Sensitive Equilibrium Sampling To Study Polychlorinated Biphenyl Disposition in Baltic Sea Sediment

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S *Supporting Information*

ABSTRACT: An equilibrium sampling approach using glass jars with μm thin coatings of the silicone polydimethylsiloxane (PDMS) was validated and applied to background sediment samples from a >50 km transect in the Stockholm Archipelago. Equilibrium between the sediment and the PDMS was demonstrated using different coating thicknesses. From the concentrations of polychlorinated biphenyls (PCBs) in the PDMS, we assessed (i) freely dissolved concentrations in the sediment interstitial porewater ($C_{Sediment\_free}$); (ii) the equilibrium status between sediment and water; (iii) the equilibrium status between sediment and biota; and (iv) site-specific sediment/water distribution ratios (K_D). The results showed that (i) Stockholm was a source of PCBs to the Baltic Sea as evidenced by significantly higher $C_{Sediment\_free}$ in Stockholm Harbor; (ii) the fugacity in sediment exceeded that in water (monitoring samples collected in February) by an average factor of 4.0; (iii) the fugacity in sediment exceeded that in herring by an average factor of 5.2; and (iv) K_D near Stockholm Harbor was 0.3−1.7 log units greater than in the outer archipelago. The coated glass jar method with its high precision and built-in QA/QC opens new possibilities to study the disposition of hydrophobic chemicals at trace levels ($C_{Sediment\_free}$ down to 1.06 fg/L) in background environments.
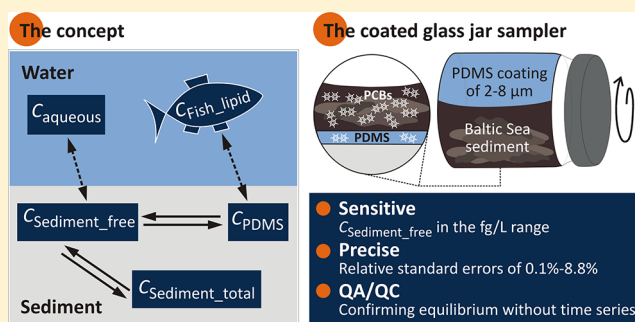
■ INTRODUCTION

In recent years, passive equilibrium samplers (PES) have become increasingly popular since they open up new research areas that focus on the availability and activity of chemicals rather than their mere presence in the environment.[1] PES require the use of a reference phase (e.g., a polymer) that is brought into contact with the sample in order to allow a partitioning equilibrium to be established between the two phases. In this context, the silicone polydimethylsiloxane (PDMS) is a versatile sampling material that has been used in various PES with different characteristics.[2−6]

An additional benefit of PES is that they open up new opportunities in multimedia process studies: If the polymer is equilibrated with different environmental media, the concentrations of a chemical in the polymer can be measured and then be directly compared. PES can hence be used as "chemical thermometers", i.e. they allow for studies of processes such as diffusion and partitioning of chemicals from one compartment to another.

Fugacity is a very useful concept for studying the behavior of pollutants in the environment.[7,1] The fugacity of a chemical in a specific medium describes its "escaping tendency" from this phase into another phase (e.g., from sediment to water). PES can be used as tools to measure the fugacity and the closely related chemical activity of pollutants in different compartments

in the environment, thereby providing thermodynamically based insight into contaminant disposition and fate, and into processes such as bioaccumulation.

Different PES methods for various hydrophobic organic compounds (HOCs) have been described in the literature. A variety of polymers have been employed, including polyethylene,[8−11] polyoxymethylene,[11−14] ethylene vinyl acetate,[15,16] and PDMS.[11,17−21] The equilibration between the sample and the polymer has mostly been done in the laboratory, but some field applications (generally to sample water) have also been reported.[9−12,16] Some studies did not achieve equilibrium between the sampled medium and the polymer during deployment and thus used a correction employing performance reference compounds.[9,10] However, sampling in the kinetic uptake phase is subject to uncertainty related to the estimation of the sampling rate for each sampling site and event. To increase the likelihood of equilibrium being reached, a large polymer surface area to polymer mass ratio is required. However, a small polymer mass (e.g., thin solid-phase microextraction fiber coatings) sets limits to the method

sensitivity.[18] Hence, a sampler format with a large polymer mass and a large specific surface area is needed if the PES is to be applicable to background locations and equilibrate within a practical time span.

Reichenberg et al.[20] developed such a method for contaminated soil, applying glass vials with 3−12 μm PDMS coatings on the inner vertical walls. The major advantage over other approaches was the built-in validation consisting of different polymer coating thicknesses that confirmed equilibrium partitioning between each sample and the polymer while at the same time showing that no sampling artifacts such as surface abrasion of the PDMS coatings were present.[20] This method was modified to larger glass jars and used to assess contaminated sediment.[21] The comparatively large polymer mass at thicknesses of a few μm offered equilibration within 2 weeks and had potential for improved sensitivity for studies in background areas; this has however not been exploited so far.

The present study was designed to test whether the PDMS-coated glass jar approach[20,21] provides sufficient analytical sensitivity to measure polychlorinated biphenyls (PCBs) in Baltic Sea sediment at background levels. It was also intended to explore the utility of equilibrium sampling of sediments in different contexts: (i) investigating spatial gradients in sediment fugacity; (ii) assessing gradients in sediment/water fugacities; (iii) evaluating bioaccumulation by comparison of fugacities in sediment and biota; and (iv) determining site-specific sediment/water distribution ratios (K_D).

■ EXPERIMENTAL SECTION

Standards and Materials. Generally, 7 "indicator" PCB congeners were investigated: PCBs 28, 52, 101, 118, 153, 138, and 180 (numbering according to IUPAC, log K_{OW} in the range 5.67−7.36).[22] In a method sensitivity test, we analyzed 7 additional PCB congeners in selected samples: PCBs 18, 70, 110, 105, 149, 199, and 194 (log K_{OW} in the range 5.24−7.80).[22] Details about the chemicals' and solvents' suppliers and purity are given in Text S1 in the Supporting Information.

