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Equilibrium Sampling to Determine the Thermodynamic Potential for Bioaccumulation of Persistent Organic Pollutants from Sediment

Annika Jahnke,*[,†] Matthew MacLeod,[†] Håkan Wickström,[‡] and Philipp Mayer[§]

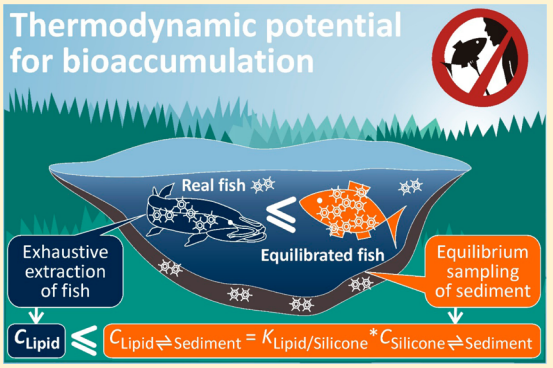
[†]Department of Applied Environmental Science (ITM), Stockholm University, Svante Arrhenius väg 8, SE-114 18 Stockholm, Sweden

[‡]Department of Aquatic Resources, Swedish University of Agricultural Sciences, Stångholmsvägen 2, SE-178 93 Drottningholm, Sweden

[§]Department of Environmental Engineering, Technical University of Denmark, Anker Engelunds Vej 1, DK-2800 Kongens Lyngby, Denmark

Supporting Information

ABSTRACT: Equilibrium partitioning (EqP) theory is currently the most widely used approach for linking sediment pollution by persistent hydrophobic organic chemicals to bioaccumulation. Most applications of the EqP approach assume (I) a generic relationship between organic carbon-normalized chemical concentrations in sediments and lipid-normalized concentrations in biota and (II) that bioaccumulation does not induce levels exceeding those expected from equilibrium partitioning. Here, we demonstrate that assumption I can be obviated by equilibrating a silicone sampler with chemicals in sediment, measuring chemical concentrations in the silicone, and applying lipid/silicone partition ratios to yield concentrations in lipid at thermodynamic equilibrium with the sediment ($C_{Lip \rightleftharpoons Sed}$). Furthermore, we evaluated the validity of assumption II by comparing $C_{Lip \rightleftharpoons Sed}$ of selected persistent, bioaccumulative and toxic pollutants (polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB)) to lipid-normalized concentrations for a range of biota from a Swedish background lake. PCBs in duck mussels, roach, eel, pikeperch, perch and pike were mostly below the equilibrium partitioning level relative to the sediment, i.e., lipid-normalized concentrations were $\leq C_{Lip \rightleftharpoons Sed}$, whereas HCB was near equilibrium between biota and sediment. Equilibrium sampling allows straightforward, sensitive and precise measurement of $C_{Lip \rightleftharpoons Sed}$. We propose $C_{Lip \rightleftharpoons Sed}$ as a metric of the thermodynamic potential for bioaccumulation of persistent organic chemicals from sediment useful to prioritize management actions to remediate contaminated sites.



INTRODUCTION

The consumption of fish is generally recommended as part of a healthy diet, and particularly species rich in long-chain omega-3 polyunsaturated fatty acids are considered beneficial (e.g., refs 1 and 2). However, persistent hydrophobic organic chemicals (HOCs) can accumulate in fish and render them unfit for human consumption. For example, in some areas of the Baltic Sea, levels of dioxins and planar polychlorinated biphenyls (PCBs) in salmon exceed regulatory thresholds (6.5 pg/g ww). Commercial fishing and trade is prohibited in these areas except by countries that have been granted derogations.[3]

Sediments have a high storage capacity for HOCs. They can act as a contaminant source to the water column, and benthic species that take chemicals up from sediments can determine the level of contamination throughout a foodweb.[4] The assessment and management of contaminated sediments requires sound and practical approaches that can link sediment contamination to HOC bioaccumulation in benthic and pelagic organisms, particularly in those species intended for human consumption. Currently, the most widely used approach for linking sediment pollution to bioaccumulation is to assess sediment quality based on organic carbon (OC)-normalized concentrations of HOCs in sediment, which is an extrapolation of the equilibrium partitioning theory.[5]

The equilibrium partitioning (EqP) approach described in detail by Di Toro et al.[5] has a thermodynamic basis, namely that distribution of pollutants in sediments tends toward a thermodynamic equilibrium characterized by equal chemical activities in sediment solids, dissolved organic carbon, interstitial pore water and benthic organisms. Di Toro et al. proposed that the freely dissolved concentration of HOCs in sediment pore water determines the potential for bioaccumulation.[5] However, accurately measuring freely dissolved chemical concentrations in pore water is difficult, especially for highly hydrophobic chemicals that strongly associate with

Received: July 9, 2014
Revised: August 27, 2014
Accepted: September 3, 2014
Published: September 3, 2014

particulate and dissolved organic carbon. Therefore, in the EqP approach the ratio of OC-normalized concentrations in sediment and a generic K_d value is used as a surrogate for freely dissolved concentrations. The original EqP method[5] was restricted to calculating effects-based sediment quality criteria for the protection of benthic organisms. However, the EqP concept has frequently been extrapolated to assess bioaccumulation of HOCs from sediment into foodwebs using biota-sediment accumulation factors (BSAFs);

$$\mathrm{BSAF} = C_{\mathrm{Bio,Lip}}/C_{\mathrm{Sed,OC}} \quad (1)$$

where $C_{\mathrm{Bio,Lip}}$ is the lipid-normalized chemical concentration in biota in the foodweb and $C_{\mathrm{Sed,OC}}$ is the OC-normalized chemical concentration in sediments.

