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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

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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

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

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

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**).

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 μM 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 d_{10}-anthracene, d_{12}-

128   benz[a]anthracene, and octachloronapthalene (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 μg 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 ($C_{PRC,t=0}$). 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):

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

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

$$f_{EQ} = 1 - \frac{C_{PRC,t}}{C_{PRC,t=0}} \tag{2}$$

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:

$$C_{PEdw,\infty} = \frac{C_{PEdw}}{f_{EQ}} \tag{3}$$

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   ($C_{PEdw,\infty}$) 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
$$C_{lip,OC} = C_{diss,OC} BAF = \frac{C_{sed} BAF}{f_{OC} K_{OC}}$$
(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_{OW}s), 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
$$C_{lip,OC+BC} = C_{diss,OC+BC}BAF = \frac{C_{sed}BAF}{f_{OC}K_{OC} + f_{BC}K_{BC}C_{diss}^{n-1}}$$
(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
$$C_{lip,PE} = C_{diss,PE}BAF = \frac{C_{PE,\infty}BAF}{K_{PE-w}}$$
(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_{EQ}s), 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 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; $1-f_{EQ}$ 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 $K_{BC}s$*

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 7× 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_{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

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_{BC}s from mean measured sediment concentrations and dissolved porewater

352   concentrations across sites. We then used these sediment-specific K_{BC}s to estimate C_{lip} at

353   individual sites, as above. Field K_{BC}s 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_{BC}s 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_{BC}s 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_{BC}s 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_{BC}s

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_{BC}s and $C_{lip,PEpw}$ were both good predictors of

364   C_{lip}, each estimator contains uncertainties related to partition coefficients; namely, K_{PE-w}s, BAFs,

365   and in the case of $C_{lip,OC+BC}$, K_{OC}s. 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_{OW}s 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_{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

443   **ACKNOWLEDGEMENTS**

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.