption. Plugged liners were heated for 19 min under helium flow in the GC injector at 250 °C and stored free from contamination in the ALEX liner tray.

For analysis, the injector temperature was increased from 20 to 260 °C at 12 °C s^{-1} to ensure thermal desorption from the fiber. Fifteen min after sample introduction, the injector was returned to split mode and the GC run started: the GC temperature was programmed from 60 °C (hold: 15 min) to 195 °C (hold: 2 min) and to 225 °C at 15 °C min^{-1}, from 225 to 260 °C at 5 °C min^{-1}, and finally to 300 °C at 20 °C min^{-1}. The final temperature was held for 10 min.

Chromatography was performed on a DB-5 fused silica column (30 m × 0.25 mm I.D., 0.25 μm; J&W Scientific), with helium (average linear velocity of 37 cm s^{-1}) as carrier phase. The detection and quantification were based on mass spectrometry (selected ion mode, quadrupole mass filter, triple-axis detector) with an Agilent 5975C instrument. The fiber samples were quantified by external standard calibration. Two to three ions per compound were monitored. One ion signal was used for quantification; the others were used for qualitative information. Group signals were monitored into time-programmed SIM groups to minimize the number of ions acquired at any one time. Dwell times for each group that yields 15−20 cycles across a peak were selected. A five-point external standard calibration curve was generated to quantify target HOCs sorbed to SPME fibers.

QA/QC and Method Verification. For quality and assurance purposes, all fibers were collected at least in triplicates. New SPME fibers were used for all work described in the study. Analytical blanks of empty GC liners and cleaned fibers were determined. Target HOCs were not detected in any procedural blank. The quality of the analytical method was evaluated by checking the recovery of the external standard solution (PAH mix No. 9 and PCB mix No. 3 for PCBs by Dr. Ehrenstorfer). Mean standard recoveries were 92% ± 12%. Method detection and quantification limits (MDLs and MQLs) were calculated using the average PAH and PCB mass in the blanks plus 3 times (MDL) or 10 times (MQL) the standard deviation and converted to C_{PDMS} (pg μL^{-1}). MQL ranges between 3.2 and 7.2 pg μL^{-1} PDMS for PCBs and 3.6−8.9 pg μL^{-1} PDMS for PAHs. MDLs are lower than 2 pg μL^{-1} PDMS for all target substances. Nine fibers were analyzed in the in situ sampling device to determine the relative standard deviation (RSD) of the analytical procedure. RSD ranged between 4.3 and 12.2% for PAHs and 2.2−14.1% for PCBs.

RESULTS AND DISCUSSION

Time to Equilibrium. Thermodynamic equilibrium between sediment and PDMS was established within a time span of roughly 5−20 d (PAHs) and 20−70 d (PCBs) for all sampling materials (Table S3). These rather short equilibrium

