

2013

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

Carey L. Friedman

Rainer Lohmann

University of Rhode Island, rlohmann@uri.edu

Follow this and additional works at: <https://digitalcommons.uri.edu/gsofacpubs>

**The University of Rhode Island Faculty have made this article openly available.
Please let us know how Open Access to this research benefits you.**

This is a pre-publication author manuscript of the final, published article.

Terms of Use

This article is made available under the terms and conditions applicable towards Open Access Policy Articles, as set forth in our [Terms of Use](#).

Citation/Publisher Attribution

Friedman, C. L., & Lohmann, R. (2014). Comparing sediment equilibrium partitioning and passive sampling techniques to estimate benthic biota PCDD/F concentrations in Newark Bay, New Jersey (U.S.A.). *Environmental Pollution*, 186, 172-179. doi: 10.1016/j.envpol.2013.12.002

Available at: <https://doi.org/10.1016/j.envpol.2013.12.002>

This Article is brought to you for free and open access by the Graduate School of Oceanography at DigitalCommons@URI. It has been accepted for inclusion in Graduate School of Oceanography Faculty Publications by an authorized administrator of DigitalCommons@URI. For more information, please contact digitalcommons@etal.uri.edu.

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

3

4 Carey L. Friedman^{a1*} and Rainer Lohmann^a

5

6 ^aUniversity of Rhode Island Graduate School of Oceanography (URI-GSO), University of Rhode
7 Island Bay Campus, 215 South Ferry Road, Narragansett, RI 02882 USA

8 Telephone: 401-874-6612

9 Fax: 401-874-6811

10 *Corresponding author (clf@mit.edu)

11

¹C.L. Friedman's current address is Center for Global Change Science, MIT E19-411n, 77 Massachusetts Ave. Cambridge, MA, USA 02139.

12 **ABSTRACT**

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

26

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

30

31 **Key Words:** polyethylene, equilibrium partitioning, PCDD, Newark

32

33 INTRODUCTION

34 Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are toxic hydrophobic
35 organic contaminants (HOCs) that sorb to particles in sediments (Luthy et al., 1997).

36 Sedimentary HOCs can be bioavailable to benthic marine organisms and accumulate up the
37 marine food chain (DeWit et al., 1995; Pickard and Clarke, 2008). The risk of aquatic organism
38 exposure to HOCs is a primary consideration when choosing an approach to clean-up HOC-
39 contaminated sites. One such site is the lower Passaic River/Newark Bay in New Jersey (USA).

40 The lower Passaic is the location of the former Diamond Alkali pesticide manufacturing
41 company, which discharged waste to adjacent waters during the 1950s/60s, severely

42 contaminating sediments with PCDD/Fs. In 1984, the sediment site was added to the U.S. EPA

43 Superfund list and is currently undergoing a two-phase clean-up process that will include

44 removal of 153,000 m³ of sediment via dredging (US EPA). Newark Bay, one of the most

45 industrialized estuaries in the United States, extends just south of the Passaic (**Fig. 1**) and is

46 known to be impacted by PCDD/Fs from the Passaic (Rappe et al., 1991). Though there have

47 been efforts to characterize contaminant dynamics in the Passaic River and Newark Bay, passive

48 sampling, a promising state-of-the-art method for determining dissolved HOC concentrations

49 (Choi et al., 2013; Fernandez et al., 2009), has not been employed. In this study, we compare

50 passive sampling-based estimates of PCDD/F concentrations in sediment-dwelling biota, and

51 conventional equilibrium partitioning-based estimates using sediment geochemical

52 characteristics (i.e., organic and black carbon, OC and BC) to PCDD/F concentrations measured

53 in biota collected from Newark Bay.

54 Passive samplers of various types have been used as tools to directly sample porewater

55 dissolved HOCs, or as surrogates for bioaccumulation organisms (Adams et al., 2007; Huckins et

56 al., 1990; Lohmann et al., 2004; Mayer et al., 2000; Schneider et al., 2006; Vinturella et al.,
57 2004). Passive samplers circumvent problems associated with traditional solvent-based
58 porewater extractions by sampling freely dissolved HOCs via diffusive uptake into the sampler
59 matrix and thus avoiding the need to isolate interstitial water and having to address related
60 artifacts. In a previous study by our group, a laboratory bioaccumulation study with field-
61 contaminated sediment demonstrated that polyethylene (PE) passive samplers can estimate freely
62 dissolved PCB concentrations organisms are exposed to within a factor of four (Friedman et al.,
63 2009). Others have similarly shown that PE can be useful for predicting uptake of PAHs in
64 benthic biota in the laboratory (Vinturella et al., 2004). PE and other samplers have also been
65 useful in determining the direction of HOC fluxes between environmental compartments; for
66 example, from the water column to the atmosphere (Morgan and Lohmann, 2008) or from
67 porewater to the overlying water column (Cornelissen et al., 2008). Only a limited number of
68 studies have demonstrated the utility of PE in predicting HOC body burdens of organisms in the
69 field, however (Cho et al., 2009).

