Interlaboratory Study of Polyethylene and Polydimethylsiloxane Polymeric Samplers for Ex Situ Measurement of Freely Dissolved Hydrophobic Organic Compounds in Sediment Porewater

Guilherme R. Lotufo,a,* Mandy M. Michalsen,a,1 Danny D. Reible,b Philip M. Gschwend,c Upal Ghosh,d Alan J. Kennedy,a Kristen M. Kerns,a Magdalena I. Rakowska,b Adesewa Odetayo,b John K. MacFarlane,c Songjing Yan,d and Mandar Bokare4

Environmental Laboratory, US Army Engineer Research and Development Center, Vicksburg, Mississippi, USA
bDepartment of Civil, Environmental, and Construction Engineering, Texas Tech University, Lubbock, Texas, USA
cDepartment of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA
dDepartment of Chemical, Biochemical, and Environmental Engineering, University of Maryland Baltimore County, Baltimore, Maryland, USA
eSeattle District, US Army Corps of Engineers, Seattle, Washington, USA

Abstract: We evaluated the precision and accuracy of multilaboratory measurements for determining freely dissolved concentrations ($C_{\text{free}}$) of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in sediment porewater using polydimethylsiloxane (PDMS) and low-density polyethylene (LDPE) polymeric samplers. Four laboratories exposed performance reference compound (PRC) preloaded polymers to actively mixed and static ex situ sediment for approximately 1 month; two laboratories had longer exposures (2 and 3 months). For $C_{\text{free}}$ results, intralaboratory precision was high for single compounds (coefficient of variation $\leq 50\%$ or less), and for most PAHs and PCBs interlaboratory variability was low (magnitude of difference was a factor of 2 or less) across polymers and exposure methods. Variability was higher for the most hydrophobic PAHs and PCBs, which were present at low concentrations and required larger PRC-based corrections, and also for naphthalene, likely due to differential volatilization losses between laboratories. Overall, intra- and interlaboratory variability between methods (PDMS vs. LDPE, actively mixed vs. static exposures) was low. The results that showed $C_{\text{free}}$ polymer equilibrium was achieved in approximately 1 month during active exposures, suggesting that the use of PRCs may be avoided for ex situ analysis using comparable active exposure; however, such ex situ testing may not reflect field conditions. Polymer-derived $C_{\text{free}}$ concentrations for most PCBs and PAHs were on average within a factor of 2 compared with concentrations in isolated porewater, which were directly measured by one laboratory; difference factors of up to 6 were observed for naphthalene and the most hydrophobic PAHs and PCBs. The $C_{\text{free}}$ results were similar for academic and private sector laboratories. The accuracy and precision that we demonstrate for determination of $C_{\text{free}}$ using polymer sampling are anticipated to increase regulatory acceptance and confidence in use of the method. Environ Toxicol Chem 2022;41:1885–1902. © 2022 The Authors. Environmental Toxicology and Chemistry published by Wiley Periodicals LLC on behalf of SETAC. This article has been contributed to by U.S. Government employees and their work is in the public domain in the USA.

Keywords: Bioavailability; Passive sampler; Polychlorinated biphenyls; Polycyclic aromatic hydrocarbons

INTRODUCTION

Freely dissolved concentrations of nonionic organic chemicals ($C_{\text{free}}$) in porewater quantify the driving force for contaminant uptake in benthic organisms and the toxic effects such influxes may cause (Di Toro et al., 1991; Lydy et al., 2014; Mayer et al., 2014). The $C_{\text{free}}$ measure is a critical exposure metric for benthic organism risk assessments (Fernandez & Gschwend, 2015; Greenberg et al., 2014; Mayer et al., 2014),
including deposit-feeding invertebrates (see Lu et al., 2011; Trimble et al., 2008; Vinturella et al., 2004). Both bio-accumulation and toxicity of hydrophobic organic compounds (HOCs) to benthic and aquatic organisms are well predicted by $C_{\text{free}}$ values. For example, Wemer et al. (2010) showed that concentrations of polychlorinated biphenyls (PCBs) in biolipids of marine species that were exposed to sediment for 28 days were well predicted by $C_{\text{free}}$. In another study, Kreitinger et al. (2007) showed that the toxicity of polycyclic aromatic hydrocarbons (PAHs) to the freshwater amphipod *Hyalella azteca* was accurately predicted by $C_{\text{free}}$, whereas no clear threshold was observed for toxicity based on bulk sediment concentrations. Therefore, measuring $C_{\text{free}}$ provides a much improved approach for compliance monitoring and managing contaminated sediments compared with bulk sediment analysis (Booij et al., 2016; Mayer et al., 2014; Parkerton & Maruya, 2014).

Obtaining accurate direct measurement of $C_{\text{free}}$ in sediment porewater using centrifugation is considered challenging (Burkhard et al., 2017). The association of contaminants with colloidal organic matter has resulted in overestimation of $C_{\text{free}}$ in porewater (Burgess & McKinney, 1999; Ghosh et al., 2000; Khalil et al., 2006; Lu et al., 2006). Moreover, $C_{\text{free}}$ is generally very low (e.g., 10 pg/gL) for strongly hydrophobic compounds (Cornelissen et al., 2008; Hawthorne et al., 2011; Jahneke et al., 2012) and typically below the limits of detection of traditional analytical methods for water. Traditional methods to predict $C_{\text{free}}$ in porewater use solvent-extractable concentrations of sediment-associated HOCs normalized to sediment organic carbon content (Di Toro et al., 1991; Park & Erstfeld, 1999). This approach is still used (see Finkelstein et al., 2017), although more complex models to estimate bioavailability have been proposed (Cornelissen & Gustafsson, 2005). However, these approaches are generally considered unsuitable by the environmental scientific community for realistic assessments of actual risks at contaminated field sites because they often have not yielded accurate predictions of $C_{\text{free}}$ (Gschwend et al., 2011; Parkerton & Maruya, 2014). The development of partitioning-based, non-depletive polymer sampling methods has allowed for the accurate determination of $C_{\text{free}}$ values in sediment porewater (Booij et al., 2003; Cornelissen et al., 2008; Fernandez et al., 2009; Lohmann et al., 2004; Mayer et al., 2000; Tomaszewski & Luthy, 2008).

Polymer-based sampling methods for determining $C_{\text{free}}$ of HOCs in sediment porewater involve direct exposure of a polymer phase to sediment either in situ at locations of interest or ex situ in the laboratory. Sediment-associated HOCs partition into the polymer, and the resulting polymer-sorbed concentration is used to calculate $C_{\text{free}}$. Ex situ applications typically involve the use of thin samplers of different polymer types and geometries under constant agitation in the laboratory, aiming to establish equilibrium between the polymer and the sediment. The in situ sampling approach involves placing a polymer sampler within the sediment in the field (Apell & Gschwend, 2016; Apell et al., 2018; Borrelli et al., 2018; Fernandez et al., 2009; Reininghaus et al., 2020; Schmidt et al., 2017; Yan et al., 2020). Equilibrium concentrations are inferred during in situ sampling through use of performance reference compounds (PRCs) or time series measurements (Apell & Gschwend, 2014; Joyce & Burgess, 2018; Joyce et al., 2020). Unlike in situ deployments, ex situ deployments typically do not incorporate field conditions by design and therefore may not reflect porewater exchange processes (Apell et al., 2018). However, bioaccumulation in deposit-feeding organisms may be less sensitive to these porewater processes (Bridges et al., 2017; Yan et al., 2020). Vertical placement of polymer samplers into the sampling media in situ allows for quantitative determination of $C_{\text{free}}$ in surface water and depth-specific profile sediment porewater (Apell et al., 2018; Fernandez et al., 2014; Lampert et al., 2013).

Polymers that are commonly applied in different forms (e.g., thicknesses and geometries) for sampling sediment porewater include polydimethylsiloxane (PDMS), low-density polyethylene (LDPE), and polyoxymethylene (POM; Lydy et al., 2014). Polymer sampling can be used to estimate $C_{\text{free}}$ for a wide range of nonionized organic chemicals of concern with octanol-water partition coefficients ($K_{\text{OW}}$) values larger than $10^3$. Polymer sampling has been successfully used and is thus recommended for use in assessing risks at contaminated sediment sites within the US Environmental Protection Agency (USEPA) Superfund Program (Apell et al., 2016; Burgess et al., 2015; Burkhard et al., 2017; Fernandez et al., 2014; USEPA, 2012). It is also considered a useful complementary tool by regulators in assessing environmental contamination under the European Union Water Framework Directive (Booij et al., 2016).

However, the large diversity of polymer classes and forms used in the past decades and the paucity of standardized methods has created challenges for widespread application in sediment contamination assessment and management projects as well as acceptance in the risk assessment and regulatory community (Greenberg et al., 2014; Jonker et al., 2018; Parkerton & Maruya, 2014). Small-scale method comparisons were previously performed either by comparing two polymer sampling methods using the same deployment system (Endo et al., 2017; Schmidt et al., 2017) or by comparing multiple polymer samplers each by a different laboratory performing independent sediment deployments (Gschwend et al., 2011). Comparisons of two methods showed overall good agreement (typically within a factor of 2), but greater differences were reported when different laboratories used different polymer samplers (PDMS, POM, or LDPE; Gschwend et al., 2011). Jonker et al. (2018) conducted the first large-scale, inter-laboratory polymer sampling methodology evaluation and concluded that overall interlaboratory variability was large (by a factor of ~10) but could be significantly reduced by standardizing methods and eliminating or reducing sources of variability extraneous to the polymer sampling method itself (e.g., chemical analysis).