Internally coated glass jars were custom-made at the Department of Environmental Science at Aarhus University in Roskilde (DK). The method was originally developed for polycyclic aromatic hydrocarbons in contaminated soil[20] and has been modified for PCB-contaminated sediment.[21] For this study, 120-mL amber glass jars (ApodanNordic PharmaPackaging A/S, Copenhagen, DK) were internally coated with PDMS (Silastic Brand Medical Adhesive Silicone Type A, Dow Corning Corporation, Midland, MI, USA). Different amounts of PDMS were applied, i.e. 24.1 ± 1.7, 44.8 ± 1.5, or 95.4 ± 7.3 mg (average ± standard deviation gravimetrically determined after cleaning), to obtain coatings of approximately 2, 4, or 8 μm thickness, respectively. The jars were precleaned with ethyl acetate and further by adding 3 mL of acetone, laying them on a Stuart SRT9D roller mixer (Bibby Scientific Limited, Staffordshire, UK), and rolling them for 30 min; this procedure was repeated once with another 3-mL aliquot of fresh acetone. The acetone was poured out and the jars were left open in a fume hood for some minutes until the solvent had evaporated, then sealed.

Sediment Sampling and Characterization. The Baltic Sea was selected for the study, as there are ample data available on PCB levels in different matrices. Surface sediment was collected on December 10, 2009 (station 9) and on November 19, 2010 (stations 1−8) from R/V *Perca* along a transect from central Stockholm toward the outer Stockholm Archipelago

(Figure S1). At each station except 6 both accumulation (A) and erosion/transport (E/T) sediments were sampled (Text S2).

The sampling locations for the different bottom types were selected based on echo sounder and side-scan sonar. Surface sediment was sampled using a Ponar grab sampler. The upper 2−3 cm were collected with a spoon and stored in polypropylene jars. All sediment samples were stored in a cold storage room until further processing in the laboratory. The samples' contents of water, total organic carbon (TOC), and soot carbon (SC)[23] were determined as described in Text S3. Details of the sampling locations and sediment properties are given in Table S1.

Equilibrium Sampling Using Coated Glass Jars. For equilibrium sampling 80 g of wet sediment was added to a precleaned and air-dried coated glass jar. In a few cases, a small volume of deionized water was added until the right consistency was achieved. A blank jar was prepared using 10 g of deionized water. To each jar, approximately 0.1 g of sodium azide was added to stabilize the sample and preclude any biological activity during further processing. The jar was covered with aluminum foil before being sealed with the lid. The jars were rolled on their sides at room temperature (20 ± 1 °C) for 2 weeks to allow establishment of a PCB partitioning equilibrium between the sample and the PDMS coating.

The method was first tested extensively with the A and E/T sediments sampled at station 9, the station most distant from Stockholm (Figure S1). The number of replicates and blanks for each coating thickness varied from 3 to 5 and 2 to 4, respectively. For the remaining stations, a sample was regularly equilibrated with two jars of each coating thickness. Further, 1−3 blank jars (8 μm of PDMS coating only since these were presumed to have the highest potential for background contamination) were processed for each batch consisting of 16−20 jars. The number of replicates is given in Table S2.

Extraction of the Coated Glass Jars, Cleanup, and Analysis. After the 2-week equilibration time, the content of the coated glass jar was poured out, 2 mL of deionized water was added, and the jar was vigorously shaken both manually and using a Vortex mixer. The content of the jar was poured out and the procedure was repeated once (4 mL total). Afterward, the inner walls of the coated glass jar were thoroughly wiped using several lint-free tissues to remove any remaining sediment and water.

In the course of this study, most of the 4-μm and approximately half of the 8-μm PDMS coatings detached from the glass walls during wiping. This was not an effect of abrasion as a result of the rolling of relatively coarse and sandy sediment since it even occurred with blank samples (i.e., particle-free water with sodium azide). It may have been caused by problems during coating or deterioration of the coatings during the 2-year storage period. Possible strategies to overcome this problem include using a different PDMS material or roughening of the inner walls before application of the PDMS coating solution, e.g. by sandblasting or etching them using hydrogen fluoride.

To extract the chemicals, 2 mL of acetone and 10 μL of the internal standard (IS) solution ($^{13}C_{12}$-labeled PCBs 28, 52, 101, 118, 138, and 180, each at approximately 100 pg/μL in toluene) were added. The jar was sealed and rolled on its side for 30 min. The acetone was pipetted into a precleaned test tube, and the extraction was repeated once (4 mL total). The acetone volume was reduced to approximately 0.5 mL in a

Table 1. Performance Parameters and End Points of the Coated Glass Jar Method

The coated glass jar method is useful for trace level studies in background areas.

Precision	Relative standard errors of the C_{PDMS} measurements of 0.1 to 8.8% (on average 2.6%). This precision is preserved when translating to other media.
Accuracy	The accuracy of $C_{Sediment\_free}$ is mainly determined by uncertainties of the applied partition ratios.
C_{PDMS}	• Calculated from the slope of the regression of PCB mass versus PDMS mass. • Useful as analytical reference and as a 'chemical thermometer' to derive fugacity gradients between environmental compartments in multimedia studies.
$C_{Sediment\_free}$	• $C_{Sediment\_free} = C_{PDMS} / K_{PDMS,water}$ • For comparison with water monitoring data to assess fugacity gradients.
$C_{Sediment\_lipid}$	• $C_{Sediment\_lipid} = C_{PDMS} \times K_{Lipid,PDMS}$ • For prediction of equilibrium partitioning levels in sediment organisms[21] and for comparison with biota monitoring data.
K_D	• $K_D = C_{Sediment\_total} / C_{Sediment\_free}$ • For site-specific assessment of sediment/water partitioning and binding to TOC and SC.

speed vac (Christ RVC 2-25, Labex, Helsingborg, Sweden). After addition of 1 mL of isooctane, the volume was again reduced to approximately 0.5 mL. The extract was submitted to a triple silica gel column cleanup as described in Text S4. Before analysis, 10 μL of the volume standard ($^{13}C_{12}$-labeled PCB 153 at approximately 100 pg/μL in toluene) was added. The final extract and injection volumes were approximately 30 and 1 μL, respectively.

All extracts were analyzed by gas chromatography coupled to either high-resolution mass spectrometry (GC/HRMS, station 9) or low-resolution mass spectrometry (GC/LRMS, stations 1−8) as described by Jahnke et al.[24]

Method Sensitivity. Method detection and quantification limits (MDLs and MQLs) of the coated glass jar approach were calculated at the pg/extract level, using the average PCB mass in the blanks plus 3 times (MDL) or 10 times (MQL) the standard deviation and converted to C_{PDMS}. The detection power of the coated glass jar method was also tested by reanalyzing selected extracts with low levels of the 7 "indicator" PCBs by GC/HRMS for 7 additional PCB congeners (see above). The selected extracts originated from a jar with 2-μm coating (7 E/T) and four jars with 8-μm coating (7 E/T, 4 E/T, 3 A, 2 A).