The use of the equilibrium partitioning approach to assess bioaccumulation of HOCs from sediment rests on two assumptions. Assumption I is that normalizing concentrations of HOCs in sediment to OC content accounts for variability in the sorptive capacity of sediments. However, research in the last two decades has shown large variability in the sorptive properties of sediments, and that normalization to the OC content of sediment is often insufficient to account for these differences.[6−8] Techniques to equilibrate micrometer-thin polymers with chemicals in sediment and to measure the chemical concentration in the polymer have been developed.[9−11] The concentration in the polymer can be translated to the freely dissolved chemical concentration in interstitial pore water, which can in turn be multiplied with a bioconcentration factor to estimate the concentration in benthic organisms.[12,13] The combination of equilibrium sampling and partitioning calculations can thus circumvent the assumption of generic sediment partitioning properties by applying a reference phase (i.e., the polymer) that has much better-defined partitioning properties than natural organic matter.

Assumption II is that bioaccumulation is largely governed by equilibrium partitioning. Recently, chemical concentrations in model lipids at thermodynamic equilibrium with sediments ($C_{\mathrm{Lip}\rightleftharpoons\mathrm{Sed}}$) have been empirically determined as the product of the measured concentrations of HOCs in silicone at equilibrium with sediment ($C_{\mathrm{Sil}\rightleftharpoons\mathrm{Sed}}$) and analyte-specific lipid/silicone partition ratios ($K_{\mathrm{Lip/Sil}}$):[14]

$$C_{\mathrm{Lip}\rightleftharpoons\mathrm{Sed}} = C_{\mathrm{Sil}\rightleftharpoons\mathrm{Sed}} \times K_{\mathrm{Lip/Sil}} \quad (2)$$

This approach allows equilibrium partitioning concentrations in lipids to be determined without applying partition ratios that involve the aqueous phase. Mäenpää et al.,[15] Jahnke et al.[16,17] and Schäfer et al.[18] described the use of silicone-coated glass jars equilibrated with sediments from a contaminated Finnish lake, the Stockholm Archipelago of the Baltic Sea, a Swedish background lake (Lake Ången) and the German part of the River Elbe. In all four studies, $C_{\mathrm{Bio,Lip}}$ of PCBs in selected benthic and pelagic biota were below the equilibrium partitioning reference relative to the sediment, i.e., $C_{\mathrm{Bio,Lip}} < C_{\mathrm{Lip}\rightleftharpoons\mathrm{Sed}}$. However, a systematic investigation including a range of species from different trophic levels that may have bioaccumulated HOCs through the foodweb has as so far been lacking; we address this issue in the present study.

The authors of the original EqP method recognized that extending the equilibrium assumption from sediment organisms to the foodweb ignores important processes that can lead to disequilibrium conditions, notably biomagnification.[5] Therefore, $C_{\mathrm{Lip}\rightleftharpoons\mathrm{Sed}}$ is not expected to provide an accurate estimate of chemical concentrations in organisms throughout the foodweb. Instead, $C_{\mathrm{Lip}\rightleftharpoons\mathrm{Sed}}$ is the concentration of HOCs in lipids of an idealized organism that is in thermodynamic equilibrium with sediment (TOC art figure). It is a well-defined, reproducible and meaningful metric of the thermodynamic potential for bioaccumulation of chemicals from sediment, which is in full accordance with EqP theory.

On the basis of our previous experience with passive equilibrium sampling, and recognizing the limitations of current extrapolations of the EqP approach, we explored the idea that risks to wildlife and human health associated with bioaccumulation of chemicals from sediment can be more effectively assessed and managed site-specifically on the basis of $C_{\mathrm{Lip}\rightleftharpoons\mathrm{Sed}}$, compared to the current practice using $C_{\mathrm{Sed,OC}}$ and assuming generic sediment partitioning properties. In this study, we pursued two research aims to evaluate this idea. The first aim was to investigate whether the bioaccumulation of the persistent, bioaccumulative and toxic model chemicals hexachlorobenzene (HCB) and PCBs in a range of benthic and pelagic species from different trophic levels in an aquatic ecosystem is characterized by biota levels below, near, or above the thermodynamic equilibrium level relative to the sediment, and thus to test the equilibrium assumption of the extrapolated EqP approach. The second aim was to investigate the utility of $C_{\mathrm{Lip}\rightleftharpoons\mathrm{Sed}}$ as a measure of the thermodynamic potential of sediments for bioaccumulation of persistent HOCs that could be used to make management decisions about contaminated sediments.

