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

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

<sup>a</sup>Environmental Laboratory, US Army Engineer Research and Development Center, Vicksburg, Mississippi, USA

<sup>b</sup>Department of Civil, Environmental, and Construction Engineering, Texas Tech University, Lubbock, Texas, USA

<sup>c</sup>Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA

<sup>d</sup>Department of Chemical, Biochemical, and Environmental Engineering, University of Maryland Baltimore County, Baltimore, Maryland, USA

<sup>e</sup>Seattle 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 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

This article includes online-only Supporting Information.

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Guilherme R. Lotufo and Mandy M. Michalsen contributed equally to this study.

\* Address correspondence to Guilherme.Lotufo@usace.army.mil

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## 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 as 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 bioaccumulation and toxicity of hydrophobic organic compounds (HOCs) to benthic and aquatic organisms are well predicted by  $C_{free}$  values. For example, Werner 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  $C_{free}$ . In another study, Kreitinger et al. (2007) showed that the toxicity of polycyclic aromatic hydrocarbons (PAHs) to the freshwater amphipod *Hyaletta azteca* was accurately predicted by  $C_{free}$ , whereas no clear threshold was observed for toxicity based on bulk sediment concentrations. Therefore, measuring  $C_{free}$  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  $C_{free}$  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  $C_{free}$  in porewater (Burgess & McKinney, 1999; Ghosh et al., 2000; Khalil et al., 2006; Lu et al., 2006). Moreover,  $C_{free}$  is generally very low (e.g., 10 pg/L) for strongly hydrophobic compounds (Cornelissen et al., 2008; Hawthorne et al., 2011; Jahnke et al., 2012) and typically below the limits of detection of traditional analytical methods for water. Traditional methods to predict  $C_{free}$  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  $C_{free}$  (Gschwend et al., 2011; Parkerton & Maruya, 2014). The development of partitioning-based, non-depletive polymer sampling methods has allowed for the accurate determination of  $C_{free}$  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  $C_{free}$  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  $C_{free}$ . 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  $C_{free}$  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  $C_{free}$  for a wide range of nonionized organic chemicals of concern with octanol–water partition coefficients ( $K_{OW}$  values) larger than  $\sim 10^3$ . 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, interlaboratory polymer sampling methodology evaluation and concluded that overall interlaboratory variability was large (by a factor of  $\sim 10$ ) 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  $C_{free}$  (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  $C_{free}$  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 micro-extraction (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  $C_{free}$  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  $C_{free}$  values of PAHs and PCBs for comparison with polymer-derived  $C_{free}$  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  $C_{free}$  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  $C_{free}$  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  $C_{free}$  results obtained via actively mixed and static exposures were then compared against the  $C_{free}$  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  $C_{free}$ . Laboratory-specific loading durations are provided in the Supporting Information, Table S3.

### Sediment exposures: Active versus static exposure conditions for determination of $C_{free}$

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 nondepletive 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 ( $22 \pm 5^\circ\text{C}$ ), 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 ( $f_{\text{eq}}$ ) 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,  $f_{\text{eq}}$  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  $f_{\text{eq}}$  values were determined according to Gschwend et al. (2014) and Apell and Gschwend (2016). Subsequently, these  $f_{\text{eq}}$  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  $C_{\text{free}}$  results using the following equation:

$$C_{\text{free}} = \frac{C_{\text{Polymer}\infty}}{K_{\text{polymer:water}}} \quad (1)$$

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

### Direct porewater extraction with colloid separation

The  $C_{\text{free}}$  results obtained via active and static exposures were compared against the  $C_{\text{free}}$  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- $\mu\text{m}$  PDMS coating (nominal) was purchased from Polymicro Technologies™. The PDMS fibers cut from this source were cleaned with hexane and acetonitrile, 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  $\mu\text{m}$  (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  $^{13}\text{C}_6$ -labeled phenanthrene, fluoranthene, chrysene, and indeno[1,2,3-*cd*]pyrene, and  $^{13}\text{C}_{12}$ -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  $4^\circ\text{C}$  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 Impellor 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 for acenaphthene 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 apportioned 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).

### Data quality and analysis

Participating laboratories submitted full Level IV data packages (USEPA, 2008) for PAH and PCB analytical data for polymers. A Level IV data package is a comprehensive report

that allows a data validator to evaluate analytical data and determine usability, including analytical data results, quality control, and sample handling information. All polymer chemistry data packages were subject to a Stage 4 validation (as defined in USEPA, 2008) per applicable data validation guidance (USEPA, 2016, 2017) by an independent chemist. Data were determined to be of suitable quality for intended use in the present interlaboratory method validation study. Data submitted by academic laboratories were not validated.

For analysis of calibration checks and polymeric samplers preloaded with PRCs, data variability was assessed using the CV (expressed as a percentage), and data accuracy was assessed by comparing the result with a reference value. Statistical comparisons of  $C_{\text{free}}$  values for PAHs and PCB congeners across laboratories were performed using SigmaStat Ver 3.5 software (SSPS). Normality was confirmed by the Shapiro–Wilk test, and equal variance was confirmed using the Brown–Forsythe test. Normality was achieved in most cases after the data were log-transformed. One-way analyses of variance (ANOVAs) were performed to determine statistically significant differences ( $\alpha=0.05$ ) across three or more treatments. The Holm–Sidak method was employed for pairwise multiple comparisons to determine statistical significance between treatments. When assumptions of parametric ANOVA were not met for log-transformed data, the nonparametric Kruskal–Wallis one-way ANOVA on ranks was applied, and the Dunn's method was employed for pairwise multiple comparisons to determine statistical significance between treatments.

