Comparing sediment equilibrium partitioning and passive sampling techniques to estimate benthic biota PCDD/F concentrations in Newark Bay, New Jersey (U.S.A.)

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Sediment and polyethylene sampler-based estimates of polychlorinated dibenzo-p-dioxin/dibenzofuran (PCDD/F) concentrations in Newark Bay, New Jersey (USA) benthic biota were compared. Biotia concentrations based on sediment were estimated using an organic carbon (OC)-water partitioning model and an OC and black carbon (BC)-water dual model. Biotia concentrations based on polyethylene were estimated from samplers deployed in the Newark Bay water column and samplers immersed in a sediment/porewater slurry in the laboratory. Porewater samplers provided the best estimates of biota concentrations (within 3.1×), with best results achieved for deposit-feeders (within 1.6×). Polyethylene deployed in deep water also provided good estimates of biota concentrations (within 4×). By contrast, OC-water partitioning overestimated biota concentrations by up to 7×, while OC and BC combined underestimated biota concentrations by up to 13×. We recommend passive samplers such as polyethylene for estimating concentrations of hydrophobic organic contaminants in field biota given its simplicity and relatively lower uncertainty compared to sediment equilibrium partitioning.

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1. Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are toxic hydrophobic organic contaminants (HOCs) that sorb to particles in sediments (Luthy et al., 1997). Sedimentary HOCs can be bioavailable to benthic marine organisms and accumulate up the marine food chain (DeWit et al., 1995; Pickard and Clarke, 2008). The risk of aquatic organism exposure to HOCs is a primary consideration when choosing an approach to clean-up HOC-contaminated sites. One such site is the lower Passaic River/Newark Bay in New Jersey (USA). The lower Passaic is the location of the former Diamond Alkali pesticide manufacturing company, which discharged waste to adjacent waters during the 1950s/60s, severely contaminating sediments with PCDD/Fs. In 1984, the sediment site was added to the U.S. EPA Superfund list and is currently undergoing a two-phase clean-up process that will include removal of 153,000 m³ of sediment via dredging (US EPA). Newark Bay, one of the most industrialized estuaries in the United States, extends just south of the Passaic (Fig. 1) and is known to be impacted by PCDD/Fs from the Passaic (Rappe et al., 1991). Though there have been efforts to characterize contaminant dynamics in the Passaic River and Newark Bay, passive sampling, a promising state-of-the-art method for determining dissolved HOC concentrations (Choi et al., 2013; Fernandez et al., 2009), has not been employed. In this study, we compare passive sampling-based estimates of PCDD/F concentrations in sediment-dwelling biota, and conventional equilibrium partitioning-based estimates using sediment geochemical characteristics (i.e., organic and black carbon, OC and BC) to PCDD/F concentrations measured in biota collected from Newark Bay.

Passive samplers of various types have been used as tools to directly sample porewater dissolved HOCs, or as surrogates for bioaccumulation organisms (Adams et al., 2007; Huckins et al., 1990; Lohmann et al., 2004; Mayer et al., 2000; Schneider et al., 2006; Vinturella et al., 2004). Passive samplers circumvent problems associated with traditional solvent-based porewater extractions by sampling freely dissolved HOCs via diffusive uptake into the sampler matrix and thus avoiding the need to isolate interstitial water and having to address related artifacts. In a previous study by our group, a laboratory bioaccumulation study with field-
contaminated sediment demonstrated that polyethylene (PE) passive samplers can estimate freely dissolved PCB concentrations organisms are exposed to within a factor of four (Friedman et al., 2009). Others have similarly shown that PE can be useful for predicting uptake of PAHs in benthic biota in the laboratory (Vinturella et al., 2004). PE and other samplers have also been useful in determining the direction of HOC fluxes between environmental compartments; for example, from the water column to the atmosphere (Morgan and Lohmann, 2008) or from porewater to the overlying water column (Cornelissen et al., 2008). Only a limited number of studies have demonstrated the utility of PE in predicting HOC body burdens of organisms in the field, however (Cho et al., 2009).

In contrast, a number of studies have discussed and used equilibrium partitioning from sediment OC, and several from OC and BC combined, to predict freely dissolved HOC concentrations and, by extension, bioavailability (Accardi-Dey and Gschwend, 2002, 2003; Burgess et al., 2013; DiToro et al., 1991; Hawthorne et al., 2007a, 2006b; Lohmann et al., 2005). In general, OC-water-based equilibrium partitioning overestimates dissolved concentrations (Hawthorne et al., 2006; Lohmann et al., 2005), and mixed results are reported when other sediment carbon phases like BC are considered, with some studies showing improvements to estimates (Accardi-Dey and Gschwend, 2003; Lohmann et al., 2005), and others showing little change or underestimates (Hawthorne et al., 2007a,b). Often these estimate errors are considered to result from inadequate equilibrium partition coefficient values.