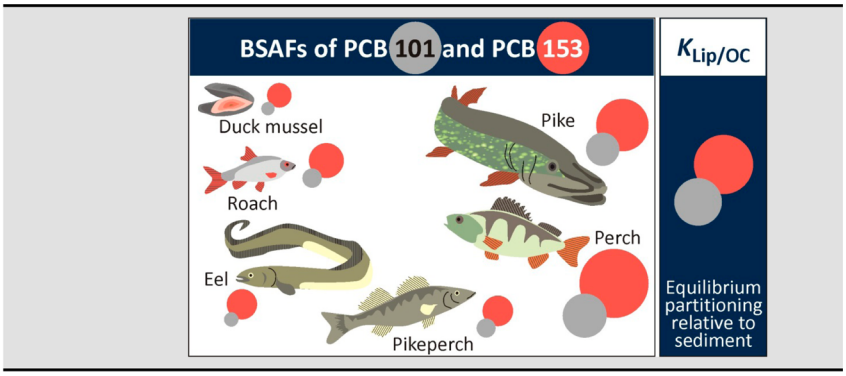
EXPERIMENTAL SECTION

Study Site. Lake Ången (58°75′15″ N, 17°18′31″ E) is a small (2.4 km^2) lake 90 km southwest of Stockholm with no known sources of pollutants other than the atmosphere. It is connected to the Baltic Sea through a 200 m long narrow stream that is blocked by an eel trap, impeding migration to and from the lake. An additional criterion for the selection of the lake was its limited depth (on average 5 m, max. 8 m), which ensures efficient vertical mixing. Further details on the study site are given in ref 17.

Sampling. Duck mussels (*Anodonta anatina*) were collected by a diver on November 24, 2012. Fish were caught with multimesh gill nets,[19] which are sectioned into parts with various mesh sizes, on November 28, 2012. The following fish species were included: Roach (*Rutilus rutilus*), pikeperch (*Sander lucioperca*), perch (*Perca fluviatilis*) and pike (*Esox lucius*). The number and characteristics of the organisms included in this study are given in Table S1 in the Supporting Information. In addition, European eels (*Anguilla anguilla*, n = 5) from an eel trap[17] were included in this study. The trophic levels of the studied fish species according to FishBase[20] are as follows (average ± standard error): 2.8 ± 0.3 (roach), 3.5 ± 0.6 (eel), 4.3 ± 0.7 (pikeperch), 4.4 ± 0.8 (perch) and 4.4 ± 0.7 (pike). In addition, δ^{15}N analysis was carried out as described below. Surface sediment was collected at five representative locations across the lake by a diver on November 19, 2011, at 2.5 m depth and 6 °C water temperature and on November 24, 2012, at 3.6−7.0 m depth and 6 °C water temperature, for details, see ref 17. All samples were transported back to the laboratory and stored at 4 °C (sediment) or −18 °C (biota) until further processing.

Standards and Materials. Seven indicator PCBs (IUPAC no.s 28, 52, 101, 118, 153, 138 and 180, AccuStandard (New

Table 1. Biota-Sediment Accumulation Factors [BSAF = $C_{Bio,Lip}/C_{Sed,OC}$] for the Six Biota Species and the Lipid/OC Partition Coefficient ($K_{Lip/OC}$) Determined Using Equilibrium Sampling[a]



	HCB	PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180
Duck mussel	(9.0)	(0.9)	(2.0)	2.4	2.5	8.2	5.3	7.6
Roach	(9.9)	(1.4)	(3.8)	5.1	6.7	16.7	10.2	12.4
Eel	(7.3)	(1.8)	(3.4)	2.7	11.8	12.7	7.1	8.9
Pikeperch	(4.7)	(0.7)	(2.6)	5.0	5.8	12.9	9.2	11.0
Perch	(16.0)	(1.5)	(9.5)	26.7	35.9	66.0	49.2	59.0
Pike	(10.3)	(2.6)	(5.7)	15.2	18.7	37.8	20.8	29.6
$K_{Lip/OC}$	(12.0)	(8.6)	(18.4)	31.2	29.3	48.3	36.1	49.7

[a]Data where the $C_{Sed,OC}$ could not be reliably quantified (see Table S4, Supporting Information) are given in brackets. Data below the thermodynamic equilibrium level relative to the sediment are highlighted in green, those near equilibrium in yellow. A visualization of the BSAFs for PCB 101, which is subject to biotransformation, and PCB 153, one of the most bioaccumulative compounds amongst the model chemicals, and the equilibrium partitioning benchmark between model lipids and the site-specific sediment organic carbon ($K_{Lip/OC}$) are also given.

Haven, CT, USA), ≥99% purity, log K_{OW} range 5.66−7.19[21]) and hexachlorobenzene (HCB, log K_{OW} 5.64[22]) were chosen as the model chemicals. Isotope-labeled internal standard (IS) compounds ($^{13}C_6$ HCB and the seven $^{13}C_{12}$ PCBs, Cambridge Isotope Laboratories (CIL, Woburn, MA, USA), ≥98% purity, approximately 2500 pg of each compound) used in the quantification of the target chemicals were spiked before sample extraction. Nonlabeled PCB 53 was used as the recovery internal standard and was spiked at approximately 2500 pg to the final extracts before analysis. All solvents and chemicals were of Suprasolv quality (Merck, Darmstadt, Germany) and used as received.