70 In contrast, a number of studies have discussed and used equilibrium partitioning from
71 sediment OC, and several from OC and BC combined, to predict freely dissolved HOC
72 concentrations and, by extension, bioavailability (Accardi-Dey and Gschwend, 2002, 2003;
73 Burgess et al., 2013; DiToro et al., 1991; Hawthorne et al., 2007a; Hawthorne et al., 2006,
74 2007b; Lohmann et al., 2005). In general, OC-water-based equilibrium partitioning
75 overestimates dissolved concentrations (Hawthorne et al., 2006; Lohmann et al., 2005), and
76 mixed results are reported when other sediment carbon phases like BC are considered, with some
77 studies showing improvements to estimates (Accardi-Dey and Gschwend, 2003; Lohmann et al.,
78 2005), and others showing little change or underestimates (Hawthorne et al., 2007a; Hawthorne

79 et al., 2007b). Often these estimate errors are considered to result from inadequate equilibrium
80 partition coefficient values.

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

90

91 MATERIALS AND METHODS

92 *Site Description and Overall Methodology*

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

99 Five sites were chosen throughout the Bay for sampling (**Fig. 1**). The “Passaic”,
100 “Hackensack”, “AK”, and “KVK” sites represent locations where the Bay converges with each
101 water channel. The mid-Bay (“MB”) site was located in the middle of Newark Bay. Water
102 column depths were ~1.5 m at the Passaic, Hackensack, and MB stations, 4 m at the KVK, and
103 8.8 m at the AK station. Sediment and biota were collected from each site and analyzed for
104 PCDD/Fs. Porewater was also analyzed for PCDD/Fs by tumbling PE and sediment together in
105 glass flasks on a shaker table in the laboratory. A separate set of PE samplers was deployed *in-*
106 *situ* at each site to determine dissolved PCDD/F concentrations above the sediment bed (“deep
107 water”). PCDD/F concentrations from all media were then converted to tissue concentrations
108 using equilibrium partition coefficients, and estimated tissue concentrations were compared to
109 those measured directly from biota. Concentrations in porewater and deep water PE were also
110 compared to determine the direction of the diffusive flux of PCDD/Fs across the sediment-water
111 interface. All extraction procedures and instrumental methods are detailed in the SI (**SI text** and
112 **Table S1**).

113

114 *Sediment and biota collection*

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

122

123 *Preparation of PEs for field deployment and laboratory tumbling experiments*

124 Sheets of PE painter's drop cloth (25 μ M thickness, Covalence Plastics) were cut into ~1
125 g pieces and cleaned by submersing in dichloromethane for 24 h twice. To gauge the equilibrium
126 status of analytes in deep water PE, performance reference compounds (PRCs) were added to PE
127 samplers before deployment. PRCs used for all analytes included d₁₀-anthracene, d₁₂-
128 benz[a]anthracene, and octachloronaphthalene (Ultra Scientific; Cambridge Isotopes). These
129 compounds were chosen because of their similar planar conformation to PCDD/Fs, and because
130 isotopically-labeled PCDD/Fs were employed as internal standard surrogates in all extractions.
131 Thus, the assumption was made that PCDD/Fs are taken up into PE at the same rate that PRCs
132 dissipate from PE (Huckins et al., 2002). This assumption introduces uncertainty into deep water
133 concentrations, addressed later in the Results. Polyethylene pieces were impregnated with PRCs
134 in an 80:20 methanol:water solution following previously published methods (Booij et al., 2002).
135 The methanol:water solution was spiked with 1 μ g PRC per 1 g sampler and samplers were
136 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 ($C_{\text{PRC},t=0}$). 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):

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

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

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

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:

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

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*

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

186

187 *Estimating biota HOC uptake*

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

$$192 \quad C_{lip,OC} = C_{diss,OC} BAF = \frac{C_{sed} BAF}{f_{OC} K_{OC}} \quad (4)$$

193 where C_{sed} is the HOC concentration in the sediment (ng/g), f_{OC} is the fraction of OC in the
 194 sediment, and K_{OC} is the OC–water partition coefficient (mL water/g OC). K_{OC} s for PCDD/Fs
 195 were derived from the literature (Xia, 1998), while PCDD/F BAFs were estimated from PCDD/F
 196 octanol-water partition coefficients (K_{OWs}), using a regression determined with PAH data at 5-
 197 24°C (Muijs and Jonker, 2009). Uncertainties associated with the BAF estimation are discussed
 198 later.