The publication of standardized methods is a necessary step to foster the use of polymer samplers as viable tools for laboratories that provide analytical services and to increase the application of this methodology for assessing long-term remediation success and informing risk management decisions. Other steps include training for unexperienced users and demonstration of successful applications (Greenberg...
et al., 2014). The large-scale interlaboratory study by Jonker et al. (2018) included only research and not commercial laboratories. Development of standardized methods is needed to improve data quality and to encourage acceptability and use of polymeric sampling by commercial laboratories and monitoring agencies in future risk assessments (Booij et al., 2016). A standard polymer-based sampling method is available to measure porewater PAHs directly at low detection limits (ng/L) from water extracted from sediment via centrifugation (ASTM International, 2013). However, the research community has only recently begun publishing protocols for directly placing polymer samplers in sediment to determine \( C_{\text{free}} \) (Burgess et al., 2017; Jonker et al., 2020).

The primary objective of the present study was to evaluate the accuracy and precision of ex situ polymer sampling for \( C_{\text{free}} \) measured by multiple academic (i.e., method-development oriented) and private sector laboratories (i.e., service oriented). Our study focused on (1) development of standard methods for polymer preparation and analysis by leading research laboratories using a phased approach focusing on methodological feedback from laboratories with varying degrees of expertise in polymer sampling, and (2) standard method validation through an interlaboratory comparison (Michalsen et al., 2021) designed to fulfill SW846 standard method application requirements (USEPA, 2015). Two polymer sampler formats were evaluated, solid phase microextraction (SPME) fibers coated with PDMS or LDPE thin sheet samplers. Each laboratory used unified Standard Operating Procedures (SOPs; Supporting Information, Section 4) for both polymers to measure \( C_{\text{free}} \) PAHs and PCBs in a homogenized field-collected sediment ex situ under continuously agitated and static exposure conditions; PRC corrections were used to correct for nonequilibrium. Four combinations (LDPE and PDMS with both actively mixed and static exposures) were assessed for interlaboratory variability. One participating laboratory analyzed isolated sediment porewater directly, to obtain the \( C_{\text{free}} \) values of PAHs and PCBs for comparison with polymer-derived \( C_{\text{free}} \) values determined by multiple laboratories. Phased study implementation allowed optimization of the unified SOPs prior to the interlaboratory method validation of LDPE and PDMS polymers for determining the \( C_{\text{free}} \) values of PAHs and PCBs in sediment porewater.

**MATERIALS AND METHODS**

**Participating laboratories**

The participating laboratories were (1) academic laboratories with research expertise in polymer sampling method development, including Texas Tech University (TTU; Lubbock, TX, USA), University of Maryland Baltimore County (UMBC; Baltimore, MD, USA), and Massachusetts Institute of Technology (MIT; Cambridge, MA, USA); and (2) private sector laboratories, including the nonprofit Battelle Memorial Institute (Norwell, MA, USA), and the commercial laboratories Analytical Resources (Tukwila, WA, USA), SGS AXYS (Sidney, BC, Canada), and TestAmerica (Knoxville, TN, USA). Vista Analytical Laboratory (El Dorado Hills, CA, USA) participated in a limited capacity. The academic laboratories prepared, provided, and updated with lessons learned the standard method unified SOPs (Supporting Information, Section 4).

**Study description**

First, intra- and interlaboratory analytical variability was checked using a reference “calibration check standard” containing known PAH and PCB concentrations (method described in the Supporting Information, Section 3). Next, variability associated with the extraction and analysis of PRC-preloaded polymers containing known PRC concentrations was checked (method described in the Supporting Information, Section 3). Finally, methodological variability was checked; all participating laboratories followed unified SOPs to load PRCs into SPME fibers coated with PDMS and into LDPE thin sheets (henceforth termed simply PDMS and LDPE polymers), to extract the polymers, and then to analyze the extract using standard analytical methods. The study culminated by determining \( C_{\text{free}} \) in subsamples of a homogenized contaminated sediment with participating laboratories performing all the following steps: (1) preparation and loading with PRCs, (2) sediment exposure, and (3) polymer extraction and analysis. The \( C_{\text{free}} \) results obtained via actively mixed and static exposures were then compared against the \( C_{\text{free}} \) results obtained from direct analysis of porewater isolated from the sediment.

**Loading of PRCs to polymeric samplers and revision of SOPs**

Each participating laboratory cut, cleaned, and loaded polymers with PRCs following SOPs supplied by the academic laboratories. All laboratories prepared their PRC loading solutions (referred to as “working standard”) in 80:20 methanol:water for LDPE and in 20:80 methanol:water for PDMS. Each participating laboratory then extracted and quantified PRC concentrations in polymer extracts. This step of loading PRCs to polymers followed by extraction and analysis was conducted twice. The first round was intended both as training and as an opportunity to identify potential problems associated with achieving uniform loading of the polymers. The SOPs were revised to address the problems encountered. The revised unified SOPs were then used for a second round of loading polymers with PRCs by each participating laboratory as part of the interlaboratory determination of \( C_{\text{free}} \). Laboratory-specific loading durations are provided in the Supporting Information, Table S3.

**Sediment exposures: Active versus static exposure conditions for determination of \( C_{\text{free}} \)**

Active exposures (i.e., actively mixed) involved inserting the polymer into the sediment, followed by continuous agitation to ensure maximal contact between the sediment porewater and the polymer. Active exposure accelerates progress toward equilibrium compared with static exposure. Static exposure...
involved inserting the polymer into the sediment without agitation, thus mimicking some in situ field conditions with no porewater flow. The protocol for this sampling approach (Supporting Information, Section 4) was adapted from Burgess et al. (2017). Polymer and sediment masses required for exposures were estimated based on the PCB and PAH concentrations in sediment, the desire to have nondepleting sampling, and expected analytical detection limits. Participating laboratories removed Indiana Harbor (East Chicago, IN, USA) sediment from refrigerated storage, allowed sediment to reach room temperature (22 ± 5 °C), opened and mixed sediment jar contents, and then inserted one PRC-loaded polymer into each jar. Six PRC-loaded polymer samples were set aside for determining initial PRC concentrations. Exposures were carried out in the dark or in amber glass bottles to minimize photodegradation. No biocides were added to the sediment. Exposures were carried out at room temperature for periods ranging from 28 to 38 days for four laboratories, but for unintended longer periods (i.e., 63 and 90 days) for two laboratories (Supporting Information, Table S3) due to COVID-19 pandemic effects on laboratory access. Constant agitation was achieved using either a roller or a shaking table. At the conclusion of the exposure periods, laboratories retrieved polymers from each jar, cleaned and extracted them in basic accordance with Ghosh et al. (2014; see the unified SOP in the Supporting Information, Section 4), and then analyzed the polymer extracts for the 16 Priority PAHs of the USEPA and the 18 PCB congeners of the National Oceanic and Atmospheric Administration. For static exposure, the procedure was identical to that just described for active exposure except without agitation. Laboratory-specific exposure duration and exposure conditions are detailed in the Supporting Information, Table S3.

Evaluation of steady-state concentrations with PRCs

The fractional approaches to equilibrium ($f_{eq}$) were modeled using measured losses (initial and final concentrations) of PRCs in the polymer samplers to adjust the measured concentrations of PAHs and PCBs to their equilibrium concentrations. For PDMS, $f_{eq}$ values for target analytes in each polymeric sampler were determined according to the procedures described in the Supporting Information, Section 4, that followed Shen and Reible (2019) and Yan et al. (2020). For LDPE, the $f_{eq}$ values were determined according to Gschwend et al. (2014) and Apell and Gschwend (2016). Subsequently, these $f_{eq}$ values for the PRCs were examined for their consistencies within and between laboratories, and then were used to make any necessary corrections of measured target compound concentrations in the polymeric samplers to their corresponding values expected at polymer–sediment equilibrium. Finally, polymer–water partition coefficients derived according to Lohmann (2012) for LDPE and according to Ghosh et al. (2014) for PDMS (see the unified SOP in the Supporting Information, Section 4) were used to convert these equilibrium polymer concentrations to $C_{free}$ results using the following equation:

$$C_{free} = \frac{C_{Polymer}}{K_{polymer:water}}$$

The $C_{Polymer}$ values were determined from the concentrations measured in LDPE or PDMS after exposure to sediment (ng kg$^{-1}$) and an adjustment for the fractional equilibration of the target PCBs ($f_{eq}$).

Direct porewater extraction with colloid separation

The $C_{free}$ results obtained via active and static exposures were compared against the $C_{free}$ results obtained from direct analysis of porewater isolated from the sediment conducted by UMBC as described in the Supporting Information, Section 3.

Materials

Polymer samplers. The SPME fiber with a 35-μm PDMS coating (nominal) was purchased from Polymicro Technologies™. The PDMS fibers cut from this source were cleaned with hexane and acetone, then rinsed with MilliQ water several times, and then dried (see the unified SOPs in the Supporting Information, Section 4). The LDPE sheets (drop-cloth or plastic tarp material) with a thickness of 25 μm (1 mil) was obtained from Husky. The LDPE strips were cut and cleaned by soaking in methylene chloride for 24 h, followed by a second 24-h methylene chloride extraction, and then a 24-h methanol extraction to remove methylene chloride from the LDPE, followed by a second 24-h methanol extraction. Finally, LDPE strips were subject to three 24-h soaks in organic-free reagent water (within the same extraction vessel) to remove residual methanol from the LDPE (see the unified SOPs in the Supporting Information, Section 4).