Here, we compare biota PCDD/F concentrations estimated from equilibrium partitioning between sedimentary carbon phases and porewater to those measured in organisms collected directly from the Newark Bay. The specific goals of the study are to determine whether (i) PE are useful in predicting benthic biota PCDD/F burdens in the field; (ii) PE-based porewater and/or water column dissolved concentrations are better predictors of in-situ bioaccumulation than sediment equilibrium partitioning; and, (iii) including BC in partitioning calculations substantially impacts estimated biota concentrations. We address these goals by collecting and analyzing Newark Bay sediment, porewater, and biota, and by deploying PE samplers directly in the Bay.

2. Materials and methods

2.1. Site description and overall methodology

Newark Bay (− 1.5 km wide, 10 km long), is part of the New York/New Jersey Harbor Estuary (Fig. 1). The Bay converges with the Passaic and Hackensack Rivers at its north and the Arthur Kill ("AK") and Kill van Kull ("KVK") at its south. The Passaic and the Hackensack Rivers are sources of freshwater to Newark Bay with a combined watershed of 3000 km², though the Hackensack is estimated to contribute only ~7% of the Passaic River on average (Caplow et al., 2003).

Five sites were chosen throughout the Bay for sampling (Fig. 1). The "Passaic", "Hackensack", "AK", and "KVK" sites represent locations where the Bay converges with each water channel. The mid-Bay ("MB") site was located in the middle of Newark Bay. Water column depths were −1.5 m at the Passaic, Hackensack, and MB stations, 4 m at the KVK, and 8.8 m at the AK station. Sediment and biota were collected from each site and analyzed for PCDD/Fs. Porewater was also analyzed for PCDD/Fs by tumbling PE and sediment together in glass flasks on a shaker table in the laboratory. A separate set of PE samplers was deployed in-situ at each site to determine dissolved PCDD/F concentrations above the sediment bed ("deep water"). PCDD/F concentrations from all media were then converted to tissue concentrations using equilibrium partition coefficients, and estimated tissue concentrations were compared to those measured directly from biota. Concentrations in porewater and deep water PE were also compared to determine the direction of the diffusive flux of PCDD/Fs across the sediment–water interface. All extraction procedures and instrumental methods are detailed in the SI (SI text and Table S1).

2.2. Sediment and biota collection

Sediment and biota were collected from the R/V Kenneth Biglane using a van Veen grab. Each grab, −250 mL of sediment was collected from the top half (~10 cm) and stored on ice. The remainder of the grab was rinsed through a 1 mm sieve. Clams (Mya arenaria) and deposit-feeding tube worms (Pectinaria gouldii) remaining on the sieve were collected and depurated in seawater in plastic bags for 4–8 h at field temperature. Collections were repeated until several grams of tissue
had been collected. Biota were rinsed with tap water, placed in muffled amber jars, and frozen on dry ice.

2.3. Preparation of PEs for field deployment and laboratory tumbling experiments

Sheets of PE painter’s drop cloth (25 μm thickness, Covalence Plastics) were cut into ~1 g pieces and cleaned by submerging in dichloromethane for 24 h twice. To gauge the equilibrium status of analytes in deep water PE, performance reference compounds (PRCs) were added to PE samplers before deployment. PRCs used for all analytes included cis-1,2,3,4-tetrachlorobenzene, cis-1,2,3,4-tetrachloroanisole, and octachloronaphthalene (Ultra Scientific; Cambridge Isotopes). These compounds were chosen because of their similar planar conformation to PCDD/Fs, and because isotopically-labeled PCDD/Fs were employed as internal standard surrogates in all extractions. Thus, the assumption was made that PCDD/Fs are taken up into PE at the same rate that PRCs dissipate from PE (Huckins et al., 2002). This assumption introduces uncertainty into deep water concentrations, addressed later in the Results. Polyethylene pieces were impregnated with PRCs in an 80:20 methanol:water solution following previously published methods (Booij et al., 2002). The methanol:water solution was spiked with 1 μg PRC per 1 g sampler and samplers were immersed in the solution for 8–12 weeks to ensure homogeneous distribution. Samplers were removed from the PRC solution and wiped dry with laboratory-grade tissues. A small snippet (~0.1 g) was cut from each sampler for initial PRC analysis (CPRC,i:0). For field deployments, the remainder of the sampler was strung on pre-cleaned stainless steel wire (Malin Co.,) wrapped in aluminum foil, and both snippet and sampler were stored at ~4 °C until deployment or analysis.