199

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

203
$$C_{lip,OC+BC} = C_{diss,OC+BC} BAF = \frac{C_{sed} BAF}{f_{OC} K_{OC} + f_{BC} K_{BC} C_{diss}^{n-1}} \quad (5)$$

204 where f_{BC} is the fraction of BC in the sediment and K_{BC} is the BC–water partition coefficient
 205 (mL water/g BC). Both literature and sediment-specific values of K_{BC} were used to calculate
 206 $C_{diss,OC+BC}$. Literature PCDD/F K_{BC} s for Newark Bay sediments (Lambert, 2010) come from an
 207 adjacent field location (the Passaic River) approximately 200 cm deeper into the sediment bed.
 208 Sediment-specific K_{BC} s were derived from porewater dissolved PCDD/F concentrations
 209 calculated from PE samplers in the present study using equation 5 (with $n=0.6, 0.7,$ and 0.8).

210

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

213
$$C_{lip,PE} = C_{diss,PE} BAF = \frac{C_{PE,\infty} BAF}{K_{PE-w}} \quad (6)$$

214 where K_{PE-w} is the PE-water partition coefficient (mL water/g PE) estimated from K_{OW} (Adams
 215 et al., 2007). Values of K_{OW} were taken from Aberg et al. (2008). K_{PE-w} s, determined at 24°C and
 216 0 ppt salinity, were adjusted to reflect deep water and porewater temperature and salinity
 217 conditions. See the SI for additional information regarding physicochemical constants used for
 218 temperature and salinity adjustments.

219

220 *Sediment total organic carbon and black carbon*

221 For total organic carbon (TOC) determinations, sediments were dried at 60°C, ground
 222 after shell material was removed, treated with HCl, and analyzed for %C on a Carlo Erba NA
 223 1500 elemental analyzer (Fisons Instruments, Beverly, MA, USA) coupled to a VG-Optima
 224 stable isotope mass spectrometer. BC was determined using previously published methods

225 (Accardi-Dey and Gschwend, 2002; Gustafsson et al., 1996). National Institute of Standards and
226 Technology Standard Reference Material 1941b analyzed with this method had a mean BC
227 content of $0.57 \pm 0.01\%$ (n=3), just within the range (0.6 – 19.7) presented by a comprehensive
228 BC quantification method intercomparison study (Hammes et al., 2007). Amorphous organic
229 carbon (i.e., the fraction of TOC not considered BC) was determined by subtracting the fraction
230 of BC from TOC.

231

232 RESULTS AND DISCUSSION

233 *Sediment*

234 Sediment OC ranged from 1.6 to 5.8% and sediment BC ranged from 0.2 to 0.3% (**Table**
235 **S2**), comparable to previous results for OC and BC of 2.6% and 0.3% in New York Harbor
236 (Lohmann et al., 2005). Sediment concentrations ranged from 0.1 (1,2,3,4,7,8-HxCDF in the
237 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,
238 OCDD was present in the greatest concentrations followed by 2,7/2,8-DiCDD. Several of the
239 mid-MW congeners (2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF) were only detected in
240 the northern half of the Bay in the Passaic and Hackensack Rivers. The most toxic dioxin
241 congener, 2,3,7,8-TCDD, was present at all sites, but was most concentrated in the Passaic and
242 Hackensack (2.1 ± 0.8 ng/g OC and 2.1 ± 0.9 ng/g OC, respectively). We compared 2,3,7,8-
243 TCDD concentrations from the present study to those found during the Contaminant Assessment
244 and Reduction Project (CARP), which measured 2,3,7,8-TCDD sediment concentrations in the
245 AK in the late 1990s/early 2000s (CARP, 2007). Concentrations of 2,3,7,8-TCDD there ranged
246 from 0.02 to 0.08 ng/g, similar to AK dry weight concentrations determined in the present study
247 (0.020 ± 0.004 ng/g).

