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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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ABSTRACT

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. Biota concentrations based on sediment were estimated using an organic carbon (OC)-water partitioning model and an OC and black carbon (BC)-water dual model. Biota 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 3.1x), with best results achieved for deposit-feeders (within 1.6x). Polyethylene deployed in deep water also provided good estimates of biota concentrations (within 4x). By contrast, OC-water partitioning overestimated biota concentrations by up to 7x, while OC and BC combined underestimated biota concentrations by up to 13x. We recommend polyethylene for estimating concentrations of hydrophobic organic contaminants in field biota given its simplicity and relatively lower uncertainty compared to sediment equilibrium partitioning.

Capsule: Using polyethylene samplers to measure porewater concentrations is a more efficient approach for estimating site-specific bioavailable organic contaminants than equilibrium partitioning.

Key Words: polyethylene, equilibrium partitioning, PCDD, Newark

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 m^3 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; Hawthorne et al., 2006, 2007b; 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; Hawthorne

et al., 2007b). 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.

MATERIALS AND METHODS

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 km^2, 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**).

Sediment and biota collection

Sediment and biota were collected from the R/V Kenneth Biglane using a van Veen grab. From 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 hours 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.

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 submersing 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 d_{10}-anthracene, d_{12}-benz[a]anthracene, and octachloronapthalene (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

137 removed from the PRC solution and wiped dry with laboratory-grade tissues. A small snippet
138 (~0.1 g) was cut from each sampler for initial PRC analysis ($C_{PRC,t=0}$). For field deployments, the
139 remainder of the sampler was strung on pre-cleaned stainless steel wire (Malin Co.), wrapped in
140 aluminum foil, and both snippet and sampler were stored at -4°C until deployment or analysis.
141
142 *PE-porewater tumbling experiments*
143 Three different sized samplers were cut from PRC-impregnated PE (~0.25, 0.50, and 0.75
144 g) for each sampling location. This was done to assess whether PEs had reached equilibrium with
145 porewater during tumbling, and sizes were chosen such that PCDD/Fs were not depleted from
146 the sediment-porewater system (calculation in the SI). Samplers were added to 125 mL muffled
147 round bottom flasks with 50-60 g wet sediment. Ten mL of 1 mg/mL sodium azide was added to
148 each flask to limit bacterial growth, and flasks were filled to air-tight level with Milli-Q water.
149 PEs were left to tumble with sediments in the dark on a shaker table at room temperature (24°C)
150 for eight weeks, sufficient for PCDD/Fs to reach equilibrium as per previous work in our group
151 (Lambert et al., 2011).
152
153 *Deep water PE-field deployments*
154 Three replicate PE samplers were deployed from June 16 to July 6, 2009 at the same sites
155 as sediment and tissue collection (**Fig. 1**). Samplers were deployed at the bottom of the water
156 column using cement cinder blocks attached to a line and buoy, and PE were placed ~30 cm
157 above the sediment bed. After every 10 deployments, a clean PE sampler was exposed to
158 ambient air momentarily and collected as a field blank. After collection, all PEs were wrapped in

159 clean aluminum foil, stored on ice, and returned to the laboratory. Samplers were deployed and
160 collected from the R/V Kenneth Biglane.
161
162 *Adjustments to concentrations*
163 To adjust field-deployed deep water PE concentrations for disequilibrium, linear
164 relationships were determined between PRC fraction equilibrium reached (f_{EQ}) and PRC
165 molecular weight (MW) for each set of PEs undergoing the same sampling scheme (i.e.,
166 replicates deployed at the same site or in the same tumbling experiment):

167 $$f_{EQ} = m(MW) + b \quad (1)$$

168 where m is the slope, b is the intercept and f_{EQ} is determined as:

169 $$f_{EQ} = 1 - \frac{C_{PRC,t}}{C_{PRC,t=0}} \quad (2)$$

170 where $C_{PRC,t}$ is the concentration of a PRC in PE at time t. The mean p-value for statistical
171 correlation between MW and f_{EQ} was 0.04. The linear relationships were then used with PCDD/F
172 MW to estimate each analyte's equilibrium status, and C_{PEdw}s were adjusted as follows:

173 $$C_{PEdw,\infty} = \frac{C_{PEdw}}{f_{EQ}} \quad (3)$$

174 where $C_{PEdw,\infty}$ is the concentration in deep water PE adjusted to 100% equilibrium. Using this
175 method, PCDD/Fs in deep water PE had reached between 73% and 98% equilibrium. No
176 concentration adjustments were made to PEs tumbled with sediment, as equilibrium was
177 determined by comparing concentrations in different sized samplers.
178
179 *Calculation of HOC activity gradients*

Activity gradients are defined as the equilibrium concentration in the deep water PE ($C_{PEdw,\infty}$) divided by the equilibrium concentration in the porewater PE ($C_{PEpw,\infty}$) for the same compound at a given sampling site. To derive activity gradients at sites where a compound was detected in only one PE of the pair, one-half of the analytical detection limit was substituted for zero to calculate a ratio. Uncertainties introduced by this substitution are discussed in the Results.