Characteristics of the Sediment and Biota Samples. Wet sediment was dried in a 60 °C oven for 4 days, and the dried residue was subtracted from the initial sample weight to yield the water content. To determine the sediment's content of total organic carbon (TOC), wet sediment was freeze-dried and homogenized using a mortar and pestle. Subsequently, 5−10 mg were weighed into silver capsules (n = 6) onto which an excess of hydrochloric acid was pipetted to remove inorganic carbonates. The capsules were dried in a 60 °C oven overnight and the % TOC content was then determined at the Department of Geological Sciences (Stockholm University) using a Carlo Erba NC2500 elemental analyzer. In addition, stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope analysis of the homogenized and freeze-dried biota samples was carried out using continuous flow isotope ratio mass spectrometry following the same sample preparation as for sediment except for the acidification step and using the same analyzer.

Extraction, Cleanup and Analysis. Generally, 3−6 organisms were pooled for analysis (Table S1); exceptions were pikeperch, where only one individual was available, and the eels (n = 5) that were analyzed individually. Whole mussels (without the shells) or ca. 20 g of fish muscle tissue dissected from close to the dorsal fin were homogenized using an Ultra-Turrax. Target compounds were extracted from the tissue homogenates by two exhaustive extraction methods: The "classical" Jensen method,[23] with modifications as described in ref 24, and a modified Jensen method[25] specifically developed for lean tissues. The concentrations in the eels have been reported in ref 17; here, we reanalyzed one individual ("eel A") to ensure comparability with the additional samples. For sediment, we used Soxhlet extraction[26] with minor modifications.[16] For details, see Text S1 in the Supporting Information.

Passive equilibrium sampling of sediment was done using micrometer-thin layers of the silicone DC1-2577 (Dow Corning, Seneffe, BE) coated on the inner vertical walls of glass jars. The approach is described elsewhere,[27,15,16] and details for the processing of Lake Ången sediment are given in ref 17.

The extracts were submitted to similar cleanup methods (Text S1, Supporting Information). The analysis of the target compounds was done by gas chromatography coupled to high-resolution mass spectrometry in the electron impact ionization mode as detailed elsewhere.[28] A HP 6890 GC (Agilent Technologies, Santa Clara, USA) coupled to a Micromass AutoSpec Ultima mass spectrometer (Waters Corporation, Milford, USA) equipped with an Agilent Technologies FS Deactivated precolumn (0.53 mm) and a Supelco PTE-5 analytical column (30 m × 0.25 mm × 0.25 μm) was used.

RESULTS AND DISCUSSION

Characteristics of the Biota and the Sediment. The content of extractable organic matter (used as a surrogate for lipid content) of the investigated biota determined with the two different methods (refs 23 and 25, Text S1, Supporting

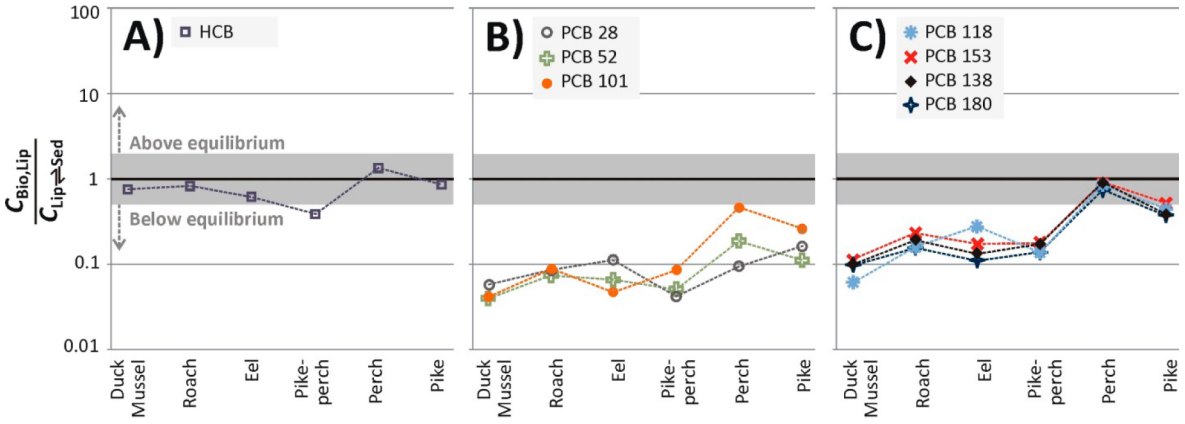


Figure 1. Ratios of lipid-normalized biota concentrations ($C_{Bio,Lip}$) for six biota species and concentrations in model lipids at thermodynamic equilibrium with the sediment ($C_{Lip\rightleftharpoons Sed}$) from passive equilibrium sampling. The shaded area highlights near equilibrium conditions (ratios between 0.5 and 2.0). Data are given for HCB that rapidly equilibrates between phases (A), lower chlorinated PCBs that are moderately bioaccumulative and subject to biotransformation (B), and higher chlorinated, highly bioaccumulative PCBs (C). Averages of all quantifiable data are plotted.