Determination of the Total PCB Concentrations in Sediment. Between 6.2 and 21.8 g (on average 13.0 g) of wet sediment was weighed into precleaned cellulose thimbles and 10 μL of the IS solution (see above) was added. The sediment was then Soxhlet extracted for ∼20 h with toluene.[25] The extracts were concentrated by rotoevaporation to approximately 100 μL and left open in a fume hood until constant weight was observed. The dry residue was reconstituted in 2 mL of isooctane. The extract was cleaned up using triple silica gel columns and copper (see Text S4), concentrated, and 10 μL of the volume standard was added.

The PCBs were determined as above, and the analyses were initially done by GC/LRMS. However, there was pronounced interference for most of the chemicals that could not be eliminated by a second round of cleanup. Therefore, these extracts were analyzed by GC/HRMS, leading to quantifiable chromatograms for all PCBs with a few exceptions at the most contaminated sites in Stockholm Harbor.

■ **RESULTS AND DISCUSSION**

Equilibrium Sampling Method Test. To test whether the PCBs had equilibrated between the sediment and the PDMS during the 2 weeks of rolling, the mass of PCBs in the PDMS

[ng] was plotted versus the mass of PDMS [mg] for the A and E/T sediment samples from station 9 (Figure S2). Linear regressions forced through the origin yielded R^2s of ≥0.96. Blanks (n = 14) showed very low levels of the 7 investigated PCBs. The observed proportionality between analyte and PDMS mass confirmed that equilibrium partitioning between sediment and PDMS had been established and that no sampling artifacts were present,[20] in agreement with the results of Mäenpää et al.[21] This confirmed that the method was well suited to study PCBs at environmental background levels in Baltic Sea sediment.

During processing of the additional sediments from stations 1−8, 9 blanks were extracted, 3 of which were lost due to coating detachment (see above). The blanks confirmed the low levels of PCBs described above. For every sediment sample, glass jars with 2-, 4-, and 8-μm coatings were processed. Between 1 and 3 data points were obtained for the 2-μm coating thickness. With the exception of sample 2 A, all jars with 4-μm coating thickness were lost (see above). Regarding the 8-μm coating thickness, the coatings were lost in approximately half of the jars. One 8-μm data point was obtained for each sample except for 1 E/T and 7 A (n = 0, Table S2).

The coated glass jar extracts from stations 1−8 were analyzed by GC/LRMS (see above). The recoveries of the IS were on average between 91% ($^{13}C_{12}$ PCB 52) and 103% ($^{13}C_{12}$ PCB 180), but higher for $^{13}C_{12}$ PCB 28 (169%), possibly due to a signal enhancement effect. There were some interferences in the chromatograms that were most pronounced for the lower chlorinated PCBs. They rendered 88% of the PCB 28, 70% of the PCB 52, and 48% of the PCB 118 data points not quantifiable.

To assess whether the sampling kinetics at stations 1−8 were consistent with those from station 9 above, the mass of PCB 138 [ng] in the PDMS was plotted against the mass of PDMS [mg] as described above (results not shown). The linear regressions forced through the origin showed R^2s of between 0.97 and 1.00 (on average 0.99), confirming equilibrium partitioning and the absence of sampling artifacts. For PCB 180, the compound that requires the most time to establish equilibrium between the sediment and the PDMS coating, the R^2s ranged from 0.79 (station 2, due to a high value for one of the jars with 2-μm coating thickness) to 1.00 (on average 0.97).

Mean C_{PDMS} at equilibrium with the sediment samples (Table S3) was derived from the slope of the linear regression of all available data from a sampling station and sediment type. The determination of C_{PDMS} was very precise with relative standard errors of between 0.1 and 8.8% (on average 2.6%, Table 1).

Performance and Sensitivity of the Equilibrium Sampling Approach. The MDLs and MQLs are plotted in Table 1 and listed in Table S4, both for GC/LRMS and GC/HRMS. C_{PDMS} were converted to $C_{Sediment\_free}$ at room temperature using the following equation:

$$C_{Sediment\_free,20°C} = C_{PDMS}/K_{PDMS,water} \tag{1}$$

where $K_{PDMS,water}$ is the compound-specific PDMS/water partition ratio. $K_{PDMS,water}$ data for, among others, a large number of PCBs for the PDMS material used in this study were determined by Smedes et al.[26] The sediment sampling was carried out in fall. During this season, the water column is typically well mixed down to the sediment sampling sites (up to 61.5 m depth, Table S1), and the average water temperature is

around 4 °C. Therefore, $C_{Sediment\_free}$ was corrected from 20 to 4 °C as described by Schwarzenbach et al.,[27] assuming that the heat of phase change for sediment/water partitioning was equal to the heat of phase change for octanol/water partitioning. Values for the latter were taken from Schenker et al.[28]

The results of the method sensitivity test analyzing additional PCBs in selected low-level extracts are given in Table S5. For the octachlorinated PCB 199, values as low as 1.06 fg/L were quantified in the E/T sediment collected at station 7. The signal in the jar with the 2-μm coating thickness was close to a signal-to-noise ratio of 10, but the jars with 8-μm coating thicknesses still showed very clear peaks. In addition, PCB 28 and PCB 52 were quantified in these extracts since interferences had originally impeded their quantification in the GC/LRMS runs (see above).

Altogether, PDMS-coated glass jars were shown to be useful tools for assessing the equilibrium status of PCBs present in background sediments. The equilibration was done in the laboratory within 2 weeks. Thanks to different coating thicknesses, validation and quality assurance are an integral part of the equilibrium sampling for individual samples.