248

249 *Tissue*

250 The mean lipid content of deposit feeders was 0.07 g/g dry weight, while that of filter
251 feeders was 0.04 g/g. Lipid-normalized tissue concentrations shown are from deposit-feeding
252 tube worms (*Pectorina gouldii*) in the AK and filter-feeding clams (*Mya arenaria*) in the
253 Passaic, Hackensack, MB, and KVK (**Fig. S3**). Tube worms from the AK had detectable
254 concentrations of a full suite of mono- through octa-CDD/Fs (from 2.6 to 49 ng/g lipid), whereas

255 filter-feeding clams had no detectable levels of high MW PCDD/Fs (i.e., hexa- through octa-
256 CDD/Fs). The difference in high MW uptake by tissues is probably a reflection of feeding mode
257 differences, given that sediments from all sites had fairly high concentrations of hepta- and octa-
258 CDD/Fs. A difference in uptake among organisms with feeding modes has been observed
259 previously, with deposit-feeders receiving the majority of their HOC burden through sediment
260 ingestion and filter-feeders receiving roughly equal amounts from sediment ingestion and water
261 filtration (McLeod et al., 2008). Low MW congener tissue concentrations were similar across
262 sites and different feeding modes, except for clams in the Passaic and Hackensack, wherein only
263 one congener (1,2,3,7,8-PeCDF) was detected, primarily due to low biota masses collected at
264 these sites. The only tissue sample in which 2,3,7,8-TCDD was detected was AK tube worms
265 (3.2 ng/g lipid), with concentrations similar to those found in ribbed mussels (*Modiolis demissus*)
266 from the Passaic and Newark Bay during the CARP study (1.2 – 3.5 ng/g lipid and 0.62 – 1.4
267 ng/g lipid, respectively) (CARP, 2007).

268

269 *Deep water and porewater*

270 Dissolved PCDD/Fs detected in deep water ranged from 3.9 fg/L (2,3,7,8-TCDD) to 1.3
271 $\times 10^4$ fg/L (2,7/2,8-DiCDD) and from 0.6 (2,3,7,8-TCDD) to 1.7×10^4 fg/L (2,7/2,8-DiCDD) in
272 porewater. Fractions of equilibrium reached for each analyte (f_{EQS}), used for calculating
273 corresponding dissolved concentrations, are reported in **Table S3**, while PCDD/F concentrations
274 determined in the three different sizes of porewater PE are reported in **Table S4**. We divided
275 PCDD/F concentrations in PE deployed in the water column by those of PE samplers tumbled
276 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 $\frac{1}{2}$ 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; $1-f_{EQ}$ 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

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

306

307 *Estimating biota PCDD/F uptake and sediment-specific K_{BCS}*

308 To assess where native tissues received the majority of their PCDD/F exposures, we
309 calculated lipid-based tissue concentrations of PCDD/Fs based on partitioning from sediment
310 OC, sediment OC and BC, porewater PE, and deep water PE. We compared these concentrations
311 to those measured directly in Newark Bay biota (**Fig. 2**), but only for stations where more than
312 one congener was detected in tissues (the AK, the KVK, and the MB). The comparison
313 discussion is only for congeners detected in sediments, deep water, porewater, and tissues
314 concurrently at a given site (i.e., congeners with only 2 or 3 chlorines).

315

316 In the AK, where only deposit-feeders were collected, tissue concentrations calculated
317 from OC-water partitioning ($C_{lip,OC}$) overestimated C_{lip} (by 7x on average), while those from
318 OC+BC-water partitioning ($C_{lip,OC+BC}$) underestimated C_{lip} (by 4x on average) (**Fig. 2a**).
319 Concentrations calculated from porewater and deep water PE both underestimated C_{lip} , but not
320 by as much as $C_{lip,OC+BC}$. Tissue concentrations calculated from porewater PE ($C_{lip,PEpw}$) were
321 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_{BCS} (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

345 et al., 2007b), and further shows that even sediments from nearby locations but deeper depths,
346 where BC is likely older and qualitatively different, can exhibit substantially different HOC-
347 binding characteristics. Werner et al. (2010) suggested that PCB sorption to BC at low
348 concentrations is linear (i.e., $n=1$ in eq. 5), but we find that lipid concentrations are instead
349 overestimated when linear sorption is assumed (e.g., using Lambert et al.'s K_{BC} values with $n=1$
350 in eq. 5 results in C_{lip} overestimates of 3.8x). Thus, in the present study, we derived sediment and
351 depth-specific K_{BCS} from mean measured sediment concentrations and dissolved porewater
352 concentrations across sites. We then used these sediment-specific K_{BCS} to estimate C_{lip} at
353 individual sites, as above. Field K_{BCS} were determined only for congeners detected in both
354 porewater PE and sediments at three or more sites (i.e., 2,7/2,8-DiCDD, 2,4,8-TriCDF, and
355 2,3,7-TriCDD), and were calculated for Freundlich coefficients of $n = 0.6, 0.7,$ and 0.8 (**Table**
356 **1**). All sediment-specific K_{BCS} were lower in value than those of Lambert, in some instances by
357 more than an order of magnitude (e.g., 2,3,7-TriCDD). Sediment-specific K_{BCS} improved
358 $C_{lip,OC+BC}$ estimates of C_{lip} by 2 – 87 fold. For example, in the AK, $C_{lip,OC+BC}$ determined using
359 sediment-specific K_{BCS} was a factor of 1.1 higher than C_{lip} (compared to 1.6x lower for
360 porewater PE), and in the KVK and MB, $C_{lip,OC+BC}$ determined using sediment-specific K_{BCS}
361 was, on average, 4x lower than C_{lip} (compared to 3.1x lower for porewater PE).