Estimating biota HOC uptake

Lipid concentrations (ng/g) were estimated from each sorbent phase (OC, OC+BC, porewater PE, and deep water PE) and compared to those measured in tissues (C_{lip}). Lipid concentrations were estimated from sediment OC partitioning ($C_{lip,OC}$) as the product of dissolved concentrations (ng/mL) and the bioaccumulation factor (BAF; unitless) as follows:

$$C_{lip,OC} = C_{diss,OC} BAF = \frac{C_{sed} BAF}{f_{OC} K_{OC}} \quad (4)$$

where C_{sed} is the HOC concentration in the sediment (ng/g), f_{OC} is the fraction of OC in the sediment, and K_{OC} is the OC–water partition coefficient (mL water/g OC). K_{OC}s for PCDD/Fs were derived from the literature (Xia, 1998), while PCDD/F BAFs were estimated from PCDD/F octanol-water partition coefficients (K_{OW}s), using a regression determined with PAH data at 5-24°C (Muijs and Jonker, 2009). Uncertainties associated with the BAF estimation are discussed later.

Similarly, lipid concentrations based on sediment OC and BC ($C_{diss,OC+BC}$) were estimated as the product of the BAF and dissolved concentrations (Accardi-Dey and Gschwend, 2002) using a Freundlich coefficient of n = 0.7:

$$C_{lip,OC+BC} = C_{diss,OC+BC} BAF = \frac{C_{sed} BAF}{f_{OC} K_{OC} + f_{BC} K_{BC} C_{diss}^{n-1}} \quad (5)$$

where f_{BC} is the fraction of BC in the sediment and K_{BC} is the BC–water partition coefficient (mL water/g BC). Both literature and sediment-specific values of K_{BC} were used to calculate $C_{diss,OC+BC}$. Literature PCDD/F K_{BC}s 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 K_{BC}s were derived from porewater dissolved PCDD/F concentrations calculated from PE samplers in the present study using equation 5 (with n=0.6, 0.7, and 0.8).

Lastly, lipid concentrations from porewater ($C_{lip,PEpw}$) and deep water ($C_{lip,PEdw}$) were estimated from PE uptake as follows:

$$C_{lip,PE} = C_{diss,PE} BAF = \frac{C_{PE,\infty} BAF}{K_{PE-w}} \quad (6)$$

where $K_{PE\text{-}w}$ is the PE-water partition coefficient (mL water/g PE) estimated from K_{OW} (Adams et al., 2007). Values of K_{OW} were taken from Aberg et al. (2008). $K_{PE\text{-}w}$s, 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.

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 %C 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 Gschwend, 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), just within the range (0.6 – 19.7) 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.

RESULTS AND DISCUSSION

Sediment

Sediment OC ranged from 1.6 to 5.8% and sediment BC ranged from 0.2 to 0.3% (**Table S2**), comparable to previous results for OC and BC of 2.6% and 0.3% in New York Harbor (Lohmann et al., 2005). Sediment concentrations ranged from 0.1 (1,2,3,4,7,8-HxCDF in the AK) to 76 ng/g OC (OCDD in the AK), or 0.005 to 2.4 ng/g dry (**Figs. S1** and **S2**). At all sites, OCDD was present in the greatest concentrations followed by 2,7/2,8-DiCDD. Several of the mid-MW congeners (2,3,7,8-TCDF, 1,2,3,7,8-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 ± 0.8 ng/g OC and 2.1 ± 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 ± 0.004 ng/g).

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 hepta- 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 (1,2,3,7,8-PeCDF) 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).

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-DiCDD) and from 0.6 (2,3,7,8-TCDD) to 1.7 $\times 10^4$ fg/L (2,7/2,8-DiCDD) in porewater. Fractions of equilibrium reached for each analyte (f_{EQ}s), used for calculating corresponding dissolved concentrations, are reported in **Table S3**, while PCDD/F concentrations determined in the three different sizes of porewater PE are reported in **Table S4**. We divided PCDD/F concentrations in PE deployed in the water column by those of PE samplers tumbled with sediments in the laboratory to obtain deep water – porewater activity gradients (**Fig. S4**).