Exploring the Equilibrium Sampling Data. After the method test described above, different aspects of PCB disposition in the Baltic Sea were explored using the C_{PDMS} data. A schematic illustration of the work is provided in Figure 1. The aspects studied were (i) spatial trends in sediment
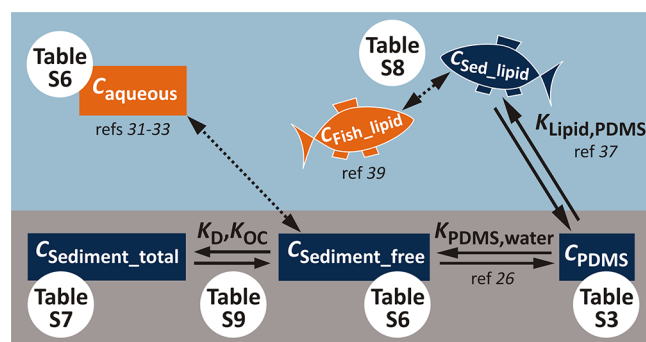
Figure 1. Schematic illustration of the aspects of PCB disposition in the Baltic Sea that were explored using the PES data. From C_{PDMS}, $C_{Sediment\_free}$ was calculated. $C_{Sediment\_free}$ was combined with $C_{Sediment\_total}$ to give K_D and K_{OC} values. $C_{Sediment\_free}$ was compared with monitoring data from the water phase ($C_{aqueous}$). Finally, C_{PDMS} was used to derive equilibrium partitioning concentrations in biota lipids that were compared to lipid-normalized biota monitoring data.

fugacity along the sampling transect and between A and E/T sediments; (ii) the equilibrium partitioning status between sediment and the water column, with the help of monitoring data from the dissolved phase in the water column ($C_{aqueous}$); (iii) bioaccumulation, by comparison of equilibrium partitioning concentrations in fish lipids ($C_{Sediment\_lipid}$) to biota monitoring data (C_{Fish_lipid}); (iv) site-specific sediment/water and organic carbon/water distribution ratios (K_D and K_{OC}, respectively). The results are described in the following sections, and the performance parameters and end points of this approach are summarized in Table 1.

Spatial Trend of PCBs along the Transect. The gradient in PCB fugacity in sediment along the transect from Stockholm Harbor to the outer reaches of the Stockholm Archipelago was assessed. From C_{PDMS}, $C_{Sediment\_free}$ [pg/L] at room temperature
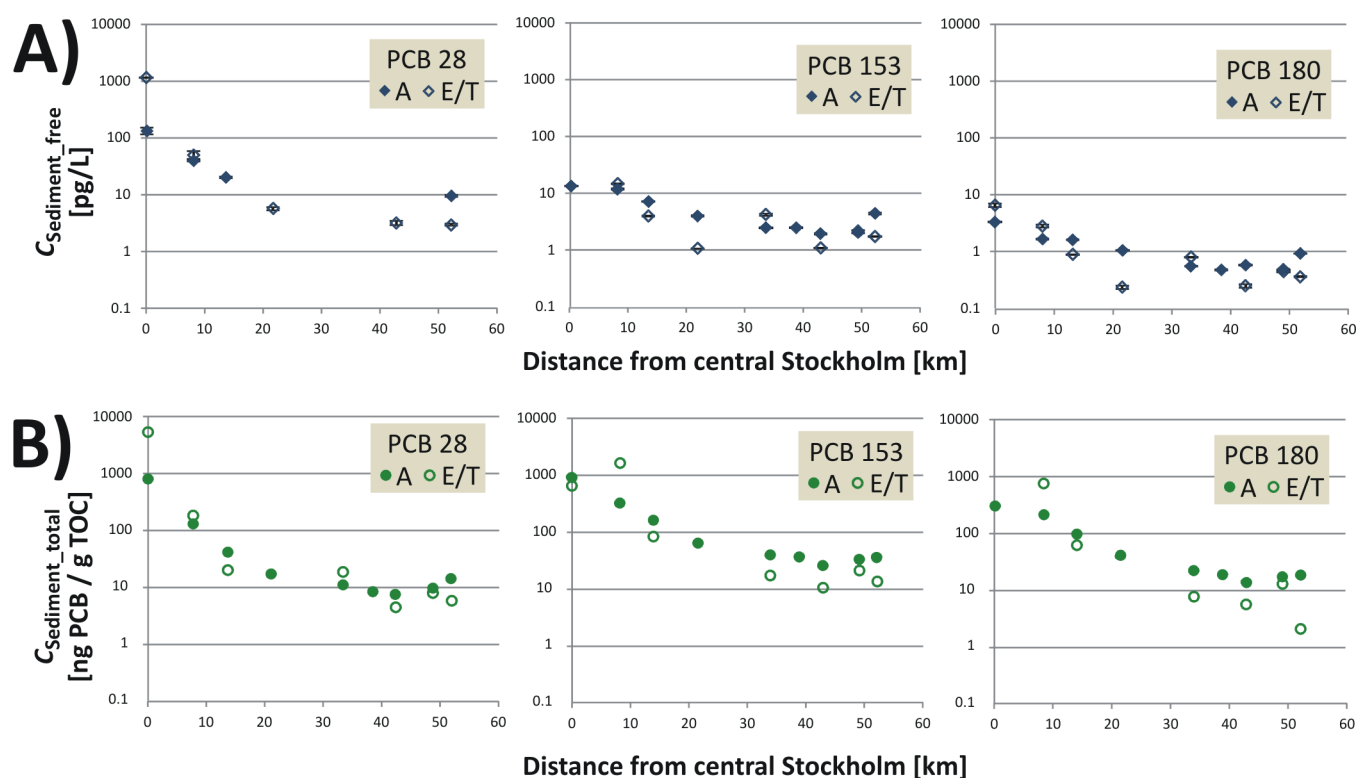
Figure 2. Spatial trends of three PCB congeners along the transect from central Stockholm Harbor into the outer Stockholm Archipelago showing (A) $C_{Sediment\_free}$ [pg/L] extrapolated to 4 °C and (B) $C_{Sediment\_total}$ [ng PCB/g TOC]. Error bars (A) reflect the relative standard error of the C_{PDMS} measurements. See Figure S5 for C_{PDMS} and $C_{Sediment\_total}$ of the additional PCB congeners.

was calculated according to eq 1 and extrapolated to 4 °C (see above). The data are given in Table S6.

Clear trends in $C_{Sediment\_free}$ were observed, with the highest levels at stations 1 and 2 in Stockholm Harbor (illustrated in Figure 2 A for PCBs 28, 153, and 180). Moving away from the harbor there was a drop, and station 3 already showed about a factor of 3 lower $C_{Sediment\_free}$. There was a smaller drop to station 4, while there was no trend in $C_{Sediment\_free}$ among stations 4−9. The trend of decreasing $C_{Sediment\_free}$ from central Stockholm into the Stockholm Archipelago was statistically significant (F test, $p < 0.05$ for all congeners except for PCB 118 ($p = 0.062$) Figure S3).