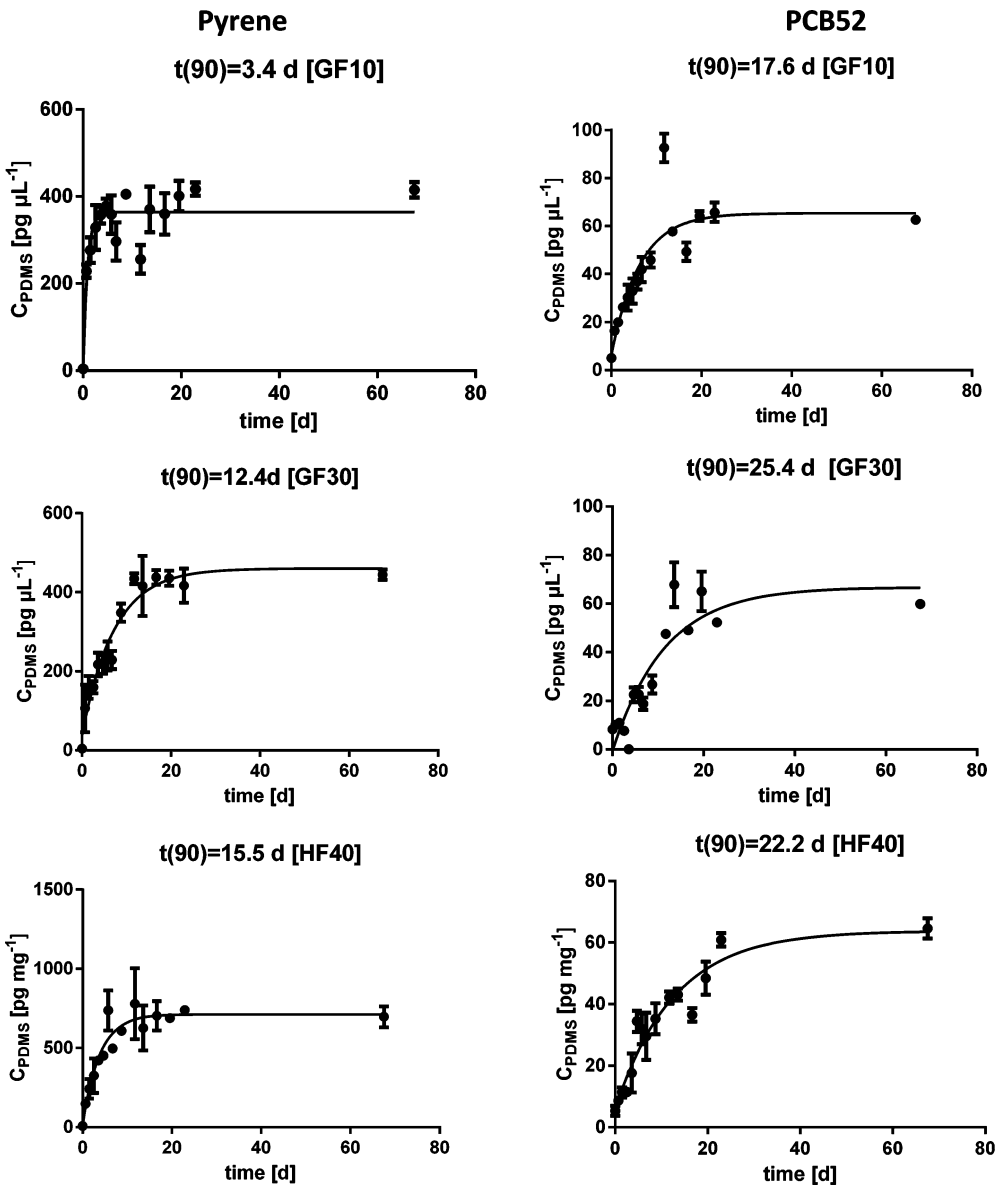

Figure 3. Example curves: uptake of contaminants into PDMS fibers with 10 and 30 μm PDMS coating as well as hollow fibers with 40 μm PDMS walls; $t(90)$ values are given based on the upper confidence limits of model parameter estimation (mean values and standard deviation); drawn lines present first-order model fit.

times for static sampling are possible due to the large area to volume ratios of the sampling phases. Furthermore, direct contact between fibers and sediment-bound analytes might have speeded up partitioning into the polymer by short cutting the unstirred aqueous boundary layer, which constitutes a high resistance for the diffusive mass transfer of hydrophobic organic chemicals. The uptake of PAHs and PCBs into the three different samplers was plotted against time (Figure 3) and a simple exponential function (eq 5) was fitted to the data. The concentration ratios between the fibers were then determined, and these ratios were later used for confirming equilibrium under field conditions (Table 2). Interestingly, the ratios between the uptake rates of the three samplers did not fully fit the theory (see Table S3), which supports earlier observations that it can be more difficult to control and exactly reproduce uptake kinetics compared to the equilibrium sampling situation.[13] Fortunately, this did not introduce any error since all measurements were done in the equilibrium mode. The deviations from kinetic theory could have several reasons. It is important to realize that uptake profiles will follow a simple exponential function only when the mass transfer from sediment to polymer can be approximated by a two compartment system, where each compartment is well mixed and there is only one rate limiting step. In the laboratory, it is relatively simple to achieve this situation when mixing a sufficient amount of sediment. For in situ and static laboratory sampling, it is generally not possible to achieve these conditions. Local depletion of the sediment adjacent to the polymer or desorption resistance can then lead to more complicated uptake profiles. For instance, the uptake might first be limited by diffusion within the aqueous boundary layer. After some time, the polymer might impose a local depletion to the sediment in its vicinity. Desorption from the sediment matrix near the fiber and aqueous diffusion from further away will then both contribute to the flux into the coating, and the distributions of these two contributions will change in time.