362

363 Though $C_{lip,OC+BC}$ from sediment-specific K_{BCS} and $C_{lip,PEpw}$ were both good predictors of
364 C_{lip} , each estimator contains uncertainties related to partition coefficients; namely, K_{PE-wS} , BAFs,
365 and in the case of $C_{lip,OC+BC}$, K_{OCS} . We assumed that K_{PE-w} and K_{OC} values had relative
366 uncertainties of 100%, given that both were calculated from K_{OW} , and K_{OWS} of these congeners
367 are reported to have a high-end uncertainty of 100% (Aberg et al., 2008). We assigned a 100%

368 relative uncertainty to the conversion of dissolved concentrations to lipid-based from BAFs.
369 Considering these assumptions combined, $C_{lip,OC+BC}$ uncertainties are 200% while $C_{lip,PEpw}$
370 uncertainties are 140%; these are in addition to analytical uncertainties (see the SI for uncertainty
371 calculations). Thus, although $C_{lip,OC+BC}$ and $C_{lip,PEpw}$ are roughly equally good predictors of C_{lip} ,
372 we note that the lower relative uncertainty in $C_{lip,PEpw}$ s and their more straightforward
373 determination make them a more practical and reliable option for obtaining site-specific
374 estimates of C_{lip} .

375

376 *Implications for use of PE to predict biota uptake in the field*

377 In the present study, we predicted PCDD/F lipid concentrations in deposit feeders within
378 an average factor of 1.6 (range 1.1 – 3.8) using porewater PEs and BAFs, while in a previous
379 study comparing PCB uptake by *Nereis virens* to uptake in PE in the laboratory (Friedman et al.,
380 2009), we estimated PCB uptake within an average factor of 0.99 (range 0.06 – 3.0) using
381 porewater PE and BAFs. Collectively, this is evidence that PE samplers used to measure
382 porewater can provide consistently more reliable estimates of C_{lip} for deposit feeders in both the
383 laboratory and the field compared to the range of estimates observed from sediment equilibrium
384 partitioning.

385

386 In the present study, however, there were a number of PCDD/Fs found in tissue but not
387 porewater, particularly high MW congeners in AK deposit feeders, suggesting these congeners
388 are not taken up by diffusion from porewater. If $C_{lip,PEpw}/C_{lip}$ is plotted against $\log K_{OW}$ for
389 PCDD/F congeners detected in both phases for AK tube worms, a slight decreasing trend in the
390 ratio is observed with increasing K_{OW} , though the relationship is not statistically significant at

391 $\alpha=0.05$ (**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_{BCS} initially employed were determined
431 with sediment from an adjacent location. When we used porewater concentrations to find
432 sediment- and depth-specific K_{BCS} , we improved predictions of biota PCDD/F uptake estimates.
433 Given the additional laboratory time and uncertainty involved in determining sediment-specific
434 K_{BCS} , 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 be 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

443 **ACKNOWLEDGEMENTS**

444 We thank Robert Chant (Rutgers University) and Christopher Sommerfield (University of
445 Delaware) for time aboard the R/V Caleta, use of data and sediment samples, and insightful
446 discussions, as well as Eric Stern, Nicole Bujalski, and Mark Reiss (U.S. EPA) for time aboard
447 the R/V Kenneth Biglane and assistance with sampling. Mark Cantwell (U.S. EPA) assisted with
448 instrumental analysis and Julia Sullivan (URI-GSO) with OC and BC analysis. We thank
449 anonymous reviewers for constructive comments. This work was supported by the Hudson River
450 Foundation through grant 07/007A to R. Lohmann and GF/01/09 to C. Friedman.

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.