The difference between the harbor and the outer part of the archipelago was a factor of ∼5. The difference was largest for PCB 28 (a factor of ∼10), although this is based on few data. This fugacity gradient indicates that Stockholm Harbor continues to be a source of PCBs to the Baltic Sea. This could be due to ongoing emissions or the mobilization of older emissions stored in the harbor sediment. However, despite the significant difference in fugacity between the harbor and the outer archipelago, we expect the source strength of Stockholm to be relatively minor as compared with the total inventory of PCBs in the Baltic Sea due to the small spatial extent of the contaminated sediment.

The spatial trend in $C_{Sediment\_total}$ is given in Figure 2 B for PCBs 28, 153, and 180, and the complete data set is given in Table S7. $C_{Sediment\_total}$ also decreased significantly moving from central Stockholm into the outer archipelago ($p \leq 0.0001$, Figure S3). This observation is consistent with decreasing levels of other HOCs such as brominated flame retardants with increasing distance from Stockholm.[29] However, the gradient in $C_{Sediment\_total}$ was significantly steeper than in $C_{Sediment\_free}$

(Figures S3 and S4, F test, $p < 0.05$ for all congeners except for PCB 52, $p = 0.098$).

The spatial trends in C_{PDMS} and $C_{Sediment\_total}$ for PCB 52, PCB 101, PCB 118 and PCB 138 are illustrated in Figure S5.

Comparison of Sediment Types. Paired A and E/T sediments were sampled and analyzed at 8 of the 9 stations, and their C_{PDMS} was compared. No systematic trend in the difference in C_{PDMS} between the paired sediment samples was observed (see Figure S5 and Table S3). At stations 3, 4, 7, and 9, C_{PDMS} was lower in the E/T sediment by a factor of 1.7−4.4 (on average 2.6), while at stations 1, 2, and 5 it was lower in the A sediment by a factor of 1.2−8.5 (on average 2.2). One possible explanation for lower C_{PDMS} after equilibration with the E/T sediments is that freshly eroded material that had previously been buried had not approached equilibrium with its new environment, having only recently been exposed to PCBs. The data indicate that this is not a phenomenon that consistently affects E/T sediments in the Stockholm Archipelago.

An earlier study showed that the PCB concentrations in A and E/T sediment from the Stockholm Archipelago were similar when normalized to organic carbon.[30] This is consistent with the observations in this study (data not shown).

Equilibrium Status between Sediment and the Water Column. To evaluate the PCB equilibrium status between the sediment and the water column, the $C_{Sediment\_free}$ data (Table S6) from stations 4−9 were used since they reflect the background levels in the Stockholm Archipelago. $C_{Sediment\_free}$ was compared to $C_{aqueous}$ from an annual monitoring program of the Leibniz Institute for Baltic Sea Research (IOW) Warnemünde.[31] $C_{aqueous}$ showed little variability between different parts of the Baltic Proper and little variability between
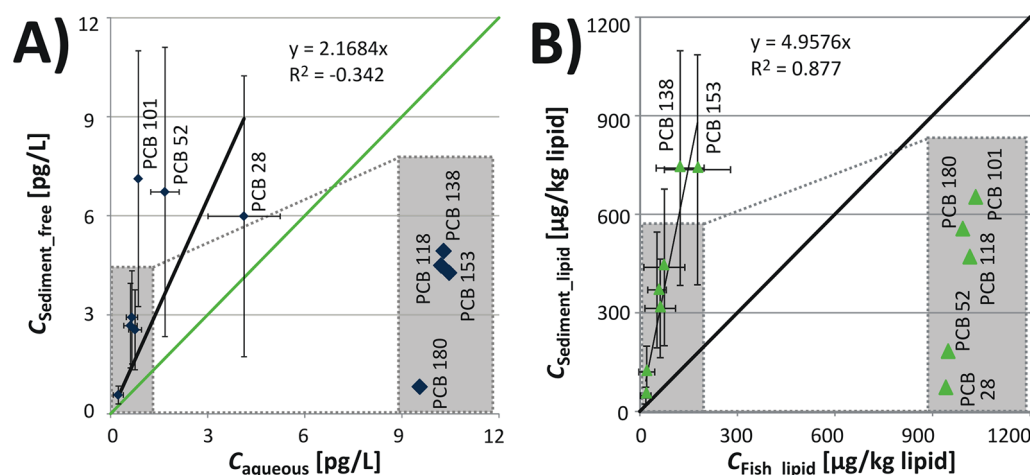
Figure 3. (A) $C_{Sediment\_free}$ [pg/L] of PCBs from this study vs $C_{aqueous}$ [pg/L] in the Arkona Sea (monitoring data, Table S6). Error bars show the standard deviations of all data points from stations 4−9 or of reported water monitoring data from 2001 to 2004, respectively. (B) Equilibrium partitioning concentrations in fish lipids ($C_{Sediment\_lipid}$) [μg/kg lipid] from this study vs lipid-normalized concentrations (C_{Fish_lipid}) [μg/kg lipid] in Baltic Sea herring (monitoring data, Table S8). Error bars demonstrate the standard deviations of all data points from stations 4−9 or of reported data from 2007 to 2010, respectively.

2001 and 2008.[32] Since tabulated data were only available for 2001−2004 (e.g., [33]), these were used (Table S6).

In Figure 3 A, $C_{Sediment\_free}$ is plotted versus $C_{aqueous}$. $C_{Sediment\_free}$ was a factor of 1.5 (PCB 28) to 8.3 (PCB 101) (on average 4.0) higher than $C_{aqueous}$. The difference in fugacity of the sediment and the aqueous phase is in agreement with model simulations which predict that the PCB fugacity in water is ~2 (PCB 28) to 10 (PCB 180) times lower than in sediment during the winter (Armitage and McLachlan, unpublished results). The fugacity gradient is related to a seasonal cycle of $C_{aqueous}$, with values in winter that are about 60% of those in summer.[34] The annual cycle in PCB fugacity in surface water is further amplified by the seasonality in the fugacity capacity of the water, which is ~6−7 times higher in winter due to the lower water temperature. This means that the PCB fugacity in the surface water is over an order of magnitude lower in winter. Consequently the fugacity in surface water is markedly lower than in sediment in winter, while it is higher in summer.