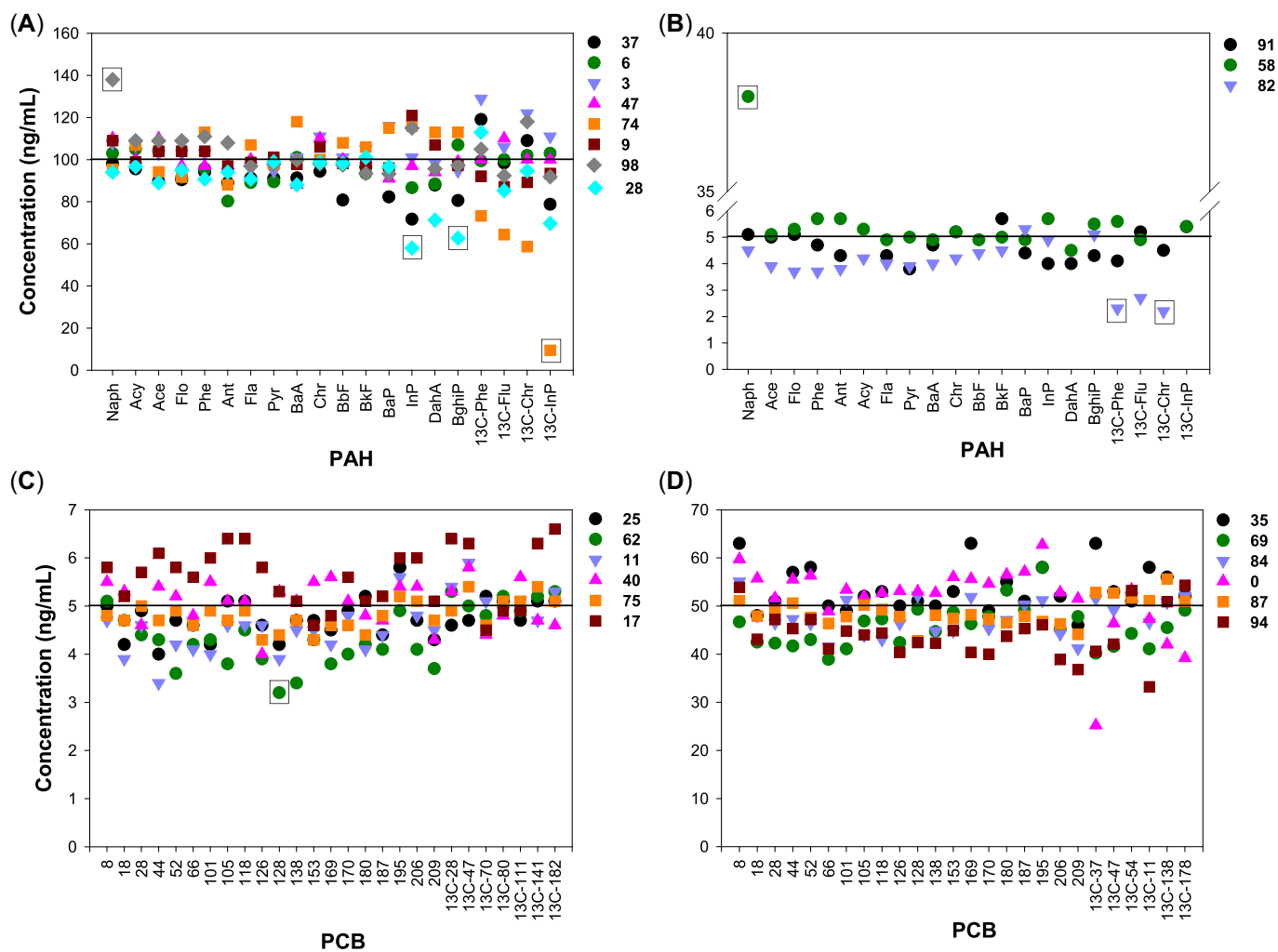
## RESULTS AND DISCUSSION

### 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  $\pm 30\%$  difference from the reference value for native target analytes and  $\pm 50\%$  for isotopically labeled analytes selected as PRCs (Figure 1). Average calibration check standard concentrations reported by laboratories were within  $\pm 30\%$  of reference concentrations for PCB and PAH natives 83% of the time and were within  $\pm 50\%$  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



**FIGURE 1:** Average concentrations of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyl (PCB) congeners, including labeled compounds selected for use as performance reference compounds (PRCs), in calibration standards by participating laboratories. **(A)** PAHs, low sensitivity; **(B)** PAHs, high sensitivity; **(C)** PCBs, low sensitivity; **(D)** PCBs, high sensitivity. Colors indicate results from six different laboratories designated by numbers. The horizontal line indicates the reference concentration. Squares around data points indicate exceedance of 2-fold difference criterion. For abbreviations, see footnote to Table 1.

replicate measurements below 20% except for  $^{13}\text{C}_6$ -indeno [1,2,3-*cd*]pyrene for three laboratories and for the  $^{13}\text{C}$ -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).  $^{13}\text{C}$ -labeled PCB PRCs were within  $\pm 50\%$  of reference concentrations for most laboratories (Supporting Information, Figure S1). A single laboratory reported an exceedance for a single PAH PRC ( $^{13}\text{C}_6$ -indeno[1,2,3-*cd*]pyrene) in PDMS. A single laboratory also reported concentrations for the  $^{13}\text{C}$ -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  $C_{free}$ , 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  $^{13}\text{C}$ -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 homogeneous 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 $C_{free}$

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  $C_{free}$  was low, with most reported CVs on replicate measurements below 50%, with an overall average of  $24\% \pm 19\%$  for active LDPE exposures,  $23\% \pm 16\%$  for static LDPE exposures,  $19\% \pm 18\%$  for active PDMS exposures, and  $15\% \pm 11\%$  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  $C_{free}$  was low, with an overall CV average of  $21\% \pm 15\%$  for active LDPE exposures,  $26\% \pm 25\%$  for static LDPE exposures,  $19\% \pm 13\%$  for active PDMS exposures, and  $11\% \pm 4\%$  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,  $C_{free}$  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, benz[*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 for acenaphthene, acenaphthylene, fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene and benzo[*ghi*]perylene for PDMS and fluoranthene and benzo[*k*]fluoranthene for LDPE