Information) were very similar. The duck mussel, roach, pikeperch, perch and pike homogenates had 0.65 or 0.74%, 0.71 or 0.73%, 0.70 or 0.74%, 0.54 or 0.57% and 0.57 or 0.58% extractable organic matter for the classical or modified Jensen extractions, respectively. On the basis of the similar extraction yields, we concluded that both methods succeeded in a complete extraction, even of these lean biota samples, and hence considered the data sets as duplicates. The lipid content of the five individual eels ranged from 19.3% to 28.5% (on average 23.3%).[17] The re-extraction of eel A yielded 23.3 and 22.4% lipid resulting from the two methods, compared to 23.2 ± 0.6% in the originally processed data set (average ± standard deviation, n = 3).[17]

The results of the stable isotope analysis of the biota samples are given in Table S2 in the Supporting Information; they indicated different energy sources of the organisms (differences in $\delta^{13}C$ of >3.6‰, Figure S1 in the Supporting Information) resulting from nonselective feeding of the species present in this nutrient-rich ecosystem. The scatter in the $\delta^{13}C$ data prevents determination of the species' relative trophic level for the complete data set. However, biomagnification was evident for some organisms and chemicals, although with shallow slopes, as shown in Figure S2 in the Supporting Information.

The sediment had a water content of 51.1 ± 0.7%, and its TOC content was 1.24 ± 0.03% (average ± standard deviation, n = 6).[17]

Total Concentrations of HOCs in Biota and Sediment. The total concentration measurements of PCBs in biota, sediment and silicone coatings yielded on average 0.006 (PCB 28, pikeperch) to 24.4 (PCB 153, eel) ng/g ww, <MQL (PCBs 28 and 52) to 109 (PCB 138) pg/g dw and 2.29 (PCB 28) to 38.2 (PCB 138) ng/g silicone, respectively. For HCB, they were between 0.026 (pikeperch) and 1.52 ng/g ww (eel), 9.4 pg/g dw and 1.01 ng/g silicone in biota, sediment and silicone coatings, respectively. Lipid-normalized HOC concentrations in biota ($C_{Bio,Lip}$) were highest in perch, ranging from 1.83 (PCB 28) to 472 (PCB 153) ng/g lipid, followed by pike, whereas the concentrations in the other species were considerably lower (Table S3 in the Supporting Information). The re-extractions of eel A generally yielded slightly lower $C_{Bio,Lip}$ for the PCBs than the published data set.[17] For this comparison, the data obtained using the "classical" and the modified Jensen methods were averaged; PCB 28 was excluded due to few quantifiable data. The newly processed data (i.e., the average concentrations obtained from both the "classical" and the modified methods) were by 4.9% (PCB 138) up to 43.7% (PCB 101) and on average 16.0% lower than the previously published $C_{Bio,Lip}$.[17]

The OC-normalized concentrations of PCBs in the sediment ($C_{Sed,OC}$)[17] ranged from <MQL (PCBs 28 and 52) to 8.82 ng/g OC (PCB 138, Table S4 in the Supporting Information).

Biota-Sediment Accumulation Factors. For PCBs with 5−7 chlorines, BSAFs ranged from 2.4 for PCB 101 in duck mussels to 66.0 for PCB 153 in perch (Table 1). It is tempting to interpret BSAFs greater than unity as an indication of bioaccumulation exceeding equilibrium partitioning relative to the sediment (i.e., biomagnification). However, differences in the sorptive capacities of biota lipids and sediment OC need to be considered when evaluating the measured BSAF values. Instead of unity, the site-specific lipid/organic carbon partition ratios ($K_{Lip/OC}$) should be used as the benchmarks for equilibrium partitioning. For Lake Ången, $K_{Lip/OC}$ ranged from 29.3 (PCB 118) to 49.7 (PCB 180, Table 1).[17] The calculation of the $K_{Lip/OC}$ data is described in Text S2 in the Supporting Information, and the Lake Ången data are set into perspective with $K_{Lip/OC}$ data of Baltic Sea sediment in Figure S3 and Table S5 in the Supporting Information.

Our measured BSAFs are generally below the site-specific $K_{Lip/OC}$ values, except for the most bioaccumulative PCBs 118, 153, 138 and 180 that slightly exceed $K_{Lip/OC}$ (up to 1.4 times, PCBs 153 and 138) in perch, the species with the highest $C_{Bio,Lip}$. We clustered all measured BSAF data (Table 1) as (i) below [at BSAF/$K_{Lip/OC}$ < 0.5], (ii) near [at 0.5 ≤ BSAF/$K_{Lip/OC}$ ≤ 2] or (iii) above [at BSAF/$K_{Lip/OC}$ > 2] the equilibrium benchmark, $K_{Lip/OC}$. In the present study, 70% (n = 21) of the BSAFs were below and 30% (n = 9) were near the equilibrium benchmark. Contrarily, there were no data that clearly indicated that biomagnification had led to elevated chemical activities in the fish relative to the sediment level.