PRCs. The PRCs were isotopically labeled versions of the contaminants of interest, which were loaded into the polymer samplers prior to sediment exposure. The PRCs were $^{13}$C$_{12}$-labeled phenanthrene, fluoranthene, chrysene, and indeno[1,2,3-cd]pyrene, and $^{13}$C$_{12}$-labeled PCB-37, -47, -54, -111, -138, and -178 congeners for use with low-resolution mass spectrometry (MS) analysis and PCB-28, -52, -47, -70, -80, -111, -141, and -182 congeners for use with high-resolution MS. All PRCs were acquired from Cambridge Isotope Laboratories.

Sediment. Indiana Harbor sediment contaminated with PAHs and PCBs was collected in fifteen 19-L (5-gallon) buckets in September 2018 and stored at 4 °C at the US Army Engineer Research Development Center Environmental Laboratory in Vicksburg (MS, USA). The Indiana Harbor sediment was homogenized in two 189-L (50-gallon) polypropylene drums using a Lightnin Impeller mixer (28-cm prop). The homogenized sediment from each drum was then distributed equally into the original 15 buckets, which had been rinsed clean with tap water. Sediment in each bucket was thoroughly hand mixed with clean stainless steel spoons, and then subsampled for...
initial total organic carbon (TOC) concentration as an indicator of homogeneity. Sediment in three buckets was excluded because TOC concentrations exhibited greater than 20% relative difference from the global average TOC concentration value (Supporting Information, Table S1). The PAH and PCB congeners were measured in sediment from the retained buckets (Supporting Information, Table S2) using USEPA methods 8270C (1996a) and 8082 (1996b), respectively. The coefficients of variation (CVs) in sediment concentrations were 11% or less for all PCB congeners and 15% or less for all PAHs except foracenaphthene and fluorene, for which the CVs were 23% and 31%, respectively. The homogenized sediment in buckets was again dispensed into a 189-L polypropylene drum, remixed, and then portioned into glass jars for shipment to the participating laboratories. The sediment was stored at 2–6 °C until use.

**Analytical methods**

The PCBs were quantified using high-resolution or low-resolution MS methods. The high-resolution gas chromatography–high resolution MS (HRGC/HRMS) USEPA method 1668C (USEPA, 2010) was used to determine target PCB congeners by SGS AXYS, TestAmerica, and Vista. The 12 World Health Organization–designated PCBs (Van den Berg et al., 2006) and the earliest and latest eluted congener at each level of chlorination were determined by the isotope dilution quantitation technique; the remaining congeners were determined by the internal standard quantitation technique. The HRGC–low sensitivity MS (HRGC/LSM) methodology modified from USEPA method 8270D (USEPA, 1998) was used to determine target PCB congeners by Analytical Resources, UMBC, MIT, and Battelle. The TTU laboratory quantified PCB congeners by using USEPA methods 8270D (1998) and 1668C (2010), employing an internal standard quantification technique, and the data for both methods were used for calculation of averages and statistical comparisons.

The PAHs were analyzed by Analytical Resources, TTU, UMBC, MIT, and Battelle with GC/MS methodology modified from USEPA (1998) method 8270D with selective ion monitoring mode to achieve lower detection limits. Both SGS AXYS and TestAmerica chose to use the isotope dilution technique for analyte quantitation, rather than the internal standard technique as stated in USEPA (1998) method 8270D. Both SGS AXYS and Vista chose to combine USEPA methods 8270D (1998) and 1625B (1984) whereby an HRGC coupled with MS is used for sample analysis, and an isotope dilution technique is applied for analyte quantitation. The TOC content of the Indiana Harbor sediment samples was determined using the Lloyd Kahn method (USEPA, 1988).

**Results and discussion**

**Instrumental performance**

For PAHs and PCBs, the CV for replicate measurements ($n = 3$) was less than 20% for all laboratory single-compound analyses, demonstrating acceptable precision for all participants. Most laboratories met the acceptance criteria of ±30% difference from the reference value for native target analytes and ±50% for isotopically labeled analytes selected as PRCs (Figure 1). Average calibration check standard concentrations reported by laboratories were within ±30% of reference concentrations for PCB and PAH natives 83% of the time and were within ±50% of reference concentrations for PCB and PAH PRCs 96% of the time. Some laboratories reported results for a few PAHs (three laboratories) and one PCB congener (one laboratory) that were out of range (Figure 1). Low interlaboratory analytical variability confirmed via calibration check standard analysis contrasts with Jonker et al. (2018), who concluded that analytical variability was a major contributor to interlaboratory variability in $C_{\text{free}}$ during their study.

**Participating laboratory analysis of polymeric samplers preloaded with PRCs**

For polymers preloaded with PRCs prepared by academic laboratories for interlaboratory comparison, precision was generally high for the PAH and PCB PRCs, with CVs for...
replicate measurements below 20% except for $^{13}$C$_6$-indeno[1,2,3-cd]pyrene for three laboratories and for the $^{13}$C-labeled congeners PCB-111, -141, and -182 for one laboratory and PCB-138 and -178 for a different laboratory (Supporting Information, Table S4).

The interlaboratory variability for the initial concentration of PRC in the polymers was low, as indicated by the magnitude of difference (MOD) for the laboratory averages (1.2–3.5, with most values below 2; Supporting Information, Table S5). $^{13}$C-labeled PCB PRCs were within ±50% of reference concentrations for most laboratories (Supporting Information, Table S4).

The interlaboratory variability for the initial concentration of PRC in the polymers was low, as indicated by the magnitude of difference (MOD) for the laboratory averages (1.2–3.5, with most values below 2; Supporting Information, Table S5). $^{13}$C-labeled PCB PRCs were within ±50% of reference concentrations for most laboratories (Supporting Information, Table S4). A single laboratory reported an exceedance for a single PAH PRC (13C$_6$-indeno[1,2,3-cd]pyrene) in PDMS. A single laboratory also reported concentrations for the 13C-labeled congeners PCB-111, -138, and -178 in LDPE samplers lower than the actual concentration by over a factor of 2 (Supporting Information, Figure S1). These deviations for PCBs were attributed to variations in the preloaded LDPE samplers. On review, it was discovered that laboratory 86 in the Supporting Information, Figure S1, may have mistakenly received LDPE sheets that were preloaded with total PRC masses that were different from those in the sheets distributed to the other laboratories.

### Evaluation of analysis of PRCs

During the first round of loading of PRCs to polymeric samplers by each participating laboratory, problems were noted by most laboratories with the use of different solvents in working standards, particularly the potential presence of two phases when low-solubility solvents were present. The PRC PCBs were received from the vendor dissolved in nonane. Failure to greatly reduce the fraction of nonane in the loading solution or to exchange it for methanol or for a solvent miscible with methanol (e.g., acetone) seems to have resulted in high variability in uptake of PRCs by PDMS and LDPE. Excessive hexane was also identified as a potential source of PDMS
delamination from the glass core. The unified SOPs were revised to require miscible carrier solvents to form a uniform PRC loading solution, and the use of an appropriate volume of loading solution/mass of polymeric samplers being prepared.

As part of the interlaboratory evaluation of polymeric sampler determination of $C_{\text{free}}$, the variability in PRC concentrations, loaded and measured separately by each of the six participating laboratories, was evaluated prior to exposing PRC-loaded polymers to the study sediment. For PDMS, PRCs met precision and accuracy criteria (i.e., a CV of 20% or less and average deviating 50% or less from target concentrations) except for an exceedingly low average concentration of PCB-138 and -178 for one laboratory (Supporting Information, Figure S2).

Precision and accuracy criteria exceedances were more frequent for LDPE (Supporting Information, Figure S3). The intra- and interlaboratory variability in the LDPE results was likely caused by variations in PRC loading resulting from LDPE strips sticking to each other while in the loading solutions or floating to the top of the PRC loading solution, or both. Corrective measures included suspending LDPE strips by "stabbing" them along glass pipet tubes or along aluminum coils or inserting the LDPE strips into stainless steel mesh (Supporting Information, Figure S4). The LDPE strips remained in the PRC loading solutions for an additional 30 days (minimum) following corrective measures (Supporting Information, Table S3). After the additional soaking period, a new set of replicate LDPE segments was retrieved from the loading solution for analysis. Even following these corrective measures, some laboratories observed variable staining of the LDPE in the PRC solutions, with some strips featuring bright yellow stains (Supporting Information, Figure S4). This suggested nonuniform loading of the yellow-colored PRC indeno[1,2,3-cd]pyrene. Following application of the corrective measures just described to improve exposure uniformity to the PRC loading solution, interlaboratory variability decreased, but precision remained low for some analytes, notably those with greater hydrophobicity (Supporting Information, Figure S5). The highest CVs, reported for one laboratory, were 68% for indeno[1,2,3-cd]pyrene, and 68%–76% for $^{13}$C-labeled PCB-111, -138, and -178. These results indicate that for this laboratory corrective measures were insufficient to overcome heterogenous uptake of those compounds into the LDPE likely resulting from the strips clumping together. It is critical to achieve homogenous PRC distribution throughout the polymer to enable appropriate use of the PRCs for disequilibrium corrections. Therefore, it is strongly recommended to confirm that the PRC concentrations are in the target range, and with acceptable precision on replicates, by analyzing multiple individual PRC-loaded LDPE and PDMS polymers before exposing them to sediment. If mean concentrations and their associated CVs are outside the acceptable range, additional PRC loading time should be provided, or other corrective actions should be conducted.

Even though it is desirable for the PRC concentrations in the polymers to approach the target concentrations, we note that it is not as important that a PRC loading level match the target concentration exactly; instead, it is most important that the PRC loading be measured accurately and be distributed homogeneously throughout the polymer (i.e., high precision on replicate PRC-loaded polymers) because initial PRC concentrations in the polymers are critical to making disequilibrium corrections post exposure.