**TABLE 1:** Polycyclic aromatic hydrocarbon  $C_{free}$  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							
	Laboratory	15	52	84	58	50	34	AVG	SD	15	52	84	58	50	34	AVG
Naph	45	37	58	70	ND	22	<b>46</b>	<b>19</b>	48	36	67	56	ND	38	<b>49</b>	<b>13</b>
Ace	28	29	50	54	27	19	<b>34</b>	<b>14</b>	44	10	39	13	18	11	<b>22</b>	<b>15</b>
Flo	30	31	51	12	18	21	<b>27</b>	<b>14</b>	47	17	39	12	15	11	<b>23</b>	<b>16</b>
Phe	28	29	49	8	15	20	<b>25</b>	<b>14</b>	44	10	31	10	8	13	<b>19</b>	<b>15</b>
Ant	26	31	49	11	15	19	<b>25</b>	<b>14</b>	43	13	34	10	8	15	<b>21</b>	<b>15</b>
Acy	13	21	37	ND	11	ND	<b>21</b>	<b>12</b>	30	14	25	ND	20	ND	<b>22</b>	<b>7</b>
Fla	23	25	42	8	12	16	<b>21</b>	<b>12</b>	36	10	21	9	9	11	<b>16</b>	<b>11</b>
Pyr	22	23	41	4	12	15	<b>20</b>	<b>13</b>	34	9	18	10	9	11	<b>15</b>	<b>10</b>
BaA	22	22	41	6	12	17	<b>20</b>	<b>12</b>	37	11	15	10	9	13	<b>16</b>	<b>11</b>
Chr	21	22	39	5	12	14	<b>19</b>	<b>11</b>	35	33	16	11	8	9	<b>19</b>	<b>12</b>
BbF	17	18	33	9	12	14	<b>17</b>	<b>9</b>	34	16	15	11	9	22	<b>18</b>	<b>9</b>
BkF	15	16	34	3	12	12	<b>15</b>	<b>10</b>	38	21	23	17	10	12	<b>20</b>	<b>10</b>
BaP	13	18	33	3	11	13	<b>15</b>	<b>10</b>	49	24	18	16	10	14	<b>22</b>	<b>14</b>
DahA	11	13	28	ND	10	13	<b>15</b>	<b>7</b>	63	30	27	ND	14	51	<b>37</b>	<b>20</b>
InP	14	10	25	5	9	11	<b>12</b>	<b>7</b>	79	42	19	18	16	35	<b>35</b>	<b>24</b>
BghiP	13	13	26	7	9	10	<b>13</b>	<b>7</b>	57	29	16	20	18	27	<b>28</b>	<b>15</b>
AVG	<b>21</b>	<b>22</b>	<b>40</b>	<b>15</b>	<b>13</b>	<b>16</b>	—	—	<b>45</b>	<b>20</b>	<b>27</b>	<b>16</b>	<b>12</b>	<b>19</b>	—	—

PAH	PDMS, active exposure								PDMS, static exposure							
	Laboratory	38	52	84	58	50	34	AVG	SD	38	52	84	58	50	34	AVG
Naph	35	34	73	61		30	<b>47</b>	<b>19</b>	21	46	31	59	ND	32	<b>38</b>	<b>15</b>
Ace	8	5	40	44	40	5	<b>24</b>	<b>20</b>	5	10	10	14	22	6	<b>11</b>	<b>6</b>
Flo	4	7	38	47	21	6	<b>21</b>	<b>18</b>	9	6	9	11	21	9	<b>11</b>	<b>5</b>
Phe	2	4	36	50	12	6	<b>18</b>	<b>20</b>	5	2	7	9	22	8	<b>9</b>	<b>7</b>
Ant	3	6	37	46	12	8	<b>19</b>	<b>18</b>	1	5	9	9	27	7	<b>10</b>	<b>9</b>
Acy	1	12	22		29	13	<b>15</b>	<b>11</b>	5	17	11	ND	23	10	<b>13</b>	<b>7</b>
Fla	9	5	33	22	4	7	<b>14</b>	<b>12</b>	9	2	6	9	20	9	<b>9</b>	<b>6</b>
Pyr	11	5	34	19	4	7	<b>13</b>	<b>11</b>	5	2	5	8	18	11	<b>8</b>	<b>6</b>
BaA	9	7	36	26	6	9	<b>16</b>	<b>13</b>	15	2	8	12	26	16	<b>13</b>	<b>8</b>
Chr	8	7	37	23	6	6	<b>14</b>	<b>13</b>	8	6	8	12	26	12	<b>12</b>	<b>7</b>
BbF	12	8	35	26	8	17	<b>18</b>	<b>11</b>	31	4	10	ND	29	17	<b>18</b>	<b>12</b>
BkF	8	12	33	12	6	12	<b>14</b>	<b>10</b>	10	3	18	ND	26	17	<b>15</b>	<b>9</b>
BaP	17	14	37	16	7	14	<b>17</b>	<b>10</b>	28	4	7	ND	27	27	<b>19</b>	<b>12</b>
DahA	80	14		ND	9	31	<b>34</b>	<b>32</b>	19	11	ND	ND	31	ND	<b>20</b>	<b>10</b>
InP	15	16	11	ND	8	18	<b>14</b>	<b>4</b>	20	4	10	ND	31	34	<b>20</b>	<b>13</b>
BghiP	8	14	9	ND	7	11	<b>10</b>	<b>3</b>	26	6	10	ND	25	34	<b>20</b>	<b>12</b>
AVG	<b>14</b>	<b>11</b>	<b>34</b>	<b>33</b>	<b>12</b>	<b>13</b>	—	—	<b>14</b>	<b>8</b>	<b>11</b>	<b>16</b>	<b>25</b>	<b>17</b>	—	—

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

Ace = acenaphthene; Acy = acenaphthylene; Ant = anthracene; AVG = average; BaA = benzo[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.