456 **LITERATURE CITED**

- 457 US EPA, USACE, NJ DEP, NJ DOT. Lower Passaic River Restoration Project
458 <<http://www.ourpassaic.org>>.
- 459 Aberg, A., MacLeod, M., Wiberg, K., 2008. Physical-chemical property data for dibenzo-*p*-
460 dioxin (DD), dibenzofuran (DF), and chlorinated DD/Fs: A critical review and recommended
461 values. *J. Phys. Chem. Ref. Data* 37, 1997-2008.
- 462 Accardi-Dey, A., Gschwend, P.M., 2002. Assessing the combined roles of natural organic matter
463 and black carbon as sorbents in sediments. *Environ. Sci. Technol.* 36, 21-29.
- 464 Accardi-Dey, A., Gschwend, P.M., 2003. Reinterpreting literature sorption data considering both
465 absorption into organic carbon and adsorption onto black carbon. *Environ. Sci. Technol.* 37, 99-
466 106.
- 467 Adams, R.G., Lohmann, R., Fernandez, L.A., Macfarlane, J.K., Gschwend, P.M., 2007.
468 Polyethylene devices: Passive samplers for measuring dissolved hydrophobic organic
469 compounds in aquatic environments. *Environ. Sci. Technol.* 41, 1317-1323.
- 470 Arp, H.P.H., Breedveld, G.D., Cornelissen, G., 2009. Estimating the in situ sediment-porewater
471 distribution of PAHs and chlorinated aromatic hydrocarbons in anthropogenic impacted
472 sediments. *Environ. Sci. Technol.* 43, 5576-5585.
- 473 Booij, K., Smedes, F., van Weerlee, E.M., 2002. Spiking of performance reference compounds in
474 low density polyethylene and silicone passive water samplers. *Chemosphere* 46, 1157-1161.
- 475 Burgess, R.M., Berry, W.J., Mount, D.R., DiToro, D.M., 2013. Mechanistic sediment quality
476 guidelines based on contaminant bioavailability: Equilibrium partitioning Sediment Benchmarks
477 (ESBs). *Environ. Toxicol. Chem.* 32, 102-114.
- 478 Caplow, T., Schlosser, P., Ho, D.T., Santella, N., 2003. Transport dynamics in a sheltered
479 estuary and connecting tidal straits: SF₆ tracer study in New York Harbor. *Environ. Sci. Technol.*
480 37, 5116-5126.
- 481 CARP, 2007. Data Archive: Water, Sediment and Biota Data collected from 1999-2003. Hudson
482 River Foundation, New York, NY. CD-ROM.
- 483 Cho, Y.-M., Ghosh, U., Kennedy, A.J., Grossman, A., Ray, G., Tomaszewski, J.E., Smithenry,
484 D.W., Bridges, T.S., Luthy, R.G., 2009. Field application of activated carbon amendment for in-
485 situ stabilization of polychlorinated biphenyls in marine sediment. *Environ. Sci. Technol.* 43,
486 3815-3823.
- 487 Choi, Y., Cho, Y.-M., Luthy, R.G., 2013. Polyethylene-water partition coefficients for parent-
488 and alkylated-polycyclic aromatic hydrocarbons and polychlorinated biphenyls. *Environ. Sci.*
489 *Technol.* Article ASAP.
- 490 Cornelissen, G., Wiberg, K., Broman, D., Arp, H.P.H., Persson, Y., Sundqvist, K., Jonsson, P.,
491 2008. Freely dissolved concentrations and sediment-water activity ratios of PCDD/Fs and PCBs
492 in the open Baltic Sea. *Environ. Sci. Technol.* 42, 8733-8739.
- 493 DeWit, C., Jansson, B., Bergek, S., Hjelt, M., Rappe, C., Olsson, M., Andersson, O., 1995.
494 Polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran levels and patterns in fish
495 and fish-eating wildlife in the Baltic Sea. *Chemosphere* 25, 185-188.
- 496 DiToro, D.M., Zarba, C.S., Hansen, D.J., Berry, W.J., Swartz, R.C., Cowan, C.E., Pavlou, S.P.,
497 Allen, H.E., Thomas, N.A., Paquin, P.R., 1991. Technical Basis for Establishing Sediment
498 Quality Criteria for Nonionic Organic Chemicals Using Equilibrium Partitioning. *Environ.*
499 *Toxicol. Chem.* 10, 1541-1583.