**Evaluation of determination of $C_{\text{free}}$**

After exposure to sediment, the fraction of PRC remaining in the polymer was determined and used to adjust the measured target concentrations of PAHs and PCBs in the polymers to their equilibrium concentrations. For LDPE active exposures, the fractions of PRCs remaining were only 5% or less (Supporting Information, Table S6). For LDPE static exposure, the fractions remaining were 56% or less and were similar across laboratories, although it must be noted that total incubation times varied (Supporting Information, Table S6). For PDMS active exposure, the fractions remaining ranged from fully depleted (concentrations reported nondetects after exposure) to 81% and varied widely across laboratories for PAHs (Supporting Information, Table S6), perhaps due to differences in agitation intensity. For PDMS static exposures, the fractions remaining ranged from fully depleted to 96%, and were overall higher compared with active exposures (Supporting Information, Table S6).

For PAHs, the intralaboratory variability in polymer-determined $C_{\text{free}}$ was low, with most reported CVs on replicate measurements below 50%, with an overall average of 24% ± 19% for active LDPE exposures, 23% ± 16% for static LDPE exposures, 19% ± 18% for active PDMS exposures, and 15% ± 11% for static PDMS exposures (Table 1). High variability (i.e., CV greater than 50%) was observed for naphthalene (Table 1), which was expected due to its volatility and potential loss from polymers (Thomas & Reible, 2015) and/or losses during extract volume reductions during sample preparations. Precision for PAHs was high and similar for active and static exposures. For PCBs, intralaboratory variability in polymer-determined $C_{\text{free}}$ was low, with an overall CV average of 21% ± 15% for active LDPE exposures, 26% ± 25 for static LDPE exposures, 19% ± 13% for active PDMS exposures, and 11% ± 4% for static PDMS exposures (Table 2). High variability (i.e., CV greater than 50%) was observed for PCB results from one laboratory for LDPE active and static, as well as PDMS active exposures (Table 2).

For PAHs, $C_{\text{free}}$ measurements were also similar across participating laboratories for all polymer sampling methods (Figure 2 and Supporting Information, Table S7). Interlaboratory variability was low for fluorene, phenanthrene, anthracene, pyrene, benzo[a]anthracene, and chrysene, with the MOD ranging from 2 to 5 for both polymers and exposures. Values of MOD between 2 and 5 were also observed foracenaphthene, acenaphthylene, fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and benzo[ghi]perylene for PDMS and fluoranthene and benzo[k]fluoranthene for LDPE.
Interlaboratory variability was higher with the MOD being 6 or higher for naphthalene, benzo[b]fluoranthene, indeno[1,2,3-cd]pyrene, and dibenz[a,h]anthracene for PDMS and for naphthalene, acenaphthene, acenaphthylene, and benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, indeno[1,2,3-cd]pyrene, and dibenz[a,h]anthracene for LDPE (Supporting Information, Table S7). Significant differences between laboratories occurred for all PAHs across both polymers and exposure methods, except for fluorene, anthracene, and benzo[ghi]perylene for the LDPE static exposure, for which no significant differences were found (Supporting Information, Table S7). For many PAHs, even though statistical differences were detected, the MOD was low. For PCBs, average $C_{\text{free}}$ measurements were similar for participating laboratories for both polymers and exposure methods (Figure 3 and Supporting Information, Table S8). Interlaboratory variability was low, with MODs ranging from 2 to 5 for all PCBs for the LDPE active exposures. Interlaboratory variability was higher, with the MODs being 6 or higher for PCB-153, -170, -180, and -187 for LDPE static exposures, for PCB-44, -153, -170, -180, and -187 for PDMS active exposures, and for PCB-44, -66, -153, -170, -180, and -187 for PDMS static exposures (Supporting Information, Table S8). Significant differences between laboratories occurred for all PCBs across all polymer sampling methods (Supporting Information, Table S8). The unified SOPs developed in the present study (Supporting Information, Section 4) included all aspects and steps of polymer exposure and extraction as well as some Indiana Harbor sediment–specific content where needed, but the SOPs were not prescriptive regarding analytical methods used for

### Table 1: Polycyclic aromatic hydrocarbon $C_{\text{free}}$ coefficient of variation by participating laboratory and average and standard deviation across laboratories for low-density polyethylene and polydimethylsiloxane using active or static exposure methods

| PAH          | LDPE, active exposure | LDPE, static exposure |
|--------------|------------------------|------------------------|
| Naph         | 15 52 84 58 50 34 AVG SD | 15 52 84 58 50 34 AVG SD |
| Ace          | 28 50 27 19 34 14         | 44 10 13 11 22 15       |
| Flo          | 30 12 21 27 14           | 47 17 11 13 23 16       |
| Phe          | 28 9 15 20 25 14         | 44 10 8 13 19 15        |
| Ant          | 26 11 15 19 25 14        | 43 13 10 8 15 21 15     |
| Acy          | 13 21 ND 11 ND 21 12     | 30 15 ND 20 ND 22 7     |
| FlA          | 23 12 16 11 22 12        | 36 10 9 11 16 11       |
| Pyr          | 22 4 12 20 12 10         | 34 9 10 11 15 10       |
| BaA          | 22 6 17 12 10 12         | 37 11 9 11 16 11       |
| Chr          | 21 12 14 19 11 12        | 35 16 8 9 19 12        |
| BbF          | 17 9 12 14 17 9          | 34 15 9 22 18 9        |
| BkF          | 15 16 3 12 15 10         | 38 23 17 10 20 10      |
| BaP          | 13 18 3 11 13 15 7      | 49 24 16 10 22 14      |
| DahA         | 11 13 28 10 11 15 7     | 63 30 27 ND 14 37 20    |
| InP          | 14 10 5 9 12 7          | 79 42 19 18 35 35       |
| BghiP        | 13 13 6 9 10 13 7       | 57 29 16 20 18 27 15    |
| AVG          | 21 22 40 15 16 12 19   | 45 20 27 16 12 19      |

**Values greater than 50% are in green. The averages and SDs are in bold.**

Ace = acenaphthene; Acy = acenaphthylene; Ant = anthracene; AVG = average; BaA = benz[a]anthracene; BaP = benzo[a]pyrene; BbF = benzo[b]fluoranthene; BghiP = benzo[ghi]perylene; BkF = benzo[k]fluoranthene; Chr = chrysene; CV = coefficients of variation; DahA = dibenz[a,h]anthracene; FlA = fluoranthene; FlO = fluorene; InP = indeno [1,2,3-cd]pyrene; LDPE = low-density polyethylene; Naph = naphthalene; PAH = polycyclic aromatic hydrocarbon; PDMS = polydimethylsiloxane; Phe = phenanthrene; Pyr = pyrene; SD = standard deviation.
polymer extracts. The polymer sampling methodology used in the present study is similar to those recently published (Jonker et al., 2020). Overall, high differences across laboratories were observed for naphthalene, the most volatile PAH, and for very hydrophobic PAHs and PCB congeners (Figures 2 and 3 and Supporting Information, Tables S7 and S8), as discussed later in Determination of C free for highly hydrophobic PAHs and PCBs.

The only comparable previous large-scale polymer sampler study on interlaboratory variability involved only research laboratories with a proven track record of measuring C free (Jonker et al., 2018). The present study included laboratories with varying degrees of expertise in polymer sampling. Interlaboratory variability in the study by Jonker et al. (2018) was large when multiple laboratories and diverse polymer materials were used, but standardization of polymer sampling methods greatly reduced interlaboratory variability.

### Polymer sampling method comparison

Six laboratories generated results for both active and static exposure for each polymer type. For each polymer type, individual laboratory C free averages for active exposure were plotted against the corresponding average for static exposure (Figure 4). For PDMS, the results from active and static exposures were in good agreement, with an average ratio of static and active of 0.93 ± 0.22 for PAHs and 0.98 ± 0.22 for PCBs, and the slopes of the log–log regressions for the plots in Figure 4 were 1.00 (±0.01; r² = 0.99) for PAHs and 0.98 (±0.01; r² = 0.99) for PCBs. The intercepts for the correlations were 0.06 ± 0.01 and 0.03 ± 0.01 log units, indicating very low bias. For LDPE, results from both active and static exposures were also in good agreement, although more variable, with an average ratio of static and active of 0.87 ± 0.84 for PAHs and 1.35 ± 2.28 for PCBs; the slopes of the log–log regressions for the plots in Figure 4 were 1.08 (±0.029; r² = 0.97) for PAHs and 0.95 (±0.026; r² = 0.94) for PCBs. For LDPE, the highest disagreement between the two methods occurred for many high-molecular-weight PAHs and many laboratories, but disagreements occurred for comparatively fewer PCB congeners and only for two laboratories (Figure 4). For LDPE, the intercept for the correlation for PAHs (0.039 ± 0.07 log unit) reflected the bias resulting from much higher concentrations for some high-molecular-weight PAHs for the active method for some laboratories. In contrast, the