(Supporting Information, Table S7). 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  $C_{free}$  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 2:** Polychlorinated biphenyl  $C_{free}$  coefficient of variation by participating laboratory and average and standard deviation across laboratories for low-density polyethylene and polydimethylsiloxane using the active or static exposure method

PCB	Active exposure								Static exposure								
	Laboratory	15	52	84	58	50	34	AVG	SD	15	52	84	58	50	34	AVG	SD
<b>LDPE</b>																	
PCB-008	27	61	16	16	7	19	25	19	25	36	18	6	4	12	17	12	
PCB-018	26	56	15	8	5	19	<b>22</b>	<b>18</b>	25	29	17	12	6	9	<b>16</b>	<b>9</b>	
PCB-028	28	59	16	9	8	18	<b>23</b>	<b>19</b>	27	33	16	5	5	9	<b>16</b>	<b>12</b>	
PCB-044	24	54	13	11	7	17	<b>21</b>	<b>17</b>	24	27	14	7	11	8	<b>15</b>	<b>8</b>	
PCB-052	26	53	14	10	12	17	<b>22</b>	<b>16</b>	22	25	14	9	13	8	<b>15</b>	<b>7</b>	
PCB-066	28	53	14	8	6	17	<b>21</b>	<b>17</b>	22	29	14	7	13	24	<b>18</b>	<b>8</b>	
PCB-101	20	50	14	6	4	15	<b>18</b>	<b>17</b>	18	27	14	6	18	39	<b>20</b>	<b>11</b>	
PCB-105	29	52	13	9	10	17	<b>22</b>	<b>17</b>	44	32	16	11	22	69	<b>32</b>	<b>22</b>	
PCB-118	20	51	14	8	7	16	<b>19</b>	<b>16</b>	21	32	15	9	21	62	<b>27</b>	<b>19</b>	
PCB-138	20	48	12	11	15	20	<b>21</b>	<b>14</b>	24	27	16	8	23	90	<b>31</b>	<b>30</b>	
PCB-153	22	46	12	10	7	16	<b>19</b>	<b>14</b>	20	26	18	11	22	95	<b>32</b>	<b>31</b>	
PCB-170	43	46	9	10	ND	16	<b>25</b>	<b>18</b>	41	28	27	ND	ND	123	<b>55</b>	<b>46</b>	
PCB-180	13	45	11	10	10	17	<b>18</b>	<b>14</b>	20	29	26	ND	17	118	<b>42</b>	<b>43</b>	
PCB-187	19	45	9	8	6	18	<b>18</b>	<b>15</b>	21	28	21	ND	34	120	<b>45</b>	<b>42</b>	
AVG	<b>25</b>	<b>51</b>	<b>13</b>	<b>10</b>	<b>8</b>	<b>17</b>	—	—	<b>25</b>	<b>29</b>	<b>17</b>	<b>8</b>	<b>16</b>	<b>56</b>	—	—	
<b>PDMS</b>																	
PCB-008	41	3	15	14	13	14	<b>17</b>	<b>13</b>	9	5	7	9	9	10	<b>8</b>	<b>2</b>	
PCB-018	43	7	13	14	13	14	<b>17</b>	<b>13</b>	10	12	5	6	7	10	<b>8</b>	<b>3</b>	
PCB-028	46	3	15	12	17	12	<b>17</b>	<b>15</b>	12	12	5	8	8	8	<b>9</b>	<b>3</b>	
PCB-044	48	5	14	14	14	14	<b>18</b>	<b>15</b>	8	8	4	7	9	8	<b>7</b>	<b>2</b>	
PCB-052	47	5	14	13	13	13	<b>17</b>	<b>15</b>	8	12	5	6	8	10	<b>8</b>	<b>2</b>	
PCB-066	52	7	15	11	12	11	<b>18</b>	<b>17</b>	8	11	6	7	11	9	<b>9</b>	<b>2</b>	
PCB-101	53	11	15	12	14	12	<b>19</b>	<b>17</b>	11	10	10	6	13	10	<b>10</b>	<b>2</b>	
PCB-105	56	10	16	4	14	4	<b>17</b>	<b>19</b>	16	11	7	ND	19	12	<b>13</b>	<b>5</b>	
PCB-118	45	11	14	15	6	15	<b>18</b>	<b>14</b>	11	14	10	ND	21	7	<b>13</b>	<b>5</b>	
PCB-138	32	12	17	16	14	16	<b>18</b>	<b>7</b>	10	15	14	ND	11	9	<b>12</b>	<b>2</b>	
PCB-153	53	13	16	11	17	11	<b>20</b>	<b>16</b>	21	15	18	ND	15	8	<b>15</b>	<b>5</b>	
PCB-170	26	21	34	9	ND	9	<b>20</b>	<b>11</b>	15	13	12	ND	ND	15	<b>14</b>	<b>2</b>	
PCB-180	36	22	17	11	17	11	<b>19</b>	<b>9</b>	29	14	16	ND	14	7	<b>16</b>	<b>8</b>	
PCB-187	33	31	28	13	20	13	<b>23</b>	<b>9</b>	9	ND	ND	ND	11	13	<b>11</b>	<b>2</b>	
AVG	<b>44</b>	<b>11</b>	<b>17</b>	<b>12</b>	<b>14</b>	<b>12</b>	—	—	<b>13</b>	<b>12</b>	<b>9</b>	<b>10</b>	<b>7</b>	<b>12</b>	—	—	

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

AVG = average; CV = coefficients of variation; LDPE = low-density polyethylene; PCB = polychlorinated biphenyl; PDMS = polydimethylsiloxane; SD = standard deviation.