In addition, it has been hypothesized that gradients in fugacity from bottom to surface water can develop as a result of a decrease in the fugacity capacity of the sediment caused by mineralization of the organic carbon (OC) in the sediment.[35] For such a gradient to develop, however, the rate constant for the decrease in sediment fugacity capacity must be greater than the rate constant for equilibration of the chemical between the sediment and the surface water.

Equilibrium Status between Sediment and Herring. To assess the equilibrium status between sediment and herring, C_{PDMS} was converted into an equivalent equilibrium partitioning concentration in lipid ($C_{Sediment\_lipid}$). This approach of using lipid as a reference phase is in line with the proposal of Webster et al.[36] and the work by Jahnke et al.[37] and Mäenpää et al.[21] The following equation was used:

$$C_{Sediment\_lipid} = C_{PDMS} \times K_{Lipid,PDMS} \qquad (2)$$

where $K_{Lipid,PDMS}$ is the compound-specific lipid/PDMS partition ratio, which has been determined for PCBs and the PDMS used in this study.[37] Recently, similar $K_{Lipid,PDMS}$ values (within 20%) were reported for the same polymer.[38] As above,

the C_{PDMS} data from stations 4−9 were selected. The $C_{Sediment\_lipid}$ data are given in Table S8.

$C_{Sediment\_lipid}$ was compared to lipid-normalized PCB concentrations in Baltic Sea herring (C_{Fish_lipid}) from the Swedish national environmental monitoring program.[39] The station Lagnö, which is close to station 9, was selected, and yearly data from pooled samples collected between 2007 and 2010 were used (Table S8).

In Figure 3 B, $C_{Sediment\_lipid}$ is plotted versus C_{Fish_lipid}. $C_{Sediment\_lipid}$ was a factor of 2.6 (PCB 28) to 7.0 (PCB 180) (on average 5.2) greater than C_{Fish_lipid}. This result suggests that there is a disequilibrium between the sediment and the herring, with the herring being at a lower fugacity. There are several issues that should be considered when interpreting this finding. Seasonal factors such as primary production and changes in particle/water distribution ratios have been shown to control the fate and distribution of HOCs in the aquatic environment in a highly dynamic way.[40] The fish are thus exposed to seasonally varying $C_{aqueous}$ (see Smith et al.[40] and the discussion above), and due to the slow bioaccumulation kinetics of PCBs the fish body burdens reflect integrated exposure over a time period of months to years. Another potential issue is a lack of representativeness of the herring; a cohort with unusually low contamination may have been sampled. However, the PCB concentrations in the herring from this station were high compared to the other monitoring stations in the Baltic Sea,[39] indicating that this is not a concern. Finally, the sediment samples might not be representative. However, our $C_{Sediment\_total}$ values were within a factor of 0.5 (PCB 52) to 1.1 (PCB 138) of $C_{Sediment\_total}$ for sediments from the open Baltic Sea reported by Cornelissen et al.[12]

The disequilibrium between sediment and herring is similar to that between sediment and water reported above. This suggests that the herring are close to equilibrium with the water, and that the disequilibrium between herring and sediment is attributable to the disequilibrium between sediment and water. As noted above, there is a strong seasonal variability in the PCB fugacity in water, while the PCB fugacity in sediment is nearly constant. Given the slow bioaccumulation kinetics of PCBs in fish (see above), the herring can only approach a pseudo equilibrium that represents some time-

integrated average of its variable exposure via water. Consequently, the disequilibrium between sediment and herring is the result of complex dynamic interactions between the seasonality in PCB fugacity in water, temperature, and other factors influencing PCB bioaccumulation in herring.

Sediment/Water Distribution Ratios (K_D). To calculate sediment/water distribution ratios (K_D) [L/kg dw], $C_{Sediment\_total}$ (on a dry weight basis, Table S7) was divided by $C_{Sediment\_free}$ (at 20 °C). PCB 28 was not included since there were too few data (see above). Both OC and SC have been proposed as the dominant sorbent for PCBs in sediments. To explore which of these sorbents was important for the sediments in this study, K_D was plotted against both OC and SC for the data from stations 3−9 (Figure S6). For SC, no correlation was observed, while for OC correlations were observed for all congeners, with R^2s of 0.49−0.70. This indicates that OC is a major sorbent of PCBs in these sediments, while SC is not.

K_D was also calculated for the sediments from stations 1 and 2. The average K_D was between 2.7 and 7.0 times higher than the average from stations 3−9. The SC values were not elevated for stations 1 A, 2 A, and 2 E/T compared to the others (0.17%, 0.20%, and 0.26% versus a range of 0.03−0.49% and a median of 0.17%), and the OC values were only slightly elevated (4.3%, 5.1%, and 7.5% versus a range of 0.5−6.1% and a median of 4.3%). This indicates that the sorptive strength of the OC (or SC) in these sediments was stronger than in the other sediments, potentially because of the strong anthropogenic impact, given that both stations are in Stockholm Harbor.

Because OC was the major sorbent in most of the sediments, the organic carbon/water partition ratio (K_{OC}, i.e. K_D normalized to the sediment's OC content) is an appropriate parameter to define their sorption properties. The results are listed in Table S9 and plotted along the transect in Figure S4. Additionally, K_{OC} is plotted for the PCB congeners in the different sediments in Figure S7. For a given PCB congener, the K_{OC} values were generally similar for the different sediments from stations 3−9, regardless of whether they were A or E/T sediments. Higher values are apparent for stations 1 and 2 in accordance with the discussion above. Different methods for predicting K_{OC} have been suggested, with one of the simplest being the following:[41]

$$K_{OC} = 0.35 \times K_{OW} \qquad (3)$$

Figure S7 also shows the K_{OC} values predicted by this equation, whereby K_{OW} from Schenker et al.,[28] extrapolated to 20 °C, were employed. With the exception of PCB 138, the agreement of these predicted K_{OC} values with those measured for stations 3−9 is good, indicating that this equation can be used to describe PCB partitioning in Baltic Sea sediments.

Final Remarks. This work shows that PDMS-coated glass jars can be used to assess the equilibrium status of PCBs present in background sediments at $C_{Sediment\_free}$ in the low fg/L up to high pg/L range. The initial problems observed with some of the PDMS coatings that detached from the glass walls during surface wiping were overcome by applying a different PDMS material in recent work, as will be reported in the near future. The equilibration is done in the laboratory, eliminating complex, time-consuming, and risky field procedures. Further advantages include short equilibration times (2 weeks), built-in validation and quality assurance as part of the equilibrium sampling (different coating thicknesses). Additionally, the

method can readily be adapted to other matrices with flexibility in the sampler geometry, the applied polymer, cleanup procedures, and measurement by the analytical method of choice.