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Table 2. Polymer−polymer Concentration Ratios (C_{poly1}:C_{poly2}) Calculated in Units of Mass Per Mass[a]

	$C_{GF30:GF10}$ (L L^{-1})		$C_{HF40:GF10}$ (L L^{-1})	
substance	mean	± RSD (%)	mean	± RSD (%)
phenanthrene	1.28	6.26	0.92	0.72
anthracene	1.08	5.16	0.94	5.78
fluoranthene	1.26	4.58	1.01	2.51
pyrene	1.41	4.25	1.49	1.17
benzo[a]anthracene	1.52	4.07	1.07	3.52
chrysene	1.20	8.47	1.27	1.25
benzo[b]fluoranthene	1.72	3.18	1.53	3.90
benzo[k]fluoranthene	1.73	3.18	1.35	4.95
benzo[a]pyrene	1.70	2.90	1.45	3.00
indeno[1,2,3-c,d]pyrene	1.59	3.25	1.27	4.45
benzo[g,h,i]perylene	1.59	2.22	1.28	9.63
PCB 28	0.89	5.71	0.93	6.50
PCB 52	0.82	6.22	1.08	3.98
PCB 101	0.83	9.11	0.89	3.01
PCB 118	0.87	3.39	1.12	2.07
PCB 153	0.84	6.83	1.23	0.37
PCB 138	0.86	9.63	1.24	2.96
PCB 180	0.89	9.92	1.24	3.83

[a]Mean values and relative standard deviation (RSD) of 9 replicates.

Sampler Design. Full functionality of the sampler design was demonstrated in the tank and field experiments. The device was sunk by its own weight and immersed in the sediment without any additional ballast or anchorage having been applied. Upon recovery, sediment coverage and position of the sampling device appeared unchanged. The perforated copper pipe had filled with sediment but all fibers were undamaged and apparently free from biofouling. As intended, the sampler housing protected the SPME fibers from breakage and other mechanical damage, while sediment particles penetrated through the perforations. Full contact between sediment and fiber surface was achieved. Microbial deterioration of the fiber surfaces was possibly prevented due to the biocidal properties of the copper. Since exposure times are rather short, alternative housing material will be tested which is less biocidal than copper, e.g. stainless steel or titanium.

In the current configuration, the device is applicable in a wide range of nonstratified soft-sediment environments, such as harbor basins, tidal flats, or lakes. Even at sites where the sediment is covered by several meters of water, deployment is generally feasible when facilities for fixture and localization exist. Since "obstacles" both on sediment surface or further down, such as pebbles, sediment-dwelling organisms, or plant roots, may result in incomplete immersion of the sampler,