2.4. PE-porewater tumbling experiments

Three different sized samplers were cut from PRC-impregnated PE (~0.25, 0.50, and 0.75 g) for each sampling location. This was done to assess whether PEs had reached equilibrium with porewater during tumbling, and sizes were chosen such that PCDD/Fs were not depleted from the sediment-porewater system (calculation in the SI). Samplers were added to 125 mL muffled round bottom flasks with 50–60 g sediment. Ten mL of 1 mg/mL sodium azide was added to each flask, PCDD/Fs were derived from the literature (Xia, 1998), while PCDD/Fs were estimated from PCDD/F octanol–water partition coefficients (Kow), using an estimation determined with PAH data at 5–24 °C (Mujis and Jonker, 2009). Uncertainties associated with the BAF estimation are discussed later.

Similarly, lipid concentrations based on sediment OC and BC (Csed,OC-BC) were estimated as the product of the BAF and dissolved concentrations (Accardi-Dey and Ghoshwendi, 2002) using a Freundlich coefficient of n = 0.7:

\[ C_{s,OC-BC} = C_{f,OC} \cdot BAF = C_{f,OC} \cdot BAF \cdot K_{OC} \cdot f_{s,OC} \cdot BC \]

where BC is the fraction of BC in the sediment and Koc is the BC–water partition coefficient (ml/water/g BC). Both literature and sediment-specific values of Koc were used to calculate Csed,OC-BC. Literature PCDD/F/Kocs for Newark Bay sediments (Lambert, 2010) come from an adjacent field location (the Passaic River) approximately 200 cm deeper into the sediment bed. Sediment-specific Kocs were derived from porewater dissolved PCDD/F concentrations calculated from PE samplers in the present study using Eq. (5) (with n = 0.6, 0.7, and 0.8).

Lastly, lipid concentrations from porewater (Clip,FlPe) were estimated from PE uptake as follows:

\[ C_{lip,PE} = f_{dis,PE} \cdot BAf \cdot Clip,PE = Clip,PE \cdot BAF \cdot f_{lip,OC} \cdot BC \]

where BC is the PE-water partition coefficient (ml/water/g PE) estimated from Kow (Adams et al., 2007). Values of Kow were taken from Aberg et al. (2008). Kf,OC,w were determined at 24 °C and 0 ppt salinity, were adjusted to reflect deep water and porewater temperature and salinity conditions. See the SI for additional information regarding physicochemical constants used for temperature and salinity adjustments.

2.9. Sediment total organic carbon and black carbon

For total organic carbon (TOC) determinations, sediments were dried at 60 °C, ground after shell material was removed, treated with HCl, and analyzed for TOC on a Carlo Erba NA 1500 elemental analyzer (Fisons Instruments, Beverly, MA, USA), coupled to a VG-Optima stable isotope mass spectrometer. BC was determined using previously published methods (Accardi-Dey and Ghoshwendi, 2002; Gustafsson et al., 1996), National Institute of Standards and Technology Standard Reference Material (1941b) analyzed with this method had a mean BC content of 0.57 ± 0.01% (n = 3), within the range (0.6–1.7%) presented by a comprehensive BC quantification method intercomparison study (Hammes et al., 2007). Amorphous organic carbon (i.e., the fraction of TOC not considered BC) was determined by subtracting the fraction of BC from TOC.

3. Results and discussion

3.1. Sediment

Sediment OC ranged from 1.6 to 5.8% and sediment BC ranged from 0.1 to 76 ng/g OC (OCDD in the AK), or 0.005–2.72/2.8-DiCDD. Several of the mid-MW congeners (2,3,7,8-TCDF, 1,3,7,8-HxCDD, 2,3,4,7,8-PeCDF, 2,3,4,7,8-PeCDF) were only detected...
in the northern half of the Bay in the Passaic and Hackensack Rivers. The most toxic dioxin congener, 2,3,7,8-TCDD, was present at all sites, but was most concentrated in the Passaic and Hackensack (2.1 \pm 0.8 ng/g OC and 2.1 \pm 0.9 ng/g OC, respectively). We compared 2,3,7,8-TCDD concentrations from the present study to those found during the Contaminant Assessment and Reduction Project (CARP), which measured 2,3,7,8-TCDD sediment concentrations in the AK in the late 1990s/early 2000s (CARP, 2007). Concentrations of 2,3,7,8-TCDD there ranged from 0.02 to 0.08 ng/g, similar to AK dry weight concentrations determined in the present study (0.020 \pm 0.004 ng/g).