The coated glass jar PES is a useful tool with a range of applications including studying spatial trends in sediment fugacity, sediment/water, and sediment/biota equilibrium status, and sediment/water distribution ratios at the concentrations present in the environment. It can provide deep insight into the environmental behavior of contaminants, e.g. by quantifying fugacity gradients in the environment and determining the resulting direction of diffusive fluxes of chemicals. Multimedia studies that equilibrate PDMS with different environmental media for process studies are desirable and possible; a recent study showed that immersion of PDMS in complex matrices does not modify its partitioning properties for nonpolar organic chemicals.[42]

The application of the described method to other HOCs in the high K_{OW} range should be explored. The main limitation will likely be the availability of analyte specific partition ratios that can link the measured concentrations in the PDMS to various environmental media; these would have to be determined.

Finally, the comparatively low variability of the equilibrium sampling concentration for each sediment sample combined with the ease of measurement suggests that this may be a more robust, informative, and cost-effective method to monitor the contaminant status of aquatic environments than, for instance, the sampling and analysis of biota or water, both of which are characterized by complex seasonal variability.

■ 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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Notes
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■ REFERENCES

(1) Mayer, P.; Tolls, J.; Hermens, J. L. M.; Mackay, D. Equilibrium sampling devices. *Environ. Sci. Technol.* **2003**, *37*, 184A−191A.

(2) Arthur, C. L.; Pawliszyn, J. Solid phase microextraction with thermal desorption using fused silica optical fibres. *Anal. Chem.* **1990**, *62*, 2145−2148.

(3) Baltussen, E.; Sandra, P.; David, F.; Cramers, C. Stir bar sorptive extraction (SBSE), a novel extraction technique for aqueous samples: Theory and principles. *J. Microcolumn Sep.* **1999**, *11*, 737−747.

(4) Mayer, P.; Vaes, W. H. J.; Wijnker, F.; Legierse, K. C. H. M.; Kraaij, R. H.; Tolls, J.; Hermens, J. L. M. Sensing dissolved sediment porewater concentrations of persistent and bioaccumulative pollutants using disposable solid-phase microextraction fibers. *Environ. Sci. Technol.* **2000**, *34*, 5177−5183.

(5) Bruheim, I.; Liu, X. C.; Pawliszyn, J. Thin-film microextraction. *Anal. Chem.* **2003**, *75*, 1002−1010.

(6) Mayer, P.; Toräng, L.; Glaesner, N.; Jönsson, J. Å. Silicone membrane equilibrator: Measuring chemical activity of nonpolar chemicals with poly(dimethylsiloxane) microtubes immersed directly in tissue and lipids. *Anal. Chem.* **2009**, *81*, 1536−1542.

(7) Mackay, D. Finding fugacity feasible. *Environ. Sci. Technol.* **1979**, *13*, 1218−1223.

(8) Booij, K.; Hoedemaker, J. R.; Bakker, J. F. Dissolved PCBs, PAHs, and HCB in Pore Waters and Overlying Waters of Contaminated Harbor Sediments. *Environ. Sci. Technol.* **2003**, *37*, 4213−4220.

(9) Morgan, E. J.; Lohmann, R. Detecting air-water and surface-deep water gradients of PCBs using polyethylene passive samplers. *Environ. Sci. Technol.* **2008**, *42*, 7248−7253.

(10) Lohmann, R.; Klanova, J.; Kukucka, P.; Yonis, S.; Bollinger, K. PCBs and OCPs on an east-to-west transect: The importance of major currents and net volatilization for PCBs in the Atlantic Ocean. *Environ. Sci. Technol.* **2012**, DOI: 10.1021/es203459e.

(11) Cornelissen, G.; Pettersen, A.; Broman, D.; Mayer, P.; Breedveld, G. D. Field testing of equilibrium passive samplers to determine freely dissolved native polycyclic aromatic hydrocarbon concentrations. *Environ. Toxicol. Chem.* **2008**, *27*, 499−508.

(12) Cornelissen, G.; Wiberg, K.; Broman, D.; Arp, H. P. H.; Persson, Y.; Sundqvist, K.; Jonsson, P. Freely dissolved concentrations and sediment-water activity ratios of PCDD/Fs and PCBs in the open Baltic Sea. *Environ. Sci. Technol.* **2008**, *42*, 8733−8739.

(13) Hawthorne, S. B.; Miller, D. J.; Grabanski, C. B. Measuring low picogram per liter concentrations of freely dissolved polychlorinated biphenyls in sediment pore water using passive sampling with polyoxymethylene. *Anal. Chem.* **2009**, *81*, 9472−9480.

(14) Hawthorne, S. B.; Jonker, M. T. O.; van der Heijden, S. A.; Grabanski, C. B.; Azzolina, N. A.; Miller, D. J. Measuring picogram per liter concentrations of freely dissolved parent and alkyl PAHs (PAH-34), using passive sampling with polyoxymethylene. *Anal. Chem.* **2011**, *83*, 6754−6761.

(15) Meloche, L. M.; deBruyn, A. M. H.; Otton, S. V.; Ikonomou, M. G.; Gobas, F. A. P. C. Assessing exposure of sediment biota to organic contaminants by thin-film solid phase extraction. *Environ. Toxicol. Chem.* **2009**, *28*, 247−253.

(16) George, T. S.; Vlahos, P.; Harner, T.; Helm, P.; Wilford, B. A rapidly equilibrating, thin film, passive water sampler for organic contaminants; characterization and field testing. *Environ. Pollut.* **2011**, *159*, 481−486.

(17) Hunter, W.; Xu, Y.; Spurlock, F.; Gan, J. Using disposable polydimethylsiloxane fibers to assess the bioavailability of permethrin in sediment. *Environ. Toxicol. Chem.* **2008**, *27*, 568−575.

(18) Hawthorne, S. B.; Grabanski, C. B.; Miller, D. J. Solid-phase-microextraction measurement of 62 polychlorinated biphenyl congeners in milliliter sediment pore water samples and determination of K_{DOC} values. *Anal. Chem.* **2009**, *81*, 6936−6943.