277 At all sites, low MW PCDD/Fs (mono- through tetra-CDD/Fs) exhibited activity gradients of
278 approximately one (mean of 2.10) that varied in direction (range of 0.45 to 12.6), implying that,
279 on average, there was little net flux between Newark Bay porewater and deep water for low MW
280 PCDD/Fs, similar to PCDD/F fluxes at other locations (Cornelissen et al., 2008). At sampling
281 stations where high MW PCDD/Fs (penta- through octa-CDD/Fs) were detected, activity
282 gradients were primarily in the direction of the deep water (mean of 0.35, range of 0.04 to 1.15),
283 indicating porewater is a potential source of these compounds to the overlying water column.
284 The only PCDD/F that had an activity gradient in the direction of the porewater at all stations
285 was 2,7/2,8-DiCDD. As discussed elsewhere (Friedman et al., 2012), this is possibly due to on-
286 going formation of 2,7/2,8-DiCDD from triclosan within Newark Bay. Overall, activity gradients
287 suggested low MW PCDD/Fs were well mixed between the porewater and water column,
288 whereas high MW PCDD/Fs were still potentially being released to the water column. These
289 results are consistent with only low MW congeners being taken up in filter feeders living at the
290 sediment-water interface, and the presence of high MW congeners in deposit feeders living
291 within the sediment.
292
293 Activity gradients should be interpreted in the context of uncertainties related to the
294 substitution of ½ the analytical detection limit for non-detects and adjustments to deep water
295 concentrations based on PRCs, however. We assumed the following relative uncertainties: 100%
296 for PE concentrations with non-detects replaced; $1\text{-}f_{EQ}$ for the equilibrium correction for each
297 deep water PE sampler (Friedman et al., 2012); relative standard deviation of PCDD/F
298 concentration in porewater PEs (**Table S4**). Resulting uncertainties were between 11% and
299 200% for the activity gradients (mean of 88%; see the SI for uncertainty calculations). This is in

addition to analytical uncertainty (shown in error bars in **Fig. S4**). The high end of this uncertainty range generally only applies to gradients with non-detects replaced, identified with asterisks in **Fig. S4**, or high MW congeners (2,3,7,8-TCDD through OCDD). The lower average gradient uncertainty of 48% for low MW congeners supports our assertion that low MW PCDD/Fs are well-mixed within the Bay, but the greater uncertainties for higher MW PCDD/Fs make it difficult to draw conclusions regarding the direction and magnitudes of their gradients.

Estimating biota PCDD/F uptake and sediment-specific K_{BC}s

To assess where native tissues received the majority of their PCDD/F exposures, we calculated lipid-based tissue concentrations of PCDD/Fs based on partitioning from sediment OC, sediment OC 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 ($C_{lip,OC}$) overestimated C_{lip} (by 7× on average), while those from OC+BC-water partitioning ($C_{lip,OC+BC}$) underestimated C_{lip} (by 4x on average) (**Fig. 2a**). Concentrations calculated from porewater and deep water PE both underestimated C_{lip}, but not by as much as $C_{lip,OC+BC}$. Tissue concentrations calculated from porewater PE ($C_{lip,PEpw}$) were underestimated C_{lip} by 1.6x on average, while those calculated from deep water PE ($C_{lip,PEdw}$)