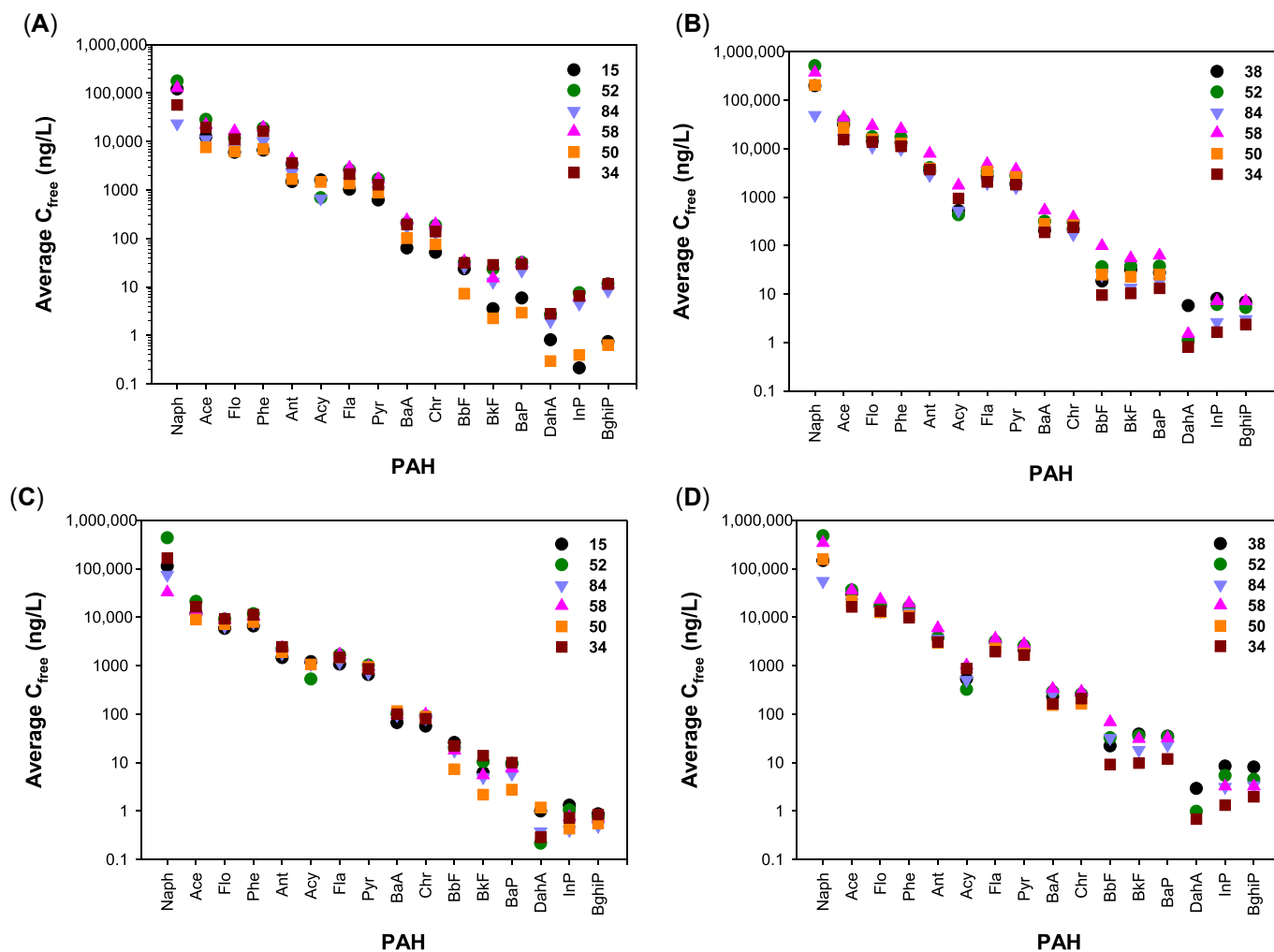
polymer extracts. The polymer sampling methodology used in the present study is similar to those recently published (Jonker et al., 2020). Overall, high differences across laboratories were observed for naphthalene, the most volatile PAH, and for very hydrophobic PAHs and PCB congeners (Figures 2 and 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  $0.93 \pm 0.22$  for PAHs and  $0.98 \pm 0.22$  for PCBs, and the slopes of the log–log regressions for the plots in Figure 4 were  $1.00 (\pm 0.01; r^2 = 0.99)$  for PAHs and  $0.98 (\pm 0.01; r^2 = 0.99)$  for PCBs. The intercepts for the correlations were  $0.06 \pm 0.01$  and  $0.03 \pm 0.01$  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  $0.87 \pm 0.84$  for PAHs and  $1.35 \pm 2.28$  for PCBs; the slopes of the log–log regressions for the plots in Figure 4 were  $1.08 (\pm 0.026; r^2 = 0.95)$  for PAHs and  $0.950 (\pm 0.026; r^2 = 0.94)$  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 ( $0.039 \pm 0.07$  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