(19) Maruya, K. A.; Zeng, E. Y.; Tsukada, D.; Bay, S. M. A passive sampler based on solid-phase microextraction for quantifying hydrophobic organic contaminants in sediment pore water. *Environ. Toxicol. Chem.* **2009**, *28*, 733−740.

(20) Reichenberg, F.; Smedes, F.; Jönsson, J. Å.; Mayer, P. Determining the chemical activity of hydrophobic organic compounds in soil using polymer coated vials. *Chem. Cent. J.* **2008**, *2*, 8.

(21) Mäenpää, K.; Leppänen, M. T.; Reichenberg, F.; Figueiredo, K.; Mayer, P. Equilibrium sampling of persistent and bioaccumulative compounds in soil and sediment − Comparison of two approaches to determine equilibrium partition concentrations in lipids. *Environ. Sci. Technol.* **2011**, *45*, 1041−1047.

(22) Hawker, D. W.; Connell, D. W. Octanol-water partition coefficients of polychlorinated biphenyl congeners. *Environ. Sci. Technol.* **1988**, *22*, 382−387.

(23) Gustafsson, Ö.; Haghseta, F.; Chan, C.; MacFarlane, J.; Gschwendt, P. M. Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability. *Environ. Sci. Technol.* **1997**, *31*, 203−209.

(24) Jahnke, A.; Mayer, P.; Broman, D.; McLachlan, M. S. Possibilities and limitations of equilibrium sampling using poly-dimethylsiloxane in fish tissue. *Chemosphere* **2009**, *77*, 764−770.

(25) Bandh, C.; Björklund, E.; Mathiasson, L.; Näf, C.; Zebühr, Y. Comparison of accelerated solvent extraction and Soxhlet extraction for the determination of PCBs in Baltic Sea sediments. *Environ. Sci. Technol.* **2000**, *34*, 4995−5000.

(26) Smedes, F.; Geertsma, R. W.; van der Zande, T.; Booij, K. Polymer-water partition coefficients of hydrophobic compounds for passive sampling: Application of cosolvent models for validation. *Environ. Sci. Technol.* **2009**, *43*, 7047−7054.

(27) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, 2nd ed.; John Wiley & Sons: Hoboken, NJ, 2003.

(28) Schenker, U.; MacLeod, M.; Scheringer, M.; Hungerbühler, K. Improving data quality for environmental fate models: A least-squares adjustment procedure for harmonizing physicochemical properties of organic compounds. *Environ. Sci. Technol.* **2005**, *39*, 8434−8441.

(29) Ricklund, N.; Kierkegaard, A.; McLachlan, M. S. Levels and potential sources of decabromodiphenyl ethane (DBDPE) and decabromodiphenyl ether (DecaBDE) in lake and marine sediments in Sweden. *Environ. Sci. Technol.* **2010**, *44*, 1987−1991.

(30) Jönsson, A.; Carman, R. Distribution of PCBs in sediment from different bottom types and water depths in Stockholm Archipelago, Baltic Sea. *Ambio* **2000**, *29*, 277−281.

(31) Wodarg, D.; Kömp, P.; McLachlan, M. S. A baseline study of polychlorinated biphenyl and hexachlorobenzene concentrations in the western Baltic Sea and Baltic Proper. *Mar. Chem.* **2004**, *87*, 23−36.

(32) German water monitoring data from the Baltic Sea is presented in annual reports (in German): Regionale Verteilung chlorierter Kohlenwasserstoffe (CKW) und polycyclischer aromatischer Kohlen-wasserstoffe (PAH) im Pelagial der Ostsee. Available at http://www.bsh.de/de/Meeresdaten/Beobachtungen/MURSYS-Umweltreportsystem/PDF/IOW_ckw-pak_Bericht_2008.pdf. Last accessed August 15, 2012.

(33) Regionale Verteilung chlorierter Kohlenwasserstoffe (CKW) und polycyclischer aromatischer Kohlenwasserstoffe (PAH) im Pelagial der Ostsee. Available at http://www.bsh.de/de/Meeresdaten/Beobachtungen/MURSYS-Umweltreportsystem/PDF/osretro012004.pdf. Last accessed August 15, 2012.

(34) Wiberg, K.; McLachlan, M. S.; Jonsson, P.; Johansson, N. *Sources, Transport, Reservoirs and Fate of Dioxins, PCBs and HCB in the Baltic Sea Environment*; Report #5912 of the Swedish Environmental Protection Agency, 2009. Available at http://www.swedishepa.se.

(35) Gobas, F. A. P. C.; MacLean, L. G. Sediment-water distribution of organic contaminants in aquatic ecosystems: The role of organic carbon mineralization. *Environ. Sci. Technol.* **2003**, *37*, 737−741.

(36) Webster, E.; Mackay, D.; Qiang, K. Equilibrium lipid partitioning concentrations as a multi-media synoptic indicator of contaminant levels and trends in aquatic ecosystems. *J. Great Lakes Res.* **1999**, *25*, 318−329.

(37) Jahnke, A.; McLachlan, M. S.; Mayer, P. Equilibrium sampling: Partitioning of organochlorine compounds from lipids into poly-dimethylsiloxane. *Chemosphere* **2008**, *73*, 1575−1581.

(38) Rusina, T. P.; Smedes, F.; Beeltje, H.; Klanova, J. Poster "Study of the partitioning between lipid and passive sampling materials in

equilibrium sampling" at the 6th SETAC World Congress, Berlin, Germany, 20−24 May 2012.

(39) Swedish monitoring data. Available at http://www.naturvardsverket.se/en/In-English/Start/State-of-the-environment/Environmental-monitoring/Environmental-monitoring-data/. Last accessed August 15, 2012.

(40) Smith, K. E. C.; McLachlan, M. S. Concentrations and partitioning of polychlorinated biphenyls in the surface waters of the southern Baltic Sea − Seasonal effects. *Environ. Toxicol. Chem.* **2006**, *25*, 2569−2575.

(41) Seth, R.; Mackay, D.; Muncke, J. Estimating the organic carbon partition coefficient and its variability for hydrophobic chemicals. *Environ. Sci. Technol.* **1999**, *33*, 2390−2394.

(42) Jahnke, A.; Mayer, P. Do complex matrices modify the sorptive properties of polydimethylsiloxane (PDMS) for non-polar organic chemicals? *J. Chromatogr., A* **2010**, *1217*, 4765−4770.