Lipid-Normalized Concentrations in Six Biota Species vs Equilibrium Partitioning Concentrations in Model Lipids. Passive equilibrium sampling of sediment using silicone-coated jars yielded equilibrium partitioning concentrations of HCB and PCBs in silicone ($C_{Sil\rightleftharpoons Sed}$). We translated $C_{Sil\rightleftharpoons Sed}$ to equilibrium partitioning concentrations in model lipids ($C_{Lip\rightleftharpoons Sed}$) using $K_{Lip/Sil}$ as described in ref 17. Both

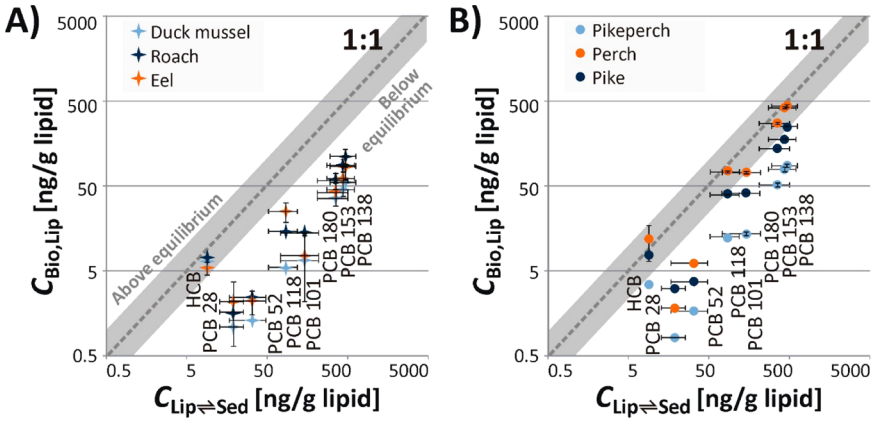


Figure 2. Lipid-normalized biota concentrations ($C_{Bio,Lip}$) vs $C_{Lip⇌Sed}$ for A) Duck mussels, roach and eel and B) Pikeperch, perch and pike. The shaded area highlights near equilibrium conditions (ratios between 0.5 and 2.0). Symbols represent single data points or means of the quantifiable replicates (Tables S3 and S6, Supporting Information). Error bars reflect absolute deviations of duplicate biota analyses (mussels, roach, pikeperch, perch and pike) or standard deviations of all quantifiable eel and sediment data for each compound.

$C_{Sil⇌Sed}$ and $C_{Lip⇌Sed}$ data are given in Table S6 in the Supporting Information.

The first aim of the present study was to compare the in situ lipid-normalized concentrations of PCBs and HCB in six aquatic species to the equilibrium partitioning reference level in the sediment. In Figure 1, we plotted the ratios of the average $C_{Bio,Lip}$ and the average $C_{Lip⇌Sed}$ for the six species. To address the first aim of the study, we categorized all measured $C_{Bio,Lip}$ data as (i) below [at $C_{Bio,Lip}/C_{Lip⇌Sed} < 0.5$], (ii) near [at $0.5 \leq C_{Bio,Lip}/C_{Lip⇌Sed} \leq 2$] or (iii) above [at $C_{Bio,Lip}/C_{Lip⇌Sed} > 2$] the equilibrium partitioning level relative to the sediment. The results reveal that (i) 76.1% (n = 51) of the data clearly indicated "below equilibrium", in agreement with comparable studies,[15−18] (ii) a limited number of observations in the highest trophic level species perch and pike and for HCB in most species indicated "near equilibrium" (23.9%, n = 16), whereas (iii) there were no observations indicating biota exceeding the equilibrium partitioning level relative to the sediment (Figure 1).

For HCB, the data are scattered around 1 (Figure 1 A), indicating near-equilibrium between biota and sediment in all species except pikeperch, which was slightly below a ratio of 0.5. However, it has to be stressed that this is based on a single quantifiable data point for HCB in silicone equilibrated with sediment (Table S6, Supporting Information). For the PCBs, $C_{Bio,Lip}$ was generally lower than $C_{Lip⇌Sed}$. The ratios for PCBs 101, 52 and 28 were consistently below the equilibrium partitioning level ($C_{Bio,Lip}/C_{Lip⇌Sed} < 0.5$, Figure 1 B), which reflects lower biomagnification potential of these lower chlorinated congeners, biotransformation/metabolism[29] and/or that the water phase in the lake might have been somewhat below the equilibrium partitioning level relative to the sediment.[17] Biotransformation of PCBs has been shown to be structure-dependent in fish, being greater for PCBs possessing vicinal hydrogen atoms in the meta/para positions such as PCBs 101 and 52.[29] For PCBs 118, 153, 138 and 180 (Figure 1C), the ratios approached the equilibrium partitioning reference level in perch and for PCB 153 in pike, the two species that showed the greatest extent of biomagnification in accordance with their trophic levels from FishBase.[20] Contrarily, the remaining species were substantially below the equilibrium partitioning level relative to the sediment even for these highly chlorinated PCBs, for which biomagnification is well-established.

The relationship between $C_{Bio,Lip}$ and $C_{Lip⇌Sed}$ for duck mussels, roach and eel (Figure 2A) and pikeperch, perch and pike (Figure 2B) consistently demonstrates biota being below the equilibrium partitioning level relative to the sediment, or, in a few cases such as HCB and PCBs in high trophic level species, near equilibrium status. Figure 2 includes error bars representing the variation in $C_{Sil⇌Sed}$ from five locations across the lake and a number of replicates having been processed, for the multiple analysis of five individual eels or duplicate analysis of the pooled biota samples, respectively. For PCB congeners with 3 or 4 chlorines, $C_{Bio,Lip}/C_{Lip⇌Sed}$ shows no distinct species-specific patterns (Figure S4, Supporting Information), whereas there is evidence of biomagnification of higher chlorinated PCBs in perch and pike (Figure S4B, Supporting Information). For PCBs with 5−7 chlorines, the perch data approach the equilibrium partitioning level relative to the sediment, which can also be seen for PCB 153 in pike.