3.2. Tissue

The mean lipid content of deposit feeders was 0.07 g/g dry weight, while that of filter feeders was 0.04 g/g. Lipid-normalized tissue concentrations shown are from deposit-feeding tube worms (Pectorina gouldii) in the AK and filter-feeding clams (Mya arenaria) in the Passaic, Hackensack, MB, and KVK (Fig. S3). Tube worms from the AK had detectable concentrations of a full suite of mono- through octa-CDD/Fs (from 2.6 to 49 ng/g lipid), whereas filter-feeding clams had no detectable levels of high MW PCDD/Fs (i.e., hexa- through octa-CDD/Fs). The difference in high MW uptake by tissues is probably a reflection of feeding mode differences, given that sediments from all sites had fairly high concentrations of hept- and octa-CDD/Fs. A difference in uptake among organisms with feeding modes has been observed previously, with deposit-feeders receiving the majority of their HOC burden through sediment ingestion and filter-feeders receiving roughly equal amounts from sediment ingestion and water filtration (McLeod et al., 2008).

Low MW congener tissue concentrations were similar across sites and different feeding modes, except for clams in the Passaic and Hackensack, wherein only one congener (12,3,7,8-4PeCDF) was detected, primarily due to low biota masses collected at these sites. The only tissue sample in which 2,3,7,8-TCDD was detected was AK tube worms (3.2 ng/g lipid), with concentrations similar to those found in ribbed mussels (Modiolis demissus) from the Passaic and Newark Bay during the CARP study (1.2–3.5 ng/g lipid and 0.62–1.4 ng/g lipid, respectively) (CARP, 2007).

3.3. Deep water and porewater

Dissolved PCDD/Fs detected in deep water ranged from 3.9 fg/L (2,3,7,8-TCDD) to 1.3 \times 10^4 fg/L (2,7,2,8-4DiCDD) and from 0.6 (2,3,7,8-TCDD) to 1.7 \times 10^4 fg/L (2,7,2,8-4DiCDD) in porewater. Fractions of equilibrium reached for each analyte (fEQ) (except for OCDD in the AK) or in deep water. The lack of high-MW congeners in sediments, deep water, and BC, porewater PE, and deep water PE. We compared these concentrations to those measured directly in Newark Bay biota (Fig. 2), but only for stations where more than one congener was detected in tissues (the AK, the KVK, and the MB). The comparison discussion is only for congeners detected in sediments, deep water, porewater, and tissues concurrently at a given site (i.e., congeners with only 2 or 3 chlorines).

In the AK, where only deposit-feeders were collected, tissue concentrations calculated from OC-water partitioning (Clip,OC) overestimated Clip by 7 \times on average, while those from OC + BC-water partitioning (Clip,OC+BC) underestimated Clip (by 4 \times on average) (Fig. 2a). Concentrations calculated from porewater and deep water PE both underestimated Clip, but not by as much as Clip,OC+BC. Tissue concentrations calculated from porewater PE (Clip,PE) underestimated Clip by 1.6 \times on average, while those calculated from deep water PE (Clip,PE,SW) underestimated Clip by 2.8 \times. Results for the AK suggest porewater PE were the best predictors of deposit-feeding tissue concentrations.

In both the KVK and MB, where only filter-feeders were collected, Clip,OC again overestimated Clip by 3.8 \times on average, while Clip,OC+BC again underestimated Clip by 13 \times on average (Fig. 2b and c). As with AK deposit feeders, concentrations calculated from porewater and deep water PE underestimated Clip, but not by as much as Clip,OC+BC (by 3.1 \times and 3.8 \times, respectively). Results for the KVK and MB also suggest porewater PE was the best predictor of filter-feeding tissue PCDD/F concentrations, and that in general PE samplers are better at estimating biota concentrations than traditional sediment equilibrium partitioning methods.

Several high-MW congeners were detected in the sediments of all three sites, but in tissues were only detected in deposit-feeders from the AK. High-MW PCDD/Fs were not detected in porewater (except for OCDD in the AK) or in deep water. The lack of high-MW
PCDD/F uptake in filter-feeders suggests porewater/deep water filtration are more important than particle ingestion, as might be expected from previous studies (Lohmann et al., 2004; McLeod et al., 2008).