322 underestimated C_{lip} by 2.8x. Results for the AK suggest porewater PE were the best predictors of
323 deposit-feeding tissue concentrations.
324
325 In both the KVK and MB, where only filter-feeders were collected, $C_{lip,OC}$ again
326 overestimated C_{lip} (by 3.8x on average), while $C_{lip,OC+BC}$ again underestimated C_{lip} (by 13x on
327 average) (**Figs. 2b and 2c**). As with AK deposit feeders, concentrations calculated from
328 porewater and deep water PE underestimated C_{lip}, but not by as much as $C_{lip,OC+BC}$ (by 3.1x and
329 3.8x, respectively). Results for the KVK and MB also suggest porewater PE was the best
330 predictor of filter-feeding tissue PCDD/F concentrations, and that in general PE samplers are
331 better at estimating biota concentrations than traditional sediment equilibrium partitioning
332 methods.
333
334 Several high-MW congeners were detected in the sediments of all three sites, but in
335 tissues were only detected in deposit-feeders from the AK. High-MW PCDD/Fs were not
336 detected in porewater (except for OCDD in the AK) or in deep water. The lack of high-MW
337 PCDD/F uptake in filter-feeders suggests porewater/deep water filtration are more important
338 than particle ingestion, as might be expected from previous studies (Lohmann et al., 2004;
339 McLeod et al., 2008).
340
341 The use of literature K_{BC}s (Lambert, 2010), determined with sediment from an adjacent
342 field site but at deeper depths, resulted in vast under-predictions of bioaccumulation for
343 PCDD/Fs due to underestimation of dissolved concentrations. This observation is consistent with
344 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 3.8x). Thus, in the present study, we derived sediment and depth-specific K_{BC}s from mean measured sediment concentrations and dissolved porewater concentrations across sites. We then used these sediment-specific K_{BC}s to estimate C_{lip} at individual sites, as above. Field K_{BC}s 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_{BC}s 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_{BC}s improved $C_{lip,OC+BC}$ estimates of C_{lip} by 2 – 87 fold. For example, in the AK, $C_{lip,OC+BC}$ determined using sediment-specific K_{BC}s was a factor of 1.1 higher than C_{lip} (compared to 1.6x lower for porewater PE), and in the KVK and MB, $C_{lip,OC+BC}$ determined using sediment-specific K_{BC}s was, on average, 4x lower than C_{lip} (compared to 3.1x lower for porewater PE).

Though $C_{lip,OC+BC}$ from sediment-specific K_{BC}s and $C_{lip,PEpw}$ were both good predictors of C_{lip}, each estimator contains uncertainties related to partition coefficients; namely, K_{PE-w}s, BAFs, and in the case of $C_{lip,OC+BC}$, K_{OC}s. We assumed that K_{PE-w} 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, $C_{lip,OC+BC}$ 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 $C_{lip,OC+BC}$ and $C_{lip,PEpw}$ are roughly equally good predictors of C_{lip}, we note that the lower relative uncertainty in $C_{lip,PEpw}$s and their more straightforward determination make them a more practical and reliable option for obtaining site-specific estimates of C_{lip}.

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, while 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 $C_{lip,PEpw}/C_{lip}$ is plotted against log K_{OW} for PCDD/F 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

391 α=0.05 (**Fig. 3**). Also included in this plot are results from our previous study with PCBs
392 (Friedman et al., 2009), which display similar behavior, but with a steeper decreasing trend that
393 is statistically significant ($p<0.001$). If the two datasets are combined, the overall decrease with
394 K_{OW} is significant ($p=0.01$), and implies that biota take up greater concentrations of high MW
395 HOCs than dictated by the chemical activity of their surroundings (i.e., porewater), most likely
396 via ingestion. The magnitude of negative slope tends to taper off at higher K_{OW}s, suggesting that
397 at a given hydrophobicity, ingestion of particle-associated HOCs outweighs partitioning from
398 porewater in governing biota uptake. From the combined data in **Fig. 3**, this switch from
399 porewater control to ingestion dominance appears to happen between log K_{OW} 6 and 7. Similar
400 results have been found in other studies, though the switch may take place at lower K_{OW}s in
401 different systems (e.g., at log K_{OW} of 5.8 for uptake of PCBs in freshwater oligochaetes (Sun et
402 al., 2009)). Benthic organisms, particularly deposit feeders, can have high levels of surfactants in
403 the gut (Mayer et al., 1997); this may contribute to higher levels of high MW PCDD/Fs in tissue
404 compared to PE. Additionally, though measures were taken to remove particles from tissue
405 extracts, it is possible that some remained, which might contribute to higher levels of high MW
406 PCDD/Fs in tissues.
407
408 Our porewater concentration results suggest that up to 62% of deposit feeder tissue
409 concentrations can be attributed to equilibrium with porewater. Others using a biodynamic model
410 (McLeod et al., 2008; McLeod, 2007) have estimated that deposit-feeding clams receive even
411 less (~10%) of their HOC body burden from porewater, and showed that HOC body burdens in
412 these organisms more closely resemble congener profiles in sediment, rather than porewater.
413 Hence, we emphasize that while PE can be more useful than sediment geochemistry in predicting