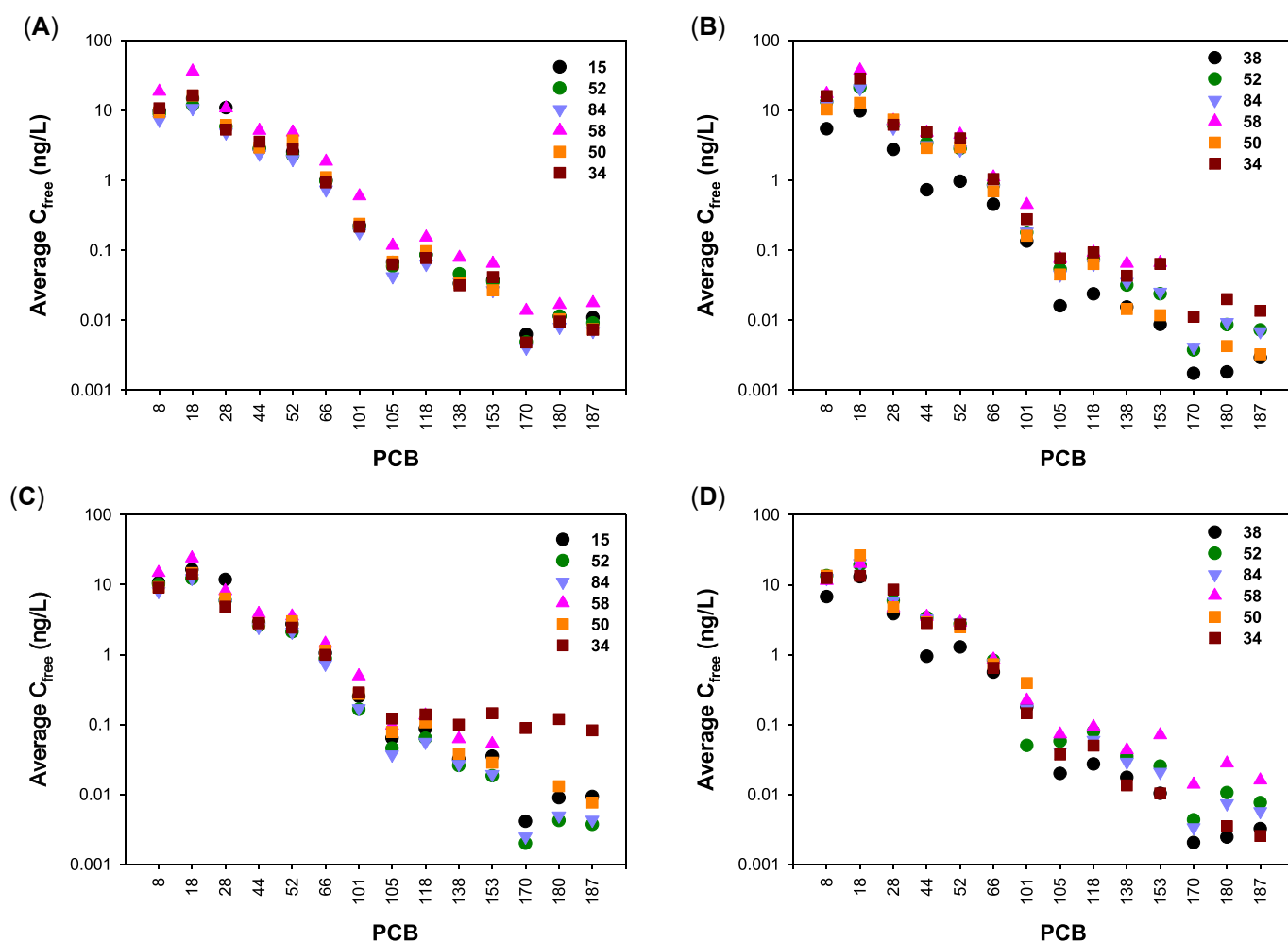
**FIGURE 2:** Plots of average freely dissolved porewater concentrations ( $C_{\text{free}}$ ) in porewater from the Indiana Harbor sediment for individual polycyclic aromatic hydrocarbons (PAHs) using active (A and B) or static (C and D) exposures of two polymers to the sediment, with low-density polyethylene (LDPE; A and C) and polydimethylsiloxane (PDMS; B and D). Colors indicate results from six different laboratories designated by numbers. For abbreviations, see footnote to Table 1.

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 regression 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 intercept for the correlations for PAHs ( $0.16 \pm 0.08$  and  $0.54 \pm 0.06$  log units for active and static methods, respectively) reflected bias resulting from higher concentrations for the PDMS sampler. For PCBs, results from both active and static exposures were also in good agreement, with an average ratio of LDPE and

PDMS of  $1.04 \pm 0.40$  for active exposure and  $1.05 \pm 0.50$  for static exposure; the slopes of the log–log regressions for the plots in Figure 5 were  $1.03 (\pm 0.018; r^2 = 0.98)$  for active exposure and  $1.03 (\pm 0.029; r^2 = 0.96)$  for static exposure. The intercepts for the correlations were  $0.02 \pm 0.02$  and  $0.05 \pm 0.03$  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



**FIGURE 3:** Plots of average freely dissolved porewater concentrations ( $C_{free}$ ) in porewater from the Indiana Harbor sediment for individual polychlorinated biphenyl (PCB) congeners using active (A and B) or static (C and D) exposures of two polymers to the sediment, with low-density polyethylene (LDPE; A and C) and polydimethylsiloxane (PDMS; B and D). Colors indicate results from six different laboratories designated by numbers.