| PCB | Active exposure | Static exposure |
|-----|----------------|----------------|
| | AVG | SD | | AVG | SD |
| **LDPE** | | | | | |
| PCB-008 | 27 | 6 | 16 | 16 | 7 | 19 | 25 | 19 | 25 | 36 | 18 | 6 | 4 | 12 | 17 | 12 |
| PCB-018 | 26 | 5 | 15 | 8 | 5 | 19 | 22 | 18 | 25 | 29 | 17 | 12 | 6 | 9 | 16 | 9 |
| PCB-028 | 28 | 5 | 16 | 9 | 9 | 18 | 23 | 19 | 27 | 33 | 16 | 5 | 5 | 9 | 16 | 12 |
| PCB-044 | 24 | 5 | 14 | 7 | 11 | 17 | 21 | 17 | 24 | 27 | 14 | 7 | 11 | 8 | 15 | 8 |
| PCB-052 | 26 | 5 | 13 | 10 | 12 | 17 | 22 | 16 | 22 | 25 | 14 | 9 | 13 | 8 | 15 | 7 |
| PCB-066 | 28 | 5 | 13 | 8 | 6 | 17 | 21 | 17 | 22 | 29 | 14 | 7 | 13 | 24 | 18 | 8 |
| PCB-101 | 20 | 5 | 14 | 4 | 6 | 15 | 18 | 17 | 18 | 27 | 14 | 6 | 18 | 39 | 20 | 11 |
| PCB-105 | 29 | 5 | 13 | 9 | 10 | 17 | 22 | 17 | 44 | 32 | 16 | 11 | 22 | 69 | 32 | 22 |
| PCB-118 | 20 | 5 | 14 | 8 | 7 | 16 | 19 | 16 | 21 | 32 | 15 | 9 | 21 | 62 | 27 | 19 |
| PCB-138 | 20 | 4 | 12 | 11 | 15 | 20 | 14 | 14 | 20 | 27 | 16 | 8 | 23 | 90 | 31 | 30 |
| PCB-153 | 22 | 6 | 12 | 7 | 16 | 19 | 14 | 14 | 20 | 26 | 18 | 11 | 22 | 95 | 32 | 31 |
| PCB-170 | 43 | 6 | 9 | 10 | ND | 16 | 25 | 18 | 41 | 28 | 27 | ND | 123 | 55 | 46 |
| PCB-180 | 13 | 5 | 11 | 10 | 10 | 17 | 18 | 14 | 20 | 29 | 26 | ND | 17 | 118 | 42 | 43 |
| PCB-187 | 19 | 4 | 5 | 9 | 8 | 18 | 18 | 15 | 21 | 28 | 21 | ND | 34 | 120 | 45 | 42 |
| AVG | 25 | 5 | 13 | 10 | 13 | 8 | 17 | — | 25 | 29 | 17 | 8 | 16 | 56 | — | — |

| **PDMS** | | | | | |
| PCB-008 | 41 | 3 | 15 | 14 | 13 | 14 | 17 | 13 | 9 | 5 | 7 | 9 | 10 | 8 | 2 |
| PCB-018 | 43 | 7 | 13 | 14 | 13 | 14 | 17 | 13 | 10 | 12 | 5 | 6 | 7 | 10 | 8 | 3 |
| PCB-028 | 46 | 3 | 15 | 12 | 17 | 12 | 17 | 15 | 12 | 12 | 5 | 8 | 8 | 8 | 9 | 3 |
| PCB-044 | 48 | 5 | 14 | 14 | 14 | 14 | 18 | 15 | 8 | 8 | 4 | 7 | 9 | 8 | 7 | 2 |
| PCB-052 | 47 | 5 | 13 | 14 | 13 | 13 | 17 | 15 | 8 | 12 | 5 | 6 | 8 | 10 | 9 | 2 |
| PCB-066 | 52 | 7 | 15 | 11 | 12 | 11 | 18 | 17 | 8 | 11 | 6 | 7 | 11 | 9 | 9 | 2 |
| PCB-101 | 53 | 11 | 15 | 12 | 14 | 12 | 19 | 17 | 11 | 10 | 10 | 6 | 13 | 10 | 10 | 2 |
| PCB-105 | 56 | 10 | 16 | 4 | 14 | 4 | 17 | 19 | 16 | 11 | 7 | ND | 19 | 12 | 13 | 5 |
| PCB-118 | 45 | 11 | 14 | 5 | 15 | 16 | 18 | 14 | 11 | 14 | 10 | ND | 21 | 7 | 13 | 5 |
| PCB-138 | 32 | 12 | 17 | 16 | 14 | 16 | 18 | 7 | 10 | 15 | 14 | ND | 11 | 9 | 12 | 2 |
| PCB-153 | 53 | 13 | 16 | 11 | 17 | 11 | 20 | 16 | 21 | 15 | 18 | ND | 15 | 8 | 15 | 5 |
| PCB-170 | 26 | 21 | 34 | 9 | ND | 9 | 20 | 11 | 15 | 13 | 12 | ND | ND | 15 | 14 | 2 |
| PCB-180 | 36 | 22 | 17 | 11 | 17 | 11 | 20 | 19 | 29 | 14 | 16 | ND | 14 | 7 | 16 | 8 |
| PCB-187 | 33 | 31 | 28 | 13 | 20 | 13 | 23 | 9 | 14 | ND | ND | ND | 11 | 13 | 11 | 2 |
| AVG | 44 | 11 | 17 | 12 | 14 | 12 | 17 | 13 | 13 | 12 | 9 | 10 | 7 | 12 | 2 | 2 |

Values greater than 50% are in green. The averages and SDs are in bold.

### Notes

**AVG** = average; **CV** = coefficients of variation; **LDPE** = low-density polyethylene; **PCB** = polychlorinated biphenyl; **PDMS** = polydimethylsiloxane; **SD** = standard deviation.
intercept for the correlation for PCBs was very low (0.00002 $\pm$ 0.03 log unit).

Five laboratories generated results for both polymer types using active and static exposures. To investigate the degree of agreement between polymers, individual laboratory $C_{\text{free}}$ averages for one polymer (i.e., LDPE or PDMS) were plotted against those for the other for either active or static exposure methods (Figure 5). For PAHs, results from the LDPE and PDMS methods were in overall good agreement, with an average ratio of LDPE and PDMS of 1.19 $\pm$ 1.41 for active exposure and 0.55 $\pm$ 0.37 for static exposure; the slopes of the log–log regressions for the plots in Figure 5 were 1.00 ($\pm$ 0.027; $r^2 = 0.95$) for active exposure and 0.903 ($\pm$ 0.022; $r^2 = 0.96$) for static exposure. The intercepts for the correlations were 0.16 $\pm$ 0.08 and 0.54 $\pm$ 0.06 log units (not significantly different from zero), indicating very low bias.

To further compare polymer sampling methods, average $C_{\text{free}}$ values and their respective standard deviations (SDs) and CVs were determined using all replicates across laboratories for each of the polymer and extraction methods (Figure 6 and Supporting Information, Table S9 and Figures S6 and S7). Overall, agreement was high across methods, with the exception of biased low measurements for high-molecular-weight PAHs and biased high measurements for high-molecular-weight PCB congeners for LDPE polymer static exposures. Differences were higher for high-molecular-weight PAHs and PCBs when comparing polymer and exposure methods. For PAHs, the ratio between averages for the correlation for PCBs was very low (0.00002 $\pm$ 0.03 log unit).

Five laboratories generated results for both polymer types using active and static exposures. To investigate the degree of agreement between polymers, individual laboratory $C_{\text{free}}$ averages for one polymer (i.e., LDPE or PDMS) were plotted against those for the other for either active or static exposure methods (Figure 5). For PAHs, results from the LDPE and PDMS methods were in overall good agreement, with an average ratio of LDPE and PDMS of 1.19 $\pm$ 1.41 for active exposure and 0.55 $\pm$ 0.37 for static exposure; the slopes of the log–log regressions for the plots in Figure 5 were 1.00 ($\pm$ 0.027; $r^2 = 0.95$) for active exposure and 0.903 ($\pm$ 0.022; $r^2 = 0.96$) for static exposure. The intercepts for the correlations were 0.16 $\pm$ 0.08 and 0.54 $\pm$ 0.06 log units (not significantly different from zero), indicating very low bias.

To further compare polymer sampling methods, average $C_{\text{free}}$ values and their respective standard deviations (SDs) and CVs were determined using all replicates across laboratories for each of the polymer and extraction methods (Figure 6 and Supporting Information, Table S9 and Figures S6 and S7). Overall, agreement was high across methods, with the exception of biased low measurements for high-molecular-weight PAHs and biased high measurements for high-molecular-weight PCB congeners for LDPE polymer static exposures. Differences were higher for high-molecular-weight PAHs and PCBs when comparing polymer and exposure methods. For PAHs, the ratio between averages for
PDMS active versus LDPE active exposures exceeded 2 (rounded to the nearest whole number) only for naphthalene and acenaphthylene. For PDMS static versus LDPE static, however, the ratio between averages exceeded 2 for a larger number of compounds: acenaphthylene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene, and these were typically higher for PDMS static. For PCBs, agreement across methods was also overall high, with the ratio between averages exceeding 2 for PDMS static versus LDPE static only for PCB-170, -180, and -187 (higher for PDMS static). The ratio between averages for PDMS active versus LDPE active was lower than 2 for all PCB congeners.

For most PRCs, the fraction remaining in both polymers following active sampling approached zero, indicating that sediment PAHs and PCBs in the sediment porewater and in the sampler approached equilibrium. For static exposures, both polymeric sampler-based porewater estimates were readily corrected for progress toward equilibrium using PRC losses measured during exposure. The overall good agreement between active and static exposures supported the expectation of similar $C_{\text{free}}$ results after appropriate correction for nonequilibrium based on studies confirming PRC-based $C_{\text{free}}$ estimates by comparison with equilibrium-estimated $C_{\text{free}}$ (Apell & Gschwend, 2016; Fernandez et al., 2014; Gschwend et al., 2011; Schmidt et al., 2017). The present study and that of Jonker et al. (2018) demonstrated that when laboratories use unified SOPs, interlaboratory variability is generally reduced even when different polymers are compared.