The use of literature $K_{BC}$ (Lambert, 2010), determined with sediment from an adjacent field site but at deeper depths, resulted in vast under-predictions of bioaccumulation for PCDD/Fs due to underestimation of dissolved concentrations. This observation is consistent with previous studies showing that the utility of $K_{BC}$ is sediment-specific (Arp et al., 2009; Hawthorne et al., 2007b), and further shows that even sediments from nearby locations but deeper depths, where BC is likely older and qualitatively different, can exhibit substantially different HOC-binding characteristics. Werner et al. (2010) suggested that PCB sorption to BC at low concentrations is linear (i.e., $n = 1$ in eq. (5)), but we find that lipid concentrations are instead overestimated when linear sorption is assumed (e.g., using Lambert et al.’s $K_{BC}$ values with $n = 1$ in eq. (5)) results in $C_{lip}$ overestimates of $3.8 \times$). Thus, in the present study, we

Fig. 2. Ratios of estimated versus measured lipid-normalized polychlorinated dibenzo-p-dioxin and dibenzofuran (PCDD/F) biota concentrations. Biota concentrations were estimated based on PCDD/F partitioning between biota and sediment organic carbon (OC), sediment OC and black carbon (BC), polyethylene (PE) in porewater, and PE in deep water in a) Arthur Kill (tube worms), b) Kill van Kull (clams), and c) mid-Bay (clams). Also shown are ratios of biota concentrations estimated from sediment OC and BC calculated using sediment-specific black carbon – water partition coefficients ($K_{BC}$) to those directly measured.
derived sediment and depth-specific $K_{OC}$ from mean measured sediment concentrations and dissolved porewater concentrations across sites. We then used these sediment-specific $K_{OC}$ to estimate $C_{lip}$ at individual sites, as above. Field $K_{OC}$ were determined only for congeners detected in both porewater PE and sediments at three or more sites (i.e., 2,7/2,8-DiCDD, 2,4,8-TriCDF, and 2,3,7-TriCDD), and were calculated for Freundlich coefficients of $n = 0.6, 0.7, and 0.8$ (Table 1). All sediment-specific $K_{OC}$ were lower in value than those of Lambert, in some instances by more than an order of magnitude (e.g., 2,3,7-TriCDD). Sediment-specific $K_{OC}$ improved $C_{lip,OC}$ estimates of $C_{lip}$ by 2–87 fold. For example, in the AK, $C_{lip,OC}$ determined using sediment-specific $K_{OC}$ was a factor of 1.1 higher than $C_{lip}$ (compared to 1.6× lower for porewater PE), and in the KVK and MB, $C_{lip,OC}$ determined using sediment-specific $K_{OC}$ was, on average, 4× lower than $C_{lip}$ (compared to 3.1× lower for porewater PE).

Though $C_{lip,OC}$ from sediment-specific $K_{OC}$ and $C_{lip,PEpw}$ were both good predictors of $C_{lip}$, each estimator contains uncertainties related to partition coefficients; namely, $K_{PE}$-ws, BAFs, and in the case of $C_{lip,OC}$, $K_{OC}$. We assumed that $K_{PE}$ and $K_{OC}$ values had relative uncertainties of 100%, given that both were calculated from $K_{OW}$, and $K_{OW,s}$ of these congeners are reported to have a high-end uncertainty of 100% (Aberg et al., 2008). We assigned a 100% relative uncertainty to the conversion of dissolved concentrations to lipid-based from BAFs. Considering these assumptions combined, $C_{lip,OC}$ uncertainties are 200% while $C_{lip,PEpw}$ uncertainties are 140%; these are in addition to analytical uncertainties (see the SI for uncertainty calculations). Thus, although $C_{lip,OC}$ and $C_{lip,PEpw}$ are roughly equally good predictors of $C_{lip}$, we note that the lower relative uncertainty in $C_{lip,PEpw}$ and their more straightforward determination make them a more practical and reliable option for obtaining site-specific estimates of $C_{lip}$.

### 3.5. Implications for use of PE to predict biota uptake in the field

In the present study, we predicted PCDD/F lipid concentrations in deposit feeders within an average factor of 1.6 (range 1.1–3.8) using porewater PEs and BAFs. In a previous study comparing PCB uptake by *Nereis virens* to uptake in PE in the laboratory (Friedman et al., 2009), we estimated PCB uptake within an average factor of 0.99 (range 0.06–3.0) using porewater PE and BAFs. Collectively, this is evidence that PE samplers used to measure porewater can provide consistently more reliable estimates of $C_{lip}$ for deposit feeders in both the laboratory and the field compared to the range of estimates observed from sediment equilibrium partitioning.