- 500 Fernandez, L.A., Macfarlane, J.K., Tcaciuc, A.P., Gschwend, P.M., 2009. Measurement of freely
501 dissolved PAH concentrations in sediment beds using passive sampling with low-density
502 polyethylene strips. *Environ. Sci. Technol.* 43, 1430-1436.
- 503 Friedman, C.L., Burgess, R.M., Perron, M.M., Cantwell, M.G., Ho, K.T., Lohmann, R., 2009.
504 Comparing polychaete bioaccumulation and passive sampler uptake to assess the effects of
505 sediment resuspension on PCB bioavailability. *Environ. Sci. Technol.* 43, 2865-2870.
- 506 Friedman, C.L., Cantwell, M.G., Lohmann, R., 2012. Passive sampling provides evidence for
507 Newark Bay as a source of PCDD/Fs to the New York/New Jersey atmosphere. *Environ.*
508 *Toxicol. Chem.* 31, 253-261.
- 509 Gustafsson, O., Haghseta, F., Chan, C., MacFarlane, J., Gschwend, P.M., 1996. Quantification of
510 the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability. *Environ.*
511 *Sci. Technol.* 31, 203-209.
- 512 Hammes, K., Schmidt, M.W.I., Smernik, R.J., Currie, L.A., Ball, W.P., Nguyen, T.H.,
513 Louchouart, P., Houel, S., Gustafsson, O., Elmquist, M., Cornelissen, G., Skjemstad, J.O.,
514 Masiello, C.A., Song, J., Peng, P., Mitra, S., Dunn, J.C., Hatcher, P.G., Hockaday, W.C., Smith,
515 D.M., Hartkopf-Froeder, C., Boehmer, A., Luer, B., Huebert, B.J., Amelung, W., Brodowski, S.,
516 Huang, L., Zhang, W., Gschwend, P.M., Flores-Cervantes, D.X., Largeau, C., Rouzaud, J.N.,
517 Rumpel, C., Guggenberger, G., Kaiser, K., Rodionov, A., Gonzalez-Vila, F.J., Gonzalez-Perez,
518 J.A., de la Rosa, J.M., Manning, D.A.C., Lopez-Capel, E., Ding, L., 2007. Comparison of
519 quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments
520 using reference materials from soil, water, sediment and the atmosphere. *Global Biogeochem.*
521 *Cycles* 21, 1-18.
- 522 Hawthorne, S.B., Azzolina, N.A., Neuhauser, E.F., Kreitinger, J.P., 2007a. Predicting
523 bioavailability of sediment polycyclic aromatic hydrocarbons to *Hyalella azteca* using
524 equilibrium partitioning, supercritical fluid extraction, and pore water concentrations. *Environ.*
525 *Sci. Technol.* 41, 6297-6304.
- 526 Hawthorne, S.B., Grabanski, C.B., Miller, D.J., 2006. Measured partitioning coefficients for
527 parent and alkyl polycyclic aromatic hydrocarbons in 114 historically contaminated sediments:
528 Part 1. K_{OC} values. *Environ. Toxicol. Chem.* 25, 2901-2911.
- 529 Hawthorne, S.B., Grabanski, C.B., Miller, D.J., 2007b. Measured partition coefficients for parent
530 and alkyl polycyclic aromatic hydrocarbons in 114 historically contaminated sediments: Part 2.
531 Testing the $K_{OC}K_{BC}$ two carbon-type model. *Environ. Toxicol. Chem.* 26, 2505-2516.
- 532 Huckins, J.N., Petty, J.D., Lebo, J.A., Almeida, F.V., Booij, K., Alvarez, D.A., Clark, R.C.,
533 Mogensen, B.B., 2002. Development of the permeability/performance reference compound
534 approach for in situ calibration of semipermeable membrane devices. *Environ. Sci. Technol.* 36,
535 85-91.
- 536 Huckins, J.N., Tubergen, M.W., Manuweera, G.K., 1990. Semipermeable membrane devices
537 containing model lipid: A new approach to monitoring the bioavailability of lipophilic
538 contaminants and estimating their bioconcentration potential. *Chemosphere* 20, 533-552.
- 539 Lambert, M., 2010. The role of black carbon in the sorption of polychlorinated dibenzo-*p*-
540 dioxins and dibenzofurans at the Diamond Alkali Superfund site, Newark Bay, NJ,
541 Oceanography. University of Rhode Island Graduate School of Oceanography, MS Thesis,
542 Narragansett.
- 543 Lambert, M., Friedman, C., Luey, P., Lohmann, R., 2011. Role of black carbon in the sorption of
544 polychlorinated dibenzo-*p*-dioxins and dibenzofurans at the Diamond Alkali Superfund site,
545 Newark Bay, New Jersey. *Environ. Sci. Technol.* 45, 4331-4338.