414 correlated biota concentrations, their use does not imply that all HOCs are taken up through
415 diffusive water-biota partitioning. Passive samplers may be less useful in predicting tissue
416 concentrations of the more hydrophobic HOCs limited by diffusive kinetics in deposit feeders.
417
418 We also note that only two species of biota were collected, providing a limited range of
419 biodiversity for both feeding modes. These two species represent the majority of the diversity
420 observed during sampling, however. The limited range is likely due to frequent navigational
421 dredging and sustained industrial traffic within Newark Bay, in addition to sediment
422 contamination. Thus, results may deviate for other species, and further studies would help
423 determine whether relationships presented here can be generalized.
424
425 *Conclusion*
426 PE samplers provide more accurate estimates of biota concentrations of PCDD/Fs in the
427 Newark Bay field than traditional sediment equilibrium partitioning methods. The traditional
428 K_{OC} partitioning model consistently overestimated biota PCDD/F uptake, by a factor of 4-7
429 times. In contrast, estimates based on K_{OC} and K_{BC} together consistently underestimated biota
430 PCDD/F uptake, by a factor of 4-13 times, even though K_{BC}s initially employed were determined
431 with sediment from an adjacent location. When we used porewater concentrations to find
432 sediment- and depth-specific K_{BC}s, we improved predictions of biota PCDD/F uptake estimates.
433 Given the additional laboratory time and uncertainty involved in determining sediment-specific
434 K_{BC}s, however, we recommend taking direct measurements of porewater concentrations using
435 PE and eliminating sediment measurements altogether as a more practical, efficient approach for
436 site-specific determinations. Careful attention needs to paid to equilibrium conditions and the

437 fact that kinetically-limited HOCs are susceptible to underestimates, though. There is little
438 diffusive exchange of low MW PCDD/Fs between the porewater and water column in Newark
439 Bay, while there is more uncertainty surrounding the exchange of high MW PCDD/Fs.
440 Equilibrium across the sediment-water interface for low MW congeners is consistent with
441 PCDD/F body burdens observed in filter feeders.
442
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451
452 *Supplementary Information*
453 The supporting information includes tables and figures relating to sediment organic and
454 black carbon content, sediment and PE PCDD/F concentrations, and porewater-deep water
455 PCDD/F gradients, as well as details regarding methods.

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592 **TABLES**

593 **Table 1.** Mean sediment-specific polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F)
594 log black carbon – water partition coefficients (log K_{BC}s) for all of Newark Bay.

PCDD/F	log K_{OW}	log K_{OC}	Field-derived log K_{BC}			Lambert [21] log K_{BC}
			n = 0.6	n = 0.7	n = 0.8	n = 0.7
2,7/2,8-DiCDD	5.59	5.30	5.18 ± 0.34	5.68 ± 0.34	6.19 ± 0.33	6.38
2,4,8-TriCDF	5.74	5.45	5.13 ± 0.32	5.73 ± 0.30	6.34 ± 0.32	5.89
2,3,7-TriCDD	6.09	5.79	4.90 ± 0.12	5.59 ± 0.08	6.28 ± 0.05	6.87

595

596 **FIGURES**

597 **Figure 1.** Newark Bay, surrounding water bodies, sampling locations (white circles), and the
598 Diamond Alkali Superfund site.

599

600 **Figure 2.** Ratios of estimated versus measured lipid-normalized polychlorinated dibenzo-*p*-
601 dioxin and dibenzofuran (PCDD/F) biota concentrations. Biota concentrations were estimated
602 based on PCDD/F partitioning between biota and sediment organic carbon (OC), sediment OC
603 and black carbon (BC), polyethylene (PE) in porewater, and PE in deep water in **a)** Arthur Kill
604 (tube worms), **b)** Kill van Kull (clams), and **c)** mid-Bay (clams). Also shown are ratios of biota
605 concentrations estimated from sediment OC and BC calculated using sediment-specific black
606 carbon – water partition coefficients (K_{BC}s) to those directly measured.

607

608 **Figure 3.** Ratio of lipid-based biota concentrations estimated from porewater PE to those
609 measured directly in deposit-feeders collected from the Arthur Kill in the current study
610 (PCDD/Fs) or from a laboratory bioaccumulation test in a previous study (PCBs) versus log
611 K_{OW}. The linear best fit for the PCDD/F dataset is y = -0.0064x + 0.56, but the regression is not
612 significant (p=0.96). The linear best fit for the PCB data is y = -1.4x + 10 with a regression

613 significance of $p<0.001$. The linear best fit for the entire dataset is $y = -0.57x + 4.4$ with an r^2 of

614 0.31 with a regression significance of $p=0.01$.