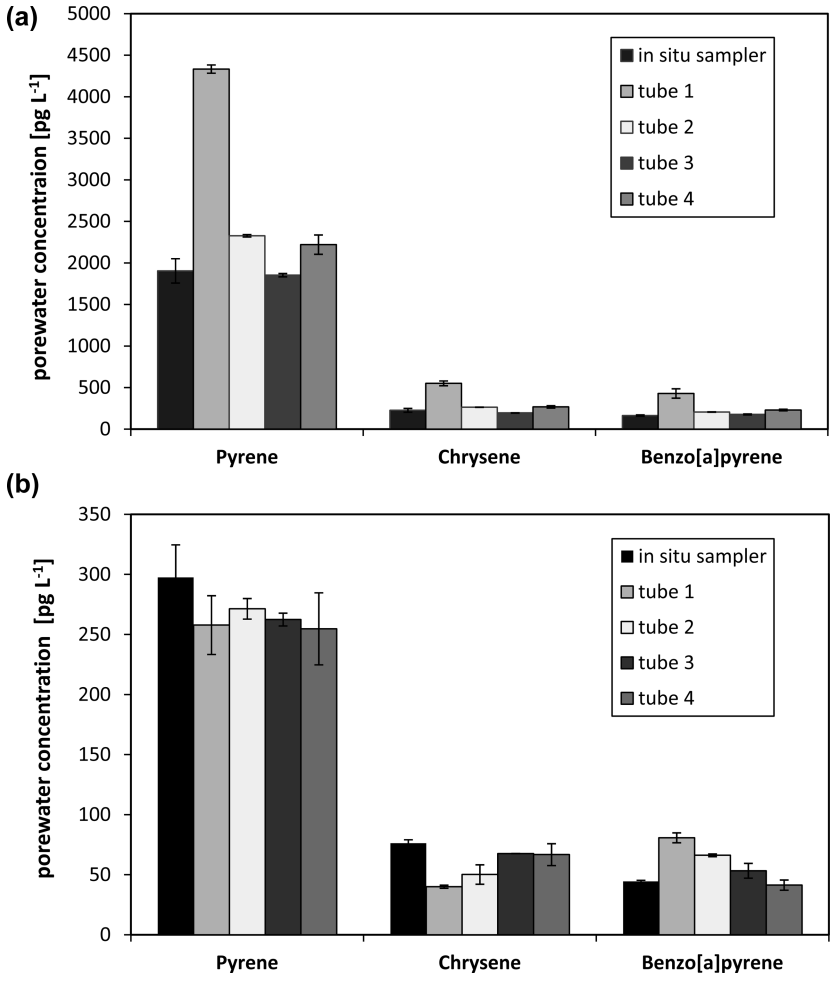

Figure 4. (a) Laboratory experiment: C_{free} from ex situ SPME (tube 1−4) vs C_{free} calculated from in situ sampler (tank experiment) under similar conditions (temperature: 20 °C, darkness) with 10-μm glass fibers (GF10) and PAHs as test substances and Hamburg Harbor (Moldauhafen) sediment. (b) Field experiment: Ex situ SPME (tube 1−4) vs in situ sampler under similar conditions (temperature: 4 °C, darkness) with GF10 fibers and PAHs as test substances (Fleet sediment; winter).

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supervision (e.g., with divers, ROVs, or video camera) of the immersion process is recommended.

Performance Testing. Laboratory measurements with matrix-SPME (agitated) and tank experiments with the new device yielded freely dissolved concentrations that were very similar and did not differ statistically (Figure 4a). Another comparison between matrix-SPME (agitated) in the laboratory and field sampling with the new device provided again very similar results, which again did not differ statistically (Figure 4b). Absence of sample agitation during tank and field sampling was successfully compensated for by prolonged equilibration times. One replicate (tube 1) of the ex situ matrix-SPME measurements deviated from the other matrix SPME replicates and the field sampling, which likely was caused by imperfect sub sampling.

The fact that laboratory and field extractions produced similar measurements does not render the in situ approach superfluous. These similarities were aimed for and laboratory conditions were adjusted to in situ conditions in order to rule out any procedural shortcomings of the new sampling method. In routine bioavailability assessment, such adjustments of laboratory conditions are impracticable, especially when samples from different locations are to be assessed. Besides, "true" field conditions (e.g., temperature, salinity, pH) would never be achieved.

Sample Analysis/Method Validation. Operating the sampling device with passive sampling phases of small volume, when compared to the high sediment volume being sampled (kinetic experiments: 160 g of wet sediment), the requirement of nondepletive extraction is fulfilled (Table S4).

Because SPME fibers are not subject to intense sample cleanup, detection and quantification limits clearly depend on levels of nontarget substances, which might disturb chromatographic analysis. The method quantification limit (MOQ) of the GF10 experiments ranged from C_{free}= 0.005 to 50 pg L^{-1} for PAHs for GF10 (fiber with the lowest fiber volume). Hence, the in situ method covers a wide range of contamination levels in natural sediment pore water systems. This is also demonstrated by the accurate PAH measurements of both a pristine (Entenfleet) and a contaminated site (Schleuseninsel Harbor) (Figure 5).

An additional field experiment was conducted in order to test the applicability of the device under field conditions and confirm the equilibrium sampling conditions via concentration ratios between the coatings (Table 2). The in situ sampler was equipped with GF10 and GF30 glass fibers (4 replicates for each material) and then deployed for 70 days in the sediment of River Elbe near Geesthacht. Concentrations of PAHs and PCBs in PDMS were determined for both fiber types. The obtained ratios from the final part of the kinetic experiment and the field experiment differed not markedly and confirmed that equilibrium partitioning between sediment and fibers had been established for all substances in the field (Figure 6). Furthermore, the field sampling has reconfirmed the PDMS to PDMS concentration ratios of the glass fibers.