In the present study, however, there were a number of PCDD/Fs found in tissue but not porewater, particularly high MW congeners in AK deposit feeders, suggesting these congeners are not taken up by diffusion from porewater. If $C_{lip,PEpw}$ is plotted against $K_{OW,PCDD/F}$ for congeners detected in both phases for AK tube worms, a slight decreasing trend in the ratio is observed with increasing $K_{OW}$, though the relationship is not statistically significant at $\alpha = 0.05$ (Fig. 3). Also included in this plot are results from our previous study with PCBs (Friedman et al., 2009), which display similar behavior, but with a steeper decreasing trend that is statistically significant ($p < 0.001$). If the two datasets are combined, the overall decrease with $K_{OW}$ is significant ($p = 0.01$), and implies that biota take up greater concentrations of high MW HOCs than dictated by the chemical activity of their surroundings (i.e., porewater), most likely via ingestion. The magnitude of negative slope tends to taper off at higher $K_{OW}$, suggesting that at a given hydrophobicity, ingestion of particle-associated HOCs outweighs
partitioning from porewater in governing biota uptake. From the combined data in Fig. 3, this switch from porewater control to ingestion dominance appears to happen between log $K_{OC}$ and 7. Similar results have been found in other studies, though the switch may take place at lower $K_{OC}$ in different systems (e.g., at log $K_{OC}$ of 5.8 for uptake of PCBs in freshwater oligochaetes (Sun et al., 2009)). Benthic organisms, particularly deposit feeders, can have high levels of surfactants in the gut (Mayer et al., 1997); this may contribute to higher levels of high MW PCDD/Fs in tissue compared to PE. Additionally, though measures were taken to remove particles from tissue extracts, it is possible that some remained, which might contribute to greater levels of high MW PCDD/Fs in tissues. Our porewater concentration results suggest that up to 62% of deposit feeder tissue concentrations can be attributed to equilibrium with porewater. Others, using a biodynamic model (McLeod et al., 2008, 2007) have estimated that deposit-feeding clams receive even less than 10% of their HOC body burden from porewater, and showed that HOC body burdens in these organisms more closely resemble congener profiles in sediment, rather than porewater. Hence, we emphasize that while PE can be more useful than sediment geochemistry in predicting correlated biota concentrations, their use does not imply that all HOCs are taken up through diffusive water-biota partitioning. Passive samplers may be less useful in predicting tissue concentrations of the more hydrophobic HOCs limited by diffusive kinetics in deposit feeders.

We also note that only two species of biota were collected, providing a limited range of biodiversity for both feeding modes. These two species represent the majority of the diversity observed during sampling. However, the limited range is likely due to frequent navigational dredging and sustained industrial traffic within Newark Bay, in addition to sediment contamination. Thus, results may deviate for other species, and further studies would help determine whether relationships presented here can be generalized.

4. Conclusion

PE samplers provide more accurate estimates of biota concentrations of PCDD/Fs in the Newark Bay field than traditional sediment equilibrium partitioning methods. The traditional $K_{OC}$ partitioning model consistently overestimated biota PCDD/F uptake, by a factor of 4–7 times. In contrast, estimates based on $K_{OC}$ and $K_{BC}$ together consistently underestimated biota PCDD/F uptake, by a factor of 4–13 times, even though $K_{BC}$ initially employed were determined with sediment from an adjacent location. When we used porewater concentrations to derive sediment- and depth-specific $K_{BC}$s, we improved predictions of biota PCDD/F uptake estimates. Given the additional laboratory time and uncertainty involved in determining sediment-specific $K_{BC}$s, we recommend taking direct measurements of porewater concentrations using passive samplers, such as PE and eliminating sediment measurements altogether as a more practical, efficient approach for site-specific determinations. Careful attention needs to be paid to equilibrium conditions and the fact that kinetically-limited HOCs are susceptible to being underestimated, though. There is little diffusive exchange of low MW PCDD/Fs between the porewater and water column in Newark Bay, while there is more uncertainty surrounding the exchange of high MW PCDD/Fs. Equilibrium across the sediment–water interface for low MW congeners is consistent with PCDD/F body burdens observed in filter feeders.

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Appendix A. Supporting information

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2013.12.002.

References