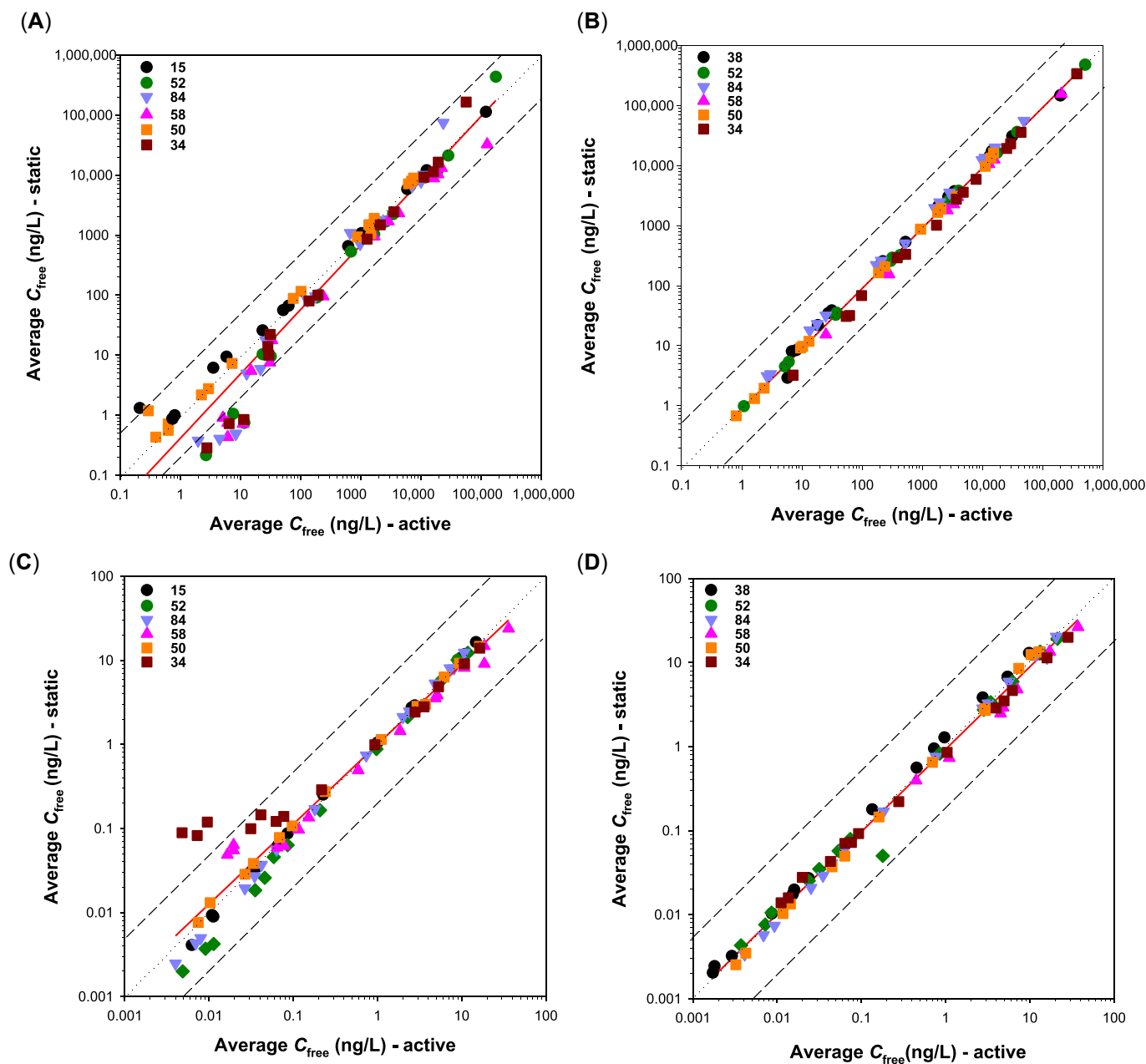
PDMS active versus LDPE active exposures exceeded 2 (rounded to the nearest whole number) only for naphthalene and acenaphthylene. For PDMS static versus LDPE static, however, the ratio between averages exceeded 2 for a larger number of compounds: acenaphthylene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[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 and 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  $C_{free}$  results after appropriate correction for nonequilibrium based on studies confirming PRC-based  $C_{free}$  estimates by comparison with equilibrium-estimated  $C_{free}$  (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 $C_{free}$ for highly hydrophobic PAHs and PCBs

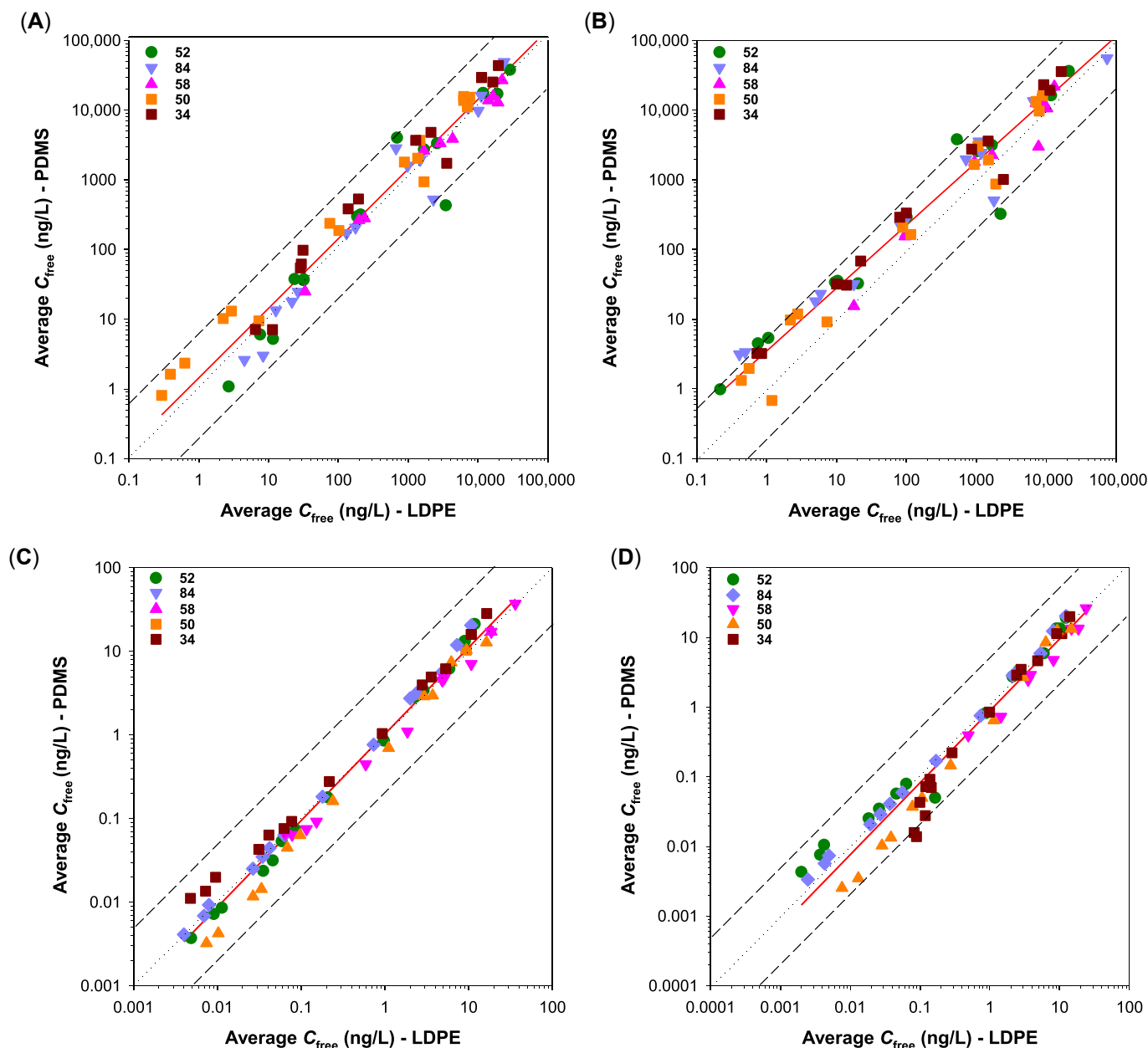
Overall, the greatest differences across laboratories for a given method or between exposure methods (i.e., active vs.