In summary, in our current study of Lake Ången, $C_{Lip⇌Sed}$ either agreed with or exceeded the lipid-normalized concentrations of PCBs and HCB in biota that result from bioaccumulation, which is in good agreement with other recent studies.[15−18,30] These results hence support the assumption of the extrapolated EqP approach that concentrations in biota would not markedly exceed the equilibrium partitioning level relative to the sediment (see assumption II in the Introduction Section). The overall picture is thus that $C_{Lip⇌Sed}$ provides the thermodynamic potential for equilibrium partitioning into the lipids of biota, and that all measured concentrations in biota of Lake Ången are below or near this level.

Reible et al.[31] suggested a closely related but still somewhat different approach in which concentrations in a polymer at equilibrium with sediment were translated to freely dissolved concentrations, which then were multiplied with the compound-specific n-octanol/water partition coefficient, K_{OW}. Consequently, this approach yields the chemical's equilibrium partitioning concentration in octanol ($C_{Oct⇌Sed}$). Recent studies have shown good correlations between these equilibrium partitioning concentrations in octanol and bioaccumulation,[30,31] which is in general agreement with the results of the present study. However, it is important to note that octanol is an imperfect surrogate for real biota lipids, and that

equilibrium partitioning into lipids often is markedly higher than for octanol,[32,33] which implies $C_{Octanol \rightleftharpoons Sed} < C_{Lip \rightleftharpoons Sed}$. Our observation of equilibrium partitioning concentrations being an indication or overestimation of lipid-normalized concentrations in real organisms can thus not be directly extrapolated to octanol-based estimations of equilibrium bioaccumulation.

Equilibrium Sampling as a Tool to Assess and Prioritize Management Actions for Contaminated Sediments. The second aim of this study is to illustrate how passive equilibrium sampling of sediment can be used to assess and manage bioaccumulation of HOCs from contaminated sediments. We propose that $C_{Lip \rightleftharpoons Sed}$ measured for contaminated sediments can be used to rapidly and precisely determine the thermodynamic potential for bioaccumulation in (i) temporal and spatial environmental monitoring, (ii) site-specific risk assessments and (iii) management of polluted sites.

Assessment and prioritization of management actions based on comparing $C_{Lip \rightleftharpoons Sed}$ between sites and against concentrations in fish that are cause for concern would be based on the assumption that elevated chemical activity in the sediments is a dominant driver of contaminant levels in biota. We note that this approach does not take into account that biomagnification and migration may result in $C_{Bio,Lip} > C_{Lip \rightleftharpoons Sed}$. However, our current study and other comparable studies that assessed sediment contamination using equilibrium sampling[15−18] have all, so far, found $C_{Bio,Lip} \leq C_{Lip \rightleftharpoons Sed}$ throughout the foodweb.

The equilibrium partitioning concentrations in lipids, $C_{Lip \rightleftharpoons Sed}$, from Stockholm Harbor and the Stockholm Archipelago of the Baltic Sea[16] and Lake Ången[17] are compared to (i) maximum allowable $C_{Bio,Lip}$ of PCBs in commercial foodstuffs such as fish provided by the European Commission[34] and (ii) $C_{Bio,Lip}$ that correspond to monthly consumption limits for PCBs in fish based on noncancer and cancer health end points, provided by the US EPA[35] in Figure 3. Generally, fish above the European thresholds must not be marketed within the EU. For foodstuffs above the strictest US EPA monthly consumption limit, <0.5 fish meals/month are recommended. The specific thresholds and adjustments that were necessary to enable this assessment are described in Text S3 in the Supporting Information.

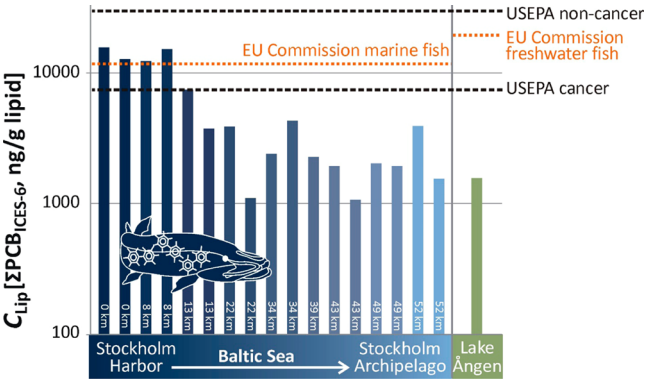


Figure 3. Sum concentrations of 6 "ICES" PCBs in model lipids at thermodynamic equilibrium with the sediment ($C_{Lip \rightleftharpoons Sed}$) from Stockholm Harbor and the Stockholm Archipelago of the Baltic Sea[16] as well as Lake Ången.[17] $C_{Lip \rightleftharpoons Sed}$ indicates the thermodynamic potential of the sediment for bioaccumulation. Maximum levels defined by the EU Commission[34] are indicated by dotted orange lines, transformed to [ng/g lipid] assuming lipid fractions corresponding to the observed levels in Lake Ången, for marine fish and freshwater fish. The risk-based consumption limits "<0.5 fish meals/month" of the US EPA[35] are given as broken black lines for noncancer and cancer health end points, transformed to [ng/g lipid] and extrapolated from total "Arochlor" PCBs to ΣPCB_{ICES-6}. See Text S3 in the Supporting Information for details.