**Determination of $C_{\text{free}}$ for highly hydrophobic PAHs and PCBs**

Overall, the greatest differences across laboratories for a given method or between exposure methods (i.e., active vs.
static) were observed for highly hydrophobic PAHs and PCB congeners (Figure 2 and Supporting Information, Tables S7 and S8), which where those associated with large PRC‐based corrections, because they were far from attaining sediment–polymer equilibrium. Heterogenous loading of some of the most hydrophobic PRCs to LDPE polymer by some laboratories (Supporting Information, Figure S5) likely contributed to higher uncertainty associated with using the initial PRC concentration, which was determined by each laboratory, to calculate equilibrium concentrations. It is well established that the use of PRCs contributes to the uncertainty of estimating $C_{\text{free}}$, especially for poorly equilibrated PRCs (Jonker et al., 2018, 2020; Joyce et al., 2020). Uncertainty associated with the use of poorly equilibrated PRCs (see Jalalizadeh & Ghosh, 2017; Sanders et al., 2018) may have contributed to the higher interlaboratory variability for the more hydrophobic compounds we observed. When selecting polymer sampler deployment methods, those that result in higher fractional loss of PRCs and a closer approach to equilibrium have been shown to result in lower uncertainty (i.e., higher
accuracy; Jalalizadeh & Ghosh, 2017) and should be employed whenever feasible.

**C<sub>free</sub> determined directly from isolated porewater**

To further evaluate the C<sub>free</sub> results found using polymeric sampling, comparisons were made with C<sub>free</sub> results from extractions of isolated porewater samples measured my UMBC (Supporting Information, Tables S7 and S8 and Figures S6 and S7). Considering the similarities between C<sub>free</sub> results for active and static exposures, comparisons focused on C<sub>free</sub> results for active exposures. Figure 7 shows compound-specific comparisons of average C<sub>free</sub> values using all replicate data across participating laboratories for polymer and active exposure combinations and average C<sub>free</sub> values determined directly from isolated porewater laboratories by a single laboratory. Polymer-determined PAH and PCB C<sub>free</sub> values were on average within a factor of 2 of C<sub>free</sub> values obtained from isolated porewater (difference factor of 2.3 ± 1.1, average ± 1 SD); difference factors of up to 6 were observed for select volatile and hydrophobic PAHs and PCBs such as chrysene, and PCB-138 (Figure 7 and...
Supporting Information, Figures S6 and S7). Four PAHs (benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, and benzo[ghi]perylene) and three PCBs (PCB-170, -180, and -187) were below detection in extracted porewater but were quantifiable using polymer samplers. Therefore, polymer sampling provided the clear advantage of requiring a much smaller volume of sediment for $C_{\text{free}}$ determination, especially for strongly hydrophobic PCBs and PAHs. Gschwend et al. (2011) previously compared polymer-sampling–derived porewater PCB concentrations with concentrations independently measured using an air-bridge approach with centrifugation and direct water extraction. They reported agreement within a factor of 2 for polymer-inferred porewater concentrations and independent porewater measures. Thus use of the polymeric sampling appears to have acceptable accuracy based on comparison with direct measurement methods.

**FIGURE 6:** Average polymer-sampler–derived freely dissolved porewater concentrations ($C_{\text{free}}$) in porewater from the Indiana Harbor sediment derived using all replicate data across all participating laboratories for two polymers, polydimethylsiloxane (PDMS) and low-density polyethylene (LDPE), and two exposure method combinations. (A) Polycyclic aromatic hydrocarbons (PAHs); (B) polychlorinated biphenyls (PCBs).

**FIGURE 7:** Comparison of average (and 1 standard deviation) freely dissolved porewater concentrations ($C_{\text{free}}$) for polycyclic aromatic hydrocarbons (PAHs; A) and polychlorinated biphenyls (PCBs; B) in actively sampled sediment measured by all participating laboratories using polymers (polydimethylsiloxane [PDMS], green; low-density polyethylene [LDPE], yellow) versus measures performed by isolation and direct measurement of porewater from the same sediment by one laboratory (blue).
CONCLUSIONS

Participating laboratories, including three academic and four private sector laboratories, successfully used polymer sampling methodologies to determine freely dissolved concentrations of HOCs in real-world sediment porewater from μg/L levels for smaller PAHs down to pg/L for larger PCB congeners. Overall, interlaboratory variability was low (i.e., precision was high), and interlaboratory variability was also low (less than a factor of 2) across laboratories for most target PAHs and PCBs for all sampling methods evaluated in spite of the number of steps and relative complexity associated with $C_{\text{free}}$ determination. Such a successful outcome was attributed to the phased approach of the interlaboratory method validation study, which allowed laboratories to identify unusually high variability, then pinpoint their sources, and ultimately improve the unified SOPs used in the final sediment exposures and polymer-determined $C_{\text{free}}$ values. The greatest differences across laboratories were associated with the most volatile targets (e.g., naphthalene) and the least water-soluble targets (e.g., indeno[1,2,3-cd]pyrene), presumably because the former suffer losses during sample processing and the latter due to uncertainties associated with the use of small PRC losses used to determine equilibrium concentrations. Precision of determination of PRC loading concentrations should be assessed prior to deployment of PRC-loaded polymers for sampling porewater, especially when using laboratory static application or in situ deployment.

Overall, the active exposure method reflected equilibrium between sediments and polymers, based on PRC losses, and the static sampling, corrected based on PRC losses, compared very well with active exposure results across laboratories, providing robust validation of the PRC correction approach. The $C_{\text{free}}$ polymer equilibrium was typically achieved in ~1 month during active exposures, suggesting that the use of PRCs may be avoided for ex situ analysis if sediment is actively sampled; however, this is done at the risk of not reflecting field conditions (e.g., effects of bioirrigation; Apell et al., 2018), which is best assessed using in situ polymer sampling corrected based on PRC losses. Overall, average $C_{\text{free}}$ polymeric results were similar to average $C_{\text{free}}$ values directly measured in extracted porewater for most PAHs and PCBs. Based on comparisons performed in the present study and previously (see Gschwend et al., 2011), the accuracy of polymeric sampling can be considered high based on comparison with direct measurement methods. Polymer sampling provided the clear advantage of successfully measuring ultra-low water concentrations of the strongly hydrophobic PCBs and PAHs.

Because detailed standard protocols were available (Supporting Information, Section 4, and also Jonker et al., 2020), the private sector laboratories were able to successfully produce results similar to those generated by academic laboratories with research expertise in polymer sampling. These findings should provide confidence to a wider group of academic, government, and private sector entities to routinely adopt polymer sampling methods as a tool for contaminated sediment research as well as site characterization and management.

Supporting Information—The Supporting Information is available on the Wiley Online Library at https://doi.org/10.1002/etc.5356.

Acknowledgments—The authors thank the private sector participating laboratories: Battelle Memorial Institute, Analytical Resources, SGS AXYS, and TestAmerica. The authors also thank A. Suess (Seattle District, US Army Corps of Engineers), M. Lin (Pyron Environmental), and M. Mills and M. Lambert (US Environmental Protection Agency). The Environmental Security Technology Certification Program (ESTCP ER-201735) funded the present study.

Disclaimer—The views and opinions expressed in the present study are those of the individual authors and not those of the US Army or other sponsor organizations. The use of trade, product, or firm names in this report is for descriptive purposes only and does not imply endorsement by the US Government. Permission was granted to publish this information by the US Army Chief of Engineers. The findings of the present study are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Author Contributions Statement—Guilherme R. Lotufo: Formal analysis; writing—original draft; writing—review & editing. Mandy M. Michalsen: Conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; project administration; writing—review & editing. Danny D. Reible: Investigation; supervision; methodology; writing—review & editing. Philip M. Gschwend: Investigation; supervision; methodology; writing—review & editing. Upal Ghosh: Investigation; supervision; methodology; writing—review & editing. Alan J. Kennedy: Investigation; methodology; writing—review & editing. Kristen M. Kerns: Investigation; methodology. Magdalena I. Rakowska: Investigation; methodology; writing—review & editing. Adesewo Odetayo: Investigation. John K. MacFarlane: Investigation; writing—review & editing. Songjing Yan: Investigation. Mandar Bokare: Investigation; writing review & editing.

Data Availability Statement—Data, associated metadata, and calculation tools are available in the Supporting Information and from the corresponding author (Guilherme.Lotufo@usace.army.mil).

REFERENCES

Apell, J. N., & Gschwend, P. M. (2014). Validating the use of performance reference compounds in passive samplers to assess porewater concentrations in sediment beds. Environmental Science & Technology, 48(17), 10301–10307. https://doi.org/10.1021/es502694g

Apell, J. N., & Gschwend, P. M. (2016). In situ passive sampling of sediments in the Lower Duwamish Waterway Superfund site: Replicability, comparison with ex situ measurements, and use of data. Environmental Pollution, 218, 95–101. https://doi.org/10.1016/j.envpol.2016.08.023

Apell, J. N., Tcaciuc, A. P., & Gschwend, P. M. (2016). Understanding the rates of nonpolar organic chemical accumulation into passive samplers...
deployed in the environment: Guidance for passive sampler deployments. Integrated Environmental Assessment and Management, 12(3), 486–492. https://doi.org/10.1002/ieam.1697

Apell, J. N., Shull, D. H., Hoyt, A. M., & Gschwend, P. M. (2018). Investigating the effect of bioirrigation on in situ porewater concentrations and fluxes of polychlorinated biphenyls using passive samplers. Environmental Science & Technology, 52, 4565–4573. https://doi.org/10.1021/acs.est.7b05809

ASTM International. (2013). Standard test method for determination of parent and alkyl polycyclic aromatic hydrocarbons in sediment pore water using solid-phase microextraction and gas chromatography/mass spectrometry in selected ion monitoring mode. Designation 7363–13.