- 546 Lohmann, R., Burgess, R.M., Cantwell, M.G., Ryba, S.A., MacFarlane, J.K., Gschwend, P.M.,
547 2004. Dependency of polychlorinated biphenyl and polycyclic aromatic hydrocarbon
548 bioaccumulation in *Mya arenaria* on both water column and sediment bed chemical activities.
549 Environ. Toxicol. Chem. 23, 2551-2562.
- 550 Lohmann, R., MacFarlane, J.K., Gschwend, P.M., 2005. Importance of black carbon to sorption
551 of native PAHs, PCBs, and PCDDs in Boston and New York, Harbor sediments. Environ. Sci.
552 Technol. 39, 141-148.
- 553 Luthy, R.G., Aiken, G.R., Brusseau, M.L., Cunningham, S.D., Gschwend, P.M., Pignatello, J.J.,
554 Reinhard, M., Traina, S.J., Weber, W.J., Westall, J.C., 1997. Sequestration of hydrophobic
555 organic contaminants by geosorbents. Environ. Sci. Technol. 31, 3341-3347.
- 556 Mayer, L.M., Schick, L.L., Self, R.F.L., Jumars, P.A., Findlay, R.H., Chen, Z., Sampson, S.,
557 1997. Digestive environments of benthic macroinvertebrate guts: Enzymes, surfactants and
558 dissolved organic matter. J. Mar. Res. 55, 785-812.
- 559 Mayer, P., Vaes, W.H.J., Wijnker, F., Legierse, K., Kraaij, R.H., Tolls, J., Hermens, J.L.M.,
560 2000. Sensing dissolved sediment porewater concentrations of persistent and bioaccumulative
561 pollutants using disposable solid-phase microextraction fibers. Environ. Sci. Technol. 34, 5177-
562 5183.
- 563 McLeod, P.B., Luoma, S.N., Luthy, R.G., 2008. Biodynamic modeling of PCB uptake by
564 *Macoma balthica* and *Corbicula fluminea* from sediment amended with activated carbon.
565 Environ. Sci. Technol. 42, 484-490.
- 566 McLeod, P.B.v.d.H.-G., M.J.; Luoma, S.N.; Luthy, R.G., 2007. Biological uptake of
567 polychlorinated biphenyls by *Macoma balthica* from sediment amended with activated carbon.
568 Environ. Toxicol. Chem. 26, 980-987.
- 569 Morgan, E., Lohmann, R., 2008. Detecting air-water and surface-deep water gradients of PCBs
570 using polyethylene passive samplers. Environ Sci Technol. 42, 7248-7253.
- 571 Muijs, B., Jonker, M., 2009. Temperature-dependent bioaccumulation of polycyclic aromatic
572 hydrocarbons. Environ. Sci. Technol. 43, 4517-4523.
- 573 Pickard, S.W., Clarke, J.U., 2008. Benthic bioaccumulation and bioavailability of
574 polychlorinated dibenzo-*p*-dioxins/dibenzofurans from surficial Lake Ontario sediments. J. Great
575 Lakes Res. 34, 418-433.
- 576 Rappe, C., Bergqvist, P.-A., Kjeller, L.-O., Swanson, S., Belton, T., Ruppel, B., Lockwood, K.,
577 Kahn, P.C., 1991. Levels and patterns of PCDD and PCDF contamination in fish, crabs, and
578 lobsters from Newark Bay and the New York Bight. Chemosphere 2, 239-266.
- 579 Schneider, A.R., Paolicchi, A., Baker, J.E., 2006. The use of solid-phase microextraction to
580 rapidly measure dissolved PCBs in natural waters. Intern. J. Environ. Anal. Chem. 86, 789-803.
- 581 Sun, X., Werner, D., Ghosh, U., 2009. Modeling PCB mass transfer and bioaccumulation in a
582 freshwater oligochaete before and after amendment of sediment with activated carbon. Environ.
583 Sci. Technol. 43, 1115-1121.
- 584 Vinturella, A.E., Burgess, R.M., Coull, B.A., Thompson, K.M., Shine, J.P., 2004. Use of passive
585 samplers to mimic uptake of polycyclic aromatic hydrocarbons by benthic polychaetes. Environ.
586 Sci. Technol. 38, 1154-1160.
- 587 Werner, D., Hale, S.E., Ghosh, U., Luthy, R.G., 2010. Polychlorinated biphenyl sorption and
588 availability in field-contaminated sediments. Environ. Sci. Technol. 44, 2809-2815.
- 589 Xia, G.S., 1998. Sorption behavior of nonpolar organic chemicals on natural sorbents. PhD
590 Dissertation, Johns Hopkins University, Baltimore MD.
- 591

592 **TABLES**

593 **Table 1.** Mean sediment-specific polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F)
 594 log black carbon – water partition coefficients ($\log K_{BCS}$) 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_{BCS}) 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 $p = 0.01$.