The thermodynamic potential of the sediment from Stockholm Harbor (showing the highest activity) for bioaccumulation with the six so-called "ICES" PCBs (ΣPCB_{ICES-6}, sum of PCBs 28, 52, 101, 153, 138 and 180 as defined by the International Council for the Exploration of the Sea, ICES) exceeds the EU maximum levels in fish and the slightly more conservative US EPA threshold for the cancer health endpoint (Figure 3, Text S3, Supporting Information). The $C_{Lip \rightleftharpoons Sed}$ from the outer Stockholm Archipelago and Lake Ången are well below the US EPA limit with regards to cancer risks.

In the present study, we found that $C_{Lip \rightleftharpoons Sed}$ for sediments from Stockholm Harbor exceeded $C_{Bio,Lip}$ regulatory limits that the European Commission and the US EPA provide for fish for human consumption (Figure 3). This result means that if fish equilibrated with the sediment in Stockholm Harbor, they would exceed the given threshold levels. Sediment in Stockholm Harbor thus has an elevated potential for bioaccumulation and may need action to reduce the bioavailability of persistent organochlorine pollutants.

Our findings are supportive of a recent strategy for the management of polluted sediment, which is based on amending a strong sorbent (e.g., activated carbon) to contaminated sediment to achieve a reduction in contaminant mobility.[36−38] Specifically, these approaches use high K_d sorbents to reduce the freely dissolved chemical concentrations in the interstitial pore water and hence also bioavailability and $C_{Lip \rightleftharpoons Sed}$. Initial research has indicated that such amendments indeed reduce exposure and bioaccumulation.[30,39,40]

We propose that passive equilibrium sampling of sediments is a useful basis to assess and compare the contamination status of different systems. Passive equilibrium sampling measures the thermodynamic potential of HOCs to bioaccumulate from sediments, and has considerable advantages over measurements of $C_{Sed,OC}$. The suggested $C_{Lip \rightleftharpoons Sed}$ approach would be highly valuable in national-level assessments aimed at the prioritization of remediation actions on contaminated sites. Equilibrium sampling of sediment thus provides a straightforward and useful new approach to determine potential HOC levels that aquatic biota may achieve provided that they reach equilibrium with the sediment. It has the potential to become a valuable tool for prioritizing further research and management actions aimed at reducing human health risks and use impairments caused by contaminated sediments.

■ ASSOCIATED CONTENT

Supporting Information

Extraction, cleanup and analysis; partitioning between lipids, organic carbon, water and polymers; regulatory perspective related to $C_{Lip \rightleftharpoons Sed}$; stable nitrogen ($\delta^{15}N$) vs carbon ($\delta^{13}C$) isotope ratios for the biota; correlations of lipid-normalized concentrations and $\delta^{15}N$; lipid/water partition ratios ($K_{Lip/W}$) and field K_{OC}; ratios of $C_{Bio,Lip}$ and $C_{Lip \rightleftharpoons Sed}$; biota length (cm) and weight (g); stable isotope ratios for the investigated biota species; lipid-normalized concentrations of HOCs in biota ($C_{Bio,Lip}$, ng/g lipid); OC-normalized concentrations of HOCs in sediment ($C_{Sed,OC}$, ng/g OC); lipid/OC partition ratios ($K_{Lip/OC}$); concentrations in silicone ($C_{Sil(DC)}$, ng/g silicone) and $C_{Lip \rightleftharpoons Sed}$ (ng/g lipid); partition ratios between the relevant

silicone polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*A. Jahnke. E-mail: annika.jahnke@itm.su.se; annika.jahnke@ufz.de.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Mona Blomqvist, Sven-Erik Blomqvist, Sören Lehmann and Johan Löwen for allowing us to carry out sampling on their property and Sören Lehmann for providing us with eel samples. We kindly acknowledge Michael S. McLachlan for helpful discussions, Urs Berger, Andreas Hägerroth, Per-Åke Hägerroth, Daniel Johansson and Dämien Bolinius for assistance during sampling, Björn Ardestam for advice and the kind provision of the fishnets and Stefan Lundberg for the identification of the mussels. We thank Margit Møller Fernqvist for the coating of the glass jars, Ulla Eriksson and Jörgen Ek for their assistance in the laboratory, Cecilia Bandh and Yngve Zebühr for the GC/HRMS analyses and Heike Siegmund for the TOC and stable isotope analyses. We thank three anonymous reviewers for their helpful comments that helped to improve this manuscript. This research was funded by The Long-range Research Initiative of The European Chemical Industry Council (CEFIC, LRI-ECO14-15.2), the Swedish Research Council Vetenskapsrådet (VR, 2011-3890), the EU Commission (OSIRIS, GOCE-037017) and carried out in preparation of a Strategic Environmental Research and Development Program (SERDP) project funded by the US-DOE and US-EPA (14 ER03-035/ER-2431).

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