Booij, K., Robinson, C. D., Burgess, R. M., Mayer, P., Roberts, C. A., Ahrens, L., Allan, I. J., Brant, J., Jones, L., Kraus, U. R., Larsen, M. M., Lepom, P., Petersen, J., Profrock, D., Roose, P., Schafer, S., Smedes, F., Tixier, C., Vorkamp, K., & Whitehouse, P. (2016). Passive sampling in regulatory chemical monitoring of nonpolar organic compounds in the aquatic environment. Environmental Science & Technology, 50(1), 3–17. https://doi.org/10.1021/acs.est.5b04050

Borrelli, R., Tcaciuc, A. P., Verginelli, I., Baciocchi, R., Guzzella, L., Cesti, P., Zaninetta, L., & Gschwend, P. M. (2018). Performance of passive sampling with low-density polyethylene membranes for the estimation of freely dissolved DDE concentrations in lake environments. Chemosphere, 200, 227–236. https://doi.org/10.1016/j.chemosphere.2018.02.077

Borges, R. M., Lohmann, R., Schubauer-Berigan, J. P., Reitsma, P., Perron, M. M., Leftovitz, L., & Cantwell, M. G. (2015). Application of passive sampling for measuring dissolved concentrations of organic contaminants in the water column at three marine superfund sites. Environmental Toxicology and Chemistry, 34(8), 1720–1733. https://doi.org/10.1002/etc.2995

Borg, R. M., & McKinney, R. A. (1999). Importance of intermittent, overlying water and whole sediment exposures to bioaccumulation by marine bivalves. Environmental Pollution, 104(3), 373–382. https://doi.org/10.1016/S0269-7491(98)00194-8

Burkhard, L. P., Mount, D. R., & Burgess, R. M. (2017). Developing sediment remediation goals at superfund sites based on porewater for the protection of benthic organisms from direct toxicity to non-ionic organic contaminants (EPA/600/R 15/289). Office of Research and Development National Human and Environmental Effects Research Laboratory; National Health and Environmental Effects Research Laboratory, Mid-Continent Ecology Division, U. S. Environmental Protection Agency.

Comelissen, G., & Gustafsson, O. (2005). Prediction of large variation in biota to sediment accumulation factors due to concentration-dependent black carbon adsorption of planar hydrophobic organic compounds. Environmental Toxicology and Chemistry, 24(3), 495–498. doi:10.1897/04-152R.1

Comelissen, G., Wiberg, K., Broman, D., Arp, H. P. H., Persson, Y., Sundqvist, K., & Jonsson, P. (2008). Freely dissolved concentrations and sediment-water activity ratios of PCDD/Fs and PCBs in the open Baltic Sea. Environmental Science & Technology, 42(23), 8733–8739. https://doi.org/10.1021/es8018579

Di Toro, D. M., Zarba, C. S., Hansen, D. J., Berry, W. J., Cowan, C. E., Pavlou, S. P., Allen, H. E., Thomas, N. A., & Paquin, P. R. (1991). Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. Environmental Toxicology and Chemistry, 10, 1541–1583. https://doi.org/10.1002/etc.5620101203

Endo, S., Yabuki, Y., & Tanaka, S. (2017). Comparing polycatenylic and poloxymethylene passive samplers for measuring sediment porewater concentrations of polychlorinated biphenyls: Mutual validation and possible correction by polymer-polymer partition experiment. Chemosphere, 184, 358–365. https://doi.org/10.1016/j.chemosphere.2017.06.005

Fernandez, L. A., & Gschwend, P. M. (2015). Predicting bioaccumulation of polycyclic aromatic hydrocarbons in soft-shelled clams (Mya arenaria) using field deployments of polystyrene passive samplers. Environmental Toxicology and Chemistry, 34(5), 993–1000. https://doi.org/10.1002/etc.2892

Fernandez, L. A., Lao, W., Maruya, K. A., & Burgess, R. M. (2014). Calculating the diffusive flux of persistent organic pollutants between sediments and the water column at the Palos Verdes Shelf superfund site using polymeric passive samplers. Environmental Science & Technology, 48(7), 3925–3934. https://doi.org/10.1021/es404475c

Fernandez, L. A., MacFarlane, J. K., Tcaciuc, A. P., & Gschwend, P. M. (2009). Measurement of freely dissolved PAH concentrations in sediment beds using passive sampling with low-density polyethylene strips. Environmental Science & Technology, 43(5), 1430–1436. https://doi.org/10.1021/es802288w

Finkelstein, K., Beckvar, N., & Dillon, T. (2017). Benthic injury dose-response models for polychlorinated biphenyl-contaminated sediment using equilibrium partitioning. Environmental Toxicology and Chemistry, 36(5), 1311–1329. https://doi.org/10.1002/etc.3662

Ghosh, U., Kan Driscoll, S., Burgess, R. M., Jonker, M. T., Reible, D., Beegan, F., & Beegan, C. (2014). Passive sampling methods for contaminated sediment remediation: Guidance for collection, calibration, and implementation. Integrated Environmental Assessment and Management, 10(2), 210–223. https://doi.org/10.1002/ieam.1507

Ghosh, U., Weber, A. S., Jensen, N. J., & Smith, J. R. (2000). Relationship between PCB desorption equilibrium, kinetics, and availability during land bioretention. Environmental Science & Technology, 34(12), 2542–2546. https://doi.org/10.1021/es9905339

Greenberg, M. S., Chapman, P. M., Allan, I. J., Anderson, K. A., Apitz, S. E., Beegan, C., Bridges, T. S., Brown, S. S., Cargill, J. G., McCulloch, M. C., Menzie, C. A., Shine, J. P., & Parkerton, T. F. (2014). Passive sampling methods for contaminated sediments: Risk assessment and management. Integrated Environmental Assessment and Management, 10(2), 224–236. https://doi.org/10.1002/ieam.1511

Gschwend, P. M., MacFarlane, J. K., Reible, D. D., Lu, X., Hawthorne, S. B., Nakles, D. V., & Thompson, T. (2011). Comparison of polymeric samplers for accurately assessing PCBs in porewaters. Environmental Toxicology and Chemistry, 30(6), 1288–1296. https://doi.org/10.1002/etc.510

Gschwend, P. M., Tcaciuc, A. P., & Apell, J. N. (2014). Passive PE sampling in support of in situ remediation of contaminated sediments—Passive sampling PCR calculation software user’s guide. ESTCP Project ER-2010. https://apps.dtic.mil/citations/ADA621918

Hawthorne, S. B., Jonker, M. T. O., Van der Heijden, S. A., Grabanski, C. B., Azzolina, N. A., & Miller, D. J. (2011). Measuring picogram per liter concentrations of freely dissolved parent and alkyl PAHs (PAH-34), using passive sampling with poloxymethylene. Analytical Chemistry, 83(17), 7654–7671. https://doi.org/10.1021/ac201411v

Jahnke, A., Mayer, P., & McLachlan, M. S. (2012). Sensitive equilbrium sampling to study polychlorinated biphenyl disposition in Baltic Sea sediment. Environmental Science & Technology, 46(18), 10114–10122. https://doi.org/10.1021/es302330v

Jalalizadeh, M., & Ghosh, U. (2017). Analysis of measurement errors in passive sampling of porewater PCB concentrations under static and periodically vibrated conditions. Environmental Science & Technology, 51(12), 7018–7027. https://doi.org/10.1021/acs.est.7b01020

Jonker, M. T. O., Burgess, R. M., Ghosh, U., Gschwend, P. M., Hale, S. E., Lohmann, R., Lydy, M. J., Marshall, A. R., Reible, D. D., & Tcaciuc, A. P. (2020). Ex situ determination of freely dissolved concentrations of hydrophobic organic chemicals in sediments and soils: Basis for interpreting toxicity and assessing bioavailability, risks and remediation necessity. Nature Protocols, 15, 1800. https://doi.org/10.1038/s41596-020-0311-y

Jonker, M. T. O., van der Heijden, S. A., Adelman, D., Apell, J. N., Burgess, R. M., Choi, Y., Fernandez, L. A., Flavetta, G. M., Ghosh, U., Gschwend, P. M., Heigele, C. E., Jalalizadeh, M., Khairy, M., Lampi, M. A., Lao, W., Lohmann, R., Lydy, M. J., Maruya, K. A., Nutile, S. A., … Wu, Y. (2018). Advancing the use of passive sampling in risk assessment and management of sediments contaminated with hydrophobic organic chemicals: Results of an international ex situ passive sampling interlaboratory comparison. Environmental Science & Technology, 52(6), 3574. https://doi.org/10.1021/acs.est.7b05752
Joyce, A. S., & Burgess, R. M. (2018). Using performance reference compounds to compare mass transfer calibration methodologies in passive samplers deployed in the water column. *Environmental Toxicology and Chemistry, 37*, 2089–2097. https://doi.org/10.1002/etc.4167

Joyce, A. S., Fernandez, L. A., & Burgess, R. M. (2020). In situ investigation of performance reference compound-based estimates of PCB equilibrated passive sampler concentrations and C_sed in the marine water column. *Environmental Toxicology and Chemistry, 39*, 1165–1173. https://doi.org/10.1002/etc.4714