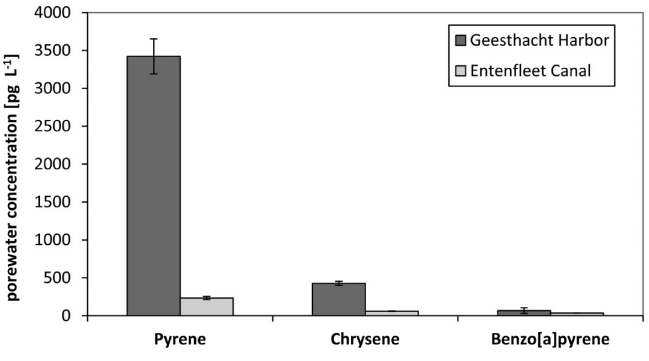

Figure 5. In-situ measurement of PAHs at a contaminated site (River Elbe near Geesthacht, Schleuseninsel Harbor; T = 20 °C) and a pristine canal (Entenfleet during winter, T = 4 °C); experiments were performed with GF10 fibers and C_{free} was temperature corrected for winter.

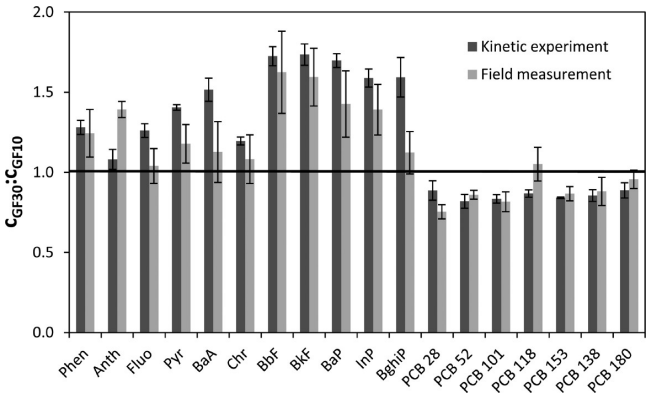

Figure 6. Concentration ratios between two coexposed PDMS coatings (C_{GF30}:C_{GF10}) from in situ deployment in River Elbe sediment and the equilibrium phase of the kinetic experiment. The good agreement of in situ and laboratory ratios supports fulfillment of the equilibrium criterion for the in situ sampling.

Final Remarks and Future Development. In this study, we introduced an equilibrium sampling device that allows in situ sampling of HOC bioavailability in sediments in terms of freely dissolved aqueous concentrations. The in situ sampling device has several advantages compared to laboratory matrix SPME or solvent-based sample extractions that make it an ideal monitoring tool: Most importantly, the ecologically relevant parameter "in situ bioavailability" is addressed instead of total sediment or pore water concentrations. The extraction and analysis of the sampler is fully automated. This strategy combines in situ sampling and automated analysis and minimizes those artifacts and errors related to sample storage, transport, and treatment. Both sampling and analysis procedures are simple, robust, and cost-effective.

The greatest amount of emphasis was put on the functionality and robustness of the sampling device. The device serves not only the purposes of fiber conveyance but those of sample protection from abrasion and biodegradation during field exposure. The versatility of the fiber assembly even offers potential for method validation. In future sampling campaigns, we will make use of internal equilibrium confirmation by employing sampling materials with different coating thicknesses. If necessary, coating thicknesses will be measured and PDMS to PDMS partition ratios applied to correct for minor differences in the partitioning properties of the coatings from different suppliers. Our future development aim is the applicability of the sampling device in open-sea sediments, e.g. alongside off-shore hydrographic stations or wind farms. Sampling in such remote places requires improved techniques for deployment and retrieval of the sampling device. Another important potential application area is the monitoring

of remediation progress when amending, e.g., activated carbon to contaminated sediments.[26] Furthermore, in situ sampling can be used to evaluate the effectiveness of sand caps for contaminated sediment management.[27,28] Finally, this in situ method for evaluating the bioavailability of sediment-associated contaminants is able to improve the assessment of the impacts of contaminated sediments.[29]

■ ASSOCIATED CONTENT

Supporting Information

Additional information as cross-referenced throughout the manuscript. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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