Khalil, M. F., Ghosh, U., & Kretjinger, J. P. (2006). Role of weathered coal tar pitch in the partitioning of polycyclic aromatic hydrocarbons in manufactured gas plant site sediments. *Environmental Science & Technology, 40*(18), 5681–5687. https://doi.org/10.1021/es0607032

Kretjinger, J. P., Neuhauser, E. F., Doherty, F. G., & Hawthorne, S. B. (2007). Greatly reduced bioavailability and toxicity of polycyclic aromatic hydrocarbons to Hyla lancea in sediments from manufactured-gas plant sites. *Environmental Toxicology and Chemistry, 26*(6), 1146–1157. https://doi.org/10.1897/06-207R.1

Lampert, D. J., Lu, X. X., & Reible, D. D. (2011). Predicting bioavailability of polycyclic aromatic hydrocarbons in field-collected sediments: Application of Tenax extraction and matrix solid phase microextraction techniques. *Chemosphere, 71*(2), 337–344. https://doi.org/10.1016/j.chemosphere.2007.09.001

Lohmann, R., Burgess, R. M., Cantwell, M. G., Ryba, S. A., MacFarlane, J. K., & Gschwend, P. M. (2004). Dependency of polychlorinated biphenyl and polycyclic aromatic hydrocarbon bioaccumulation in Mya arenaria on both water column and sediment bed chemical activities. *Environmental Toxicology and Chemistry, 23*(11), 2551–2562. https://doi.org/10.1897/03-400

Lu, X., Reible, D. D., & Fleeger, J. W. (2006). Bioavailability of polycyclic aromatic hydrocarbons in field-collected Anacostia River (Washington, DC) sediment. *Environmental Toxicology and Chemistry, 25*(11), 2829–2834. https://doi.org/10.1897/05-696R.1

Lu, X., Skwarski, A., Drake, B., & Reible, D. D. (2011). Predicting bioavailability of PAHs and PCBs with porewater concentrations measured by solid-phase microextraction fibers. *Environmental Toxicology and Chemistry, 30*(5), 1109–1116. https://doi.org/10.1002/etc.495

Lydy, M. J., Landrum, P. F., Oen, A. M. P., Allinson, M., Smedes, F., Harwood, A. D., Li, H., Maruya, K. A., & Liu, J. (2014). Passive sampling methods for contaminated sediments: State of the science for organic contaminants. In *Integrated Environmental Assessment and Management, 10*(2), 167–178. https://doi.org/10.1002/ieam.1503

Mayer, P., Parkerton, T. F., Adams, R. G., Cargill, J. G., Gan, J., Gouin, T., Gschwend, P. M., Hawthorne, S. B., Helm, P., Witt, G., You, J., & Escher, B. I. (2014). Passive sampling methods for contaminated sediments: Scientific rationale supporting use of freely dissolved concentrations. In *Integrated Environmental Assessment and Management, 10*(2), 197–209. https://doi.org/10.1002/ieam.1508

Mayer, P., Vaes, W. H. J., Wijnker, F., Legierse, K. C. H. M., Kraaij, R. H., Tolls, J., & Hermens, J. L. M. (2000). Sensing dissolved sediment porewater concentrations of persistent and bioaccumulative pollutants using disposable solid-phase microextraction fibers. *Environmental Science & Technology, 34*(24), 5177–5183. https://doi.org/10.1021/es001179g

Michalsen, M. M., Kennedy, A. J., Lotufo, G. R., Kems, K., Suess, A., Lin, M., Mill, M., Lambert, M., Reible, D. D., Rakowska, M., Odetayo, A., Ghosh, U., Bokare, M., Gschwend, P. M., & MacFarlane, J. K. (2021). Standardizing polymeric sampling method for measuring freely dissolved-organic contaminants in sediment porewater. Final technical report to the Department of Defense Environmental Security Technology Certification Program, project ER-201735.

Park, S. S., & Ertfeld, K. M. (1999). The effect of sediment organic carbon content on bioavailability of hydrophobic compounds in aquatic ecosystems. *Environmental Pollution, 105*(1), 9–15. https://doi.org/10.1016/S0269-7491(99)00216-4

Parkerton, T. F., & Maruya, K. A. (2014). Passive sampling in contaminated sediment assessment: Building consensus to improve decision making. In *Integrated Environmental Assessment and Management, 10*(2), 163–166. https://doi.org/10.1002/ieam.1488

Reinhagiu, M., Parkerton, T. F., & Witt, G. (2020). Comparison of in situ and ex situ equilibrium passive sampling for measuring freely dissolved concentrations of parent and alkylated polycyclic aromatic hydrocarbons in sediments. *Environmental Toxicology and Chemistry, 39*(11), 2169. https://doi.org/10.1002/etc.4849

Sanders, J. P., Andrade, N. A., & Ghosh, U. (2018). Evaluation of passive sampling polymers and nonequilibrium adjustment methods in a multiyear surveillance of sediment porewater PCBs. *Environmental Toxicology and Chemistry, 37*(9), 2487–2495. https://doi.org/10.1002/etc.4223

Shen, X., & Reible, D. (2019). An analytical model for the fate and transport of performance reference compounds and target compounds around cylindrical passive samplers. *Chemosphere, 232*, 489–495. https://doi.org/10.1016/j.chemosphere.2019.05.198

Schmidt, S. N., Wang, A. P., Gidley, P. T., Wooley, A. H., Lotufo, G. R., Burgess, R. M., & Mayer, P. (2017). Cross validation of two partitioning-based sampling approaches in mesocosms containing PCB contaminated field sediment, biota, and activated carbon amendment. *Environmental Science & Technology, 51*(17), 9996–10004. https://doi.org/10.1021/acs.est.7b01909

Thomas, C. L., & Reible, D. D. (2015). Modeling compound loss from polydimethylsiloxane passive samplers. *Chromatography, 2*(4), 611–624. https://doi.org/10.3390/chromatography2040611

Tomaszewski, J. E., & Luthy, R. G. (2008). Field deployment of polyethylene devices to measure PCB concentrations in porewater of contaminated sediment. *Environmental Science & Technology, 42*(16), 6086–6091. https://doi.org/10.1021/es800582a

Trimble, T. A., You, J., & Lydy, M. J. (2008). Bioavailability of PCBs from field-collected sediments: Application of Tenax extraction and matrix SPME techniques. *Chemosphere, 71*(2), 337–344. https://doi.org/10.1016/j.chemosphere.2007.09.001

U.S. Environmental Protection Agency. (1984). 40 CFR, Appendix A to Part 136, Method 1625 Revision 8, semivolatile organic compounds by isotope dilution GC/MS.

U.S. Environmental Protection Agency. (1988). Determination of total organic carbon in sediment. USEPA Region II, Environmental Services Division, Monitoring Management Branch.

U.S. Environmental Protection Agency. (1996a). Method 8270C. Semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS).

U.S. Environmental Protection Agency. (1996b). Method 8082. Polychlorinated biphenyls (PCBs) by gas chromatography.

U.S. Environmental Protection Agency. (1998). Test methods for evaluating solid waste (SW 846). Third edition and revised update III. Method 8000 and method 8270D. Office of Solid Waste and Emergency Response.

U.S. Environmental Protection Agency. (2008). USEPA contract laboratory program national functional guidelines for superfund organic methods data review (EPA-540-R-08-01).

U.S. Environmental Protection Agency. (2010). Method 1668C—Chlorinated Inorganic Compounds in water, soil, sediment, biosolids, and tissue by HRGC/HRMS.

U.S. Environmental Protection Agency. (2012). Guidelines for using passive samplers to monitor nonionic organic contaminants at superfund sediment sites. sediment assessment and monitoring sheet (Report No. OSWER Directive 9200.1-110 F5). Office of Superfund Remediation and Technology Innovation, Office of Research and Development.

U.S. Environmental Protection Agency. (2015). Guidance for methods development and methods validation for the CRCA program. https://www.epa.gov/sites/production/files/2015-10/documents/methoddev.pdf

U.S. Environmental Protection Agency. (2016). Contract laboratory program national functional guidelines for high resolution methods data review (USEPA 542-B-16-001). Office of Superfund Remediation and Technical Innovation.

U.S. Environmental Protection Agency. (2017). Contract laboratory program national functional guidelines for organic superfund data review (OLEM 9355.0-136, EPA-540-R-2017-002). Office of Superfund Remediation and Technical Innovation.

Van den Berg, M., Birbaum, L. S., Denison, M., De Vito, M., Farland, W., Feeley, M., Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D., Tohyama, C., Titzsch, A., Tuomisto, J., Tysklind, M., Walker, N., & Peterson, R. E. (2006). The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicological Sciences, 93*, 223–241. https://doi.org/10.1093/toxsci/kfn055
Vinturella, A. E., Burgess, R. M., Coull, B. A., Thompson, K. M., & Shine, J. P. (2004). Use of passive samplers to mimic uptake of polycyclic aromatic hydrocarbons by benthic polychaetes. *Environmental Science & Technology*, 38(4), 1154–1160. https://doi.org/10.1021/es034706f

Werner, D., Hale, S. E., Ghosh, U., & Luthy, R. G. (2010). Polychlorinated biphenyl sorption and availability in field-contaminated sediments. *Environmental Science & Technology*, 44(8), 2809–2815. https://doi.org/10.1021/es902325t

Yan, S., Rakowska, M., Shen, X., Himmer, T., Irvine, C., Zajac-Fay, R., Eby, J., Janda, D., Ohannessian, S., & Reible, D. D. (2020). Bioavailability assessment in activated carbon treated coastal sediment with in situ and ex situ porewater measurements. *Water Research*, 185, 116259. https://doi.org/10.1016/j.watres.2020.116259