**FIGURE 4:** Relation between average polymer-sampler-derived freely dissolved porewater concentrations ( $C_{free}$ ) in porewater from the Indiana Harbor sediment measured using static exposure and using active exposure fit to a linear regression model (solid line). Dashed lines indicate a factor of 5 deviation between  $C_{free}$  measured by the two methods. (A) Low-density polyethylene (LDPE), polycyclic aromatic hydrocarbons (PAHs); (B) polydimethylsiloxane (PDMS), PAHs; (C) LDPE, polychlorinated biphenyls (PCBs); (D) PDMS, PCBs. Colors indicate results from six different laboratories designated by numbers.

static) were observed for highly hydrophobic PAHs and PCB congeners (Figure 2 and Supporting Information, Tables S7 and S8), which were those associated with large PRC-based corrections, because they were far from attaining sediment-polymer equilibrium. Heterogeneous 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  $C_{free}$ , 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



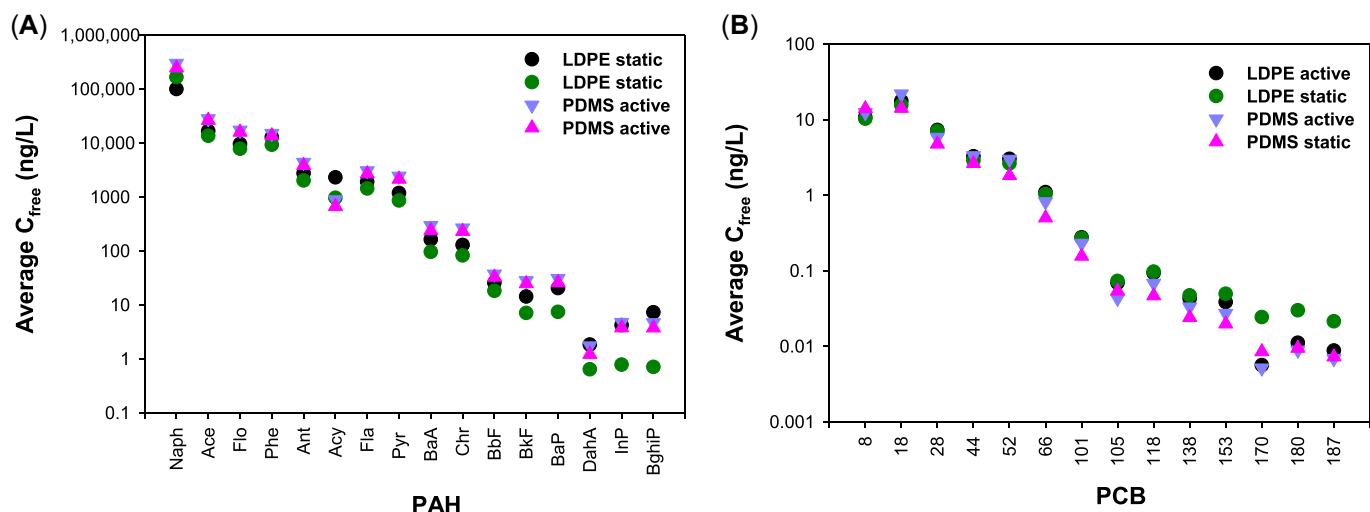
**FIGURE 5:** Relation between average polymer-sampler-derived freely dissolved porewater concentrations ( $C_{\text{free}}$ ) in porewater from the Indiana Harbor sediment measured using polydimethylsiloxane (PDMS) and using low-density polyethylene (LDPE) fit to a linear regression model (solid line). Dashed lines indicate a factor of 5 deviation between  $C_{\text{free}}$  measured by the two methods. Colors indicate results from six different laboratories designated by numbers. (A) Polycyclic aromatic hydrocarbons (PAHs), active exposure; (B) PAHs, static exposure; (C) polychlorinated biphenyls (PCBs), active exposure; (D) PCBs, static exposure.

accuracy; Jalalizadeh & Ghosh, 2017) and should be employed whenever feasible.

### $C_{\text{free}}$ determined directly from isolated porewater

To further evaluate the  $C_{\text{free}}$  results found using polymeric sampling, comparisons were made with  $C_{\text{free}}$  results from extractions of isolated porewater samples measured by UMBC (Supporting Information, Tables S7 and S8 and Figures S6 and S7). Considering the similarities between  $C_{\text{free}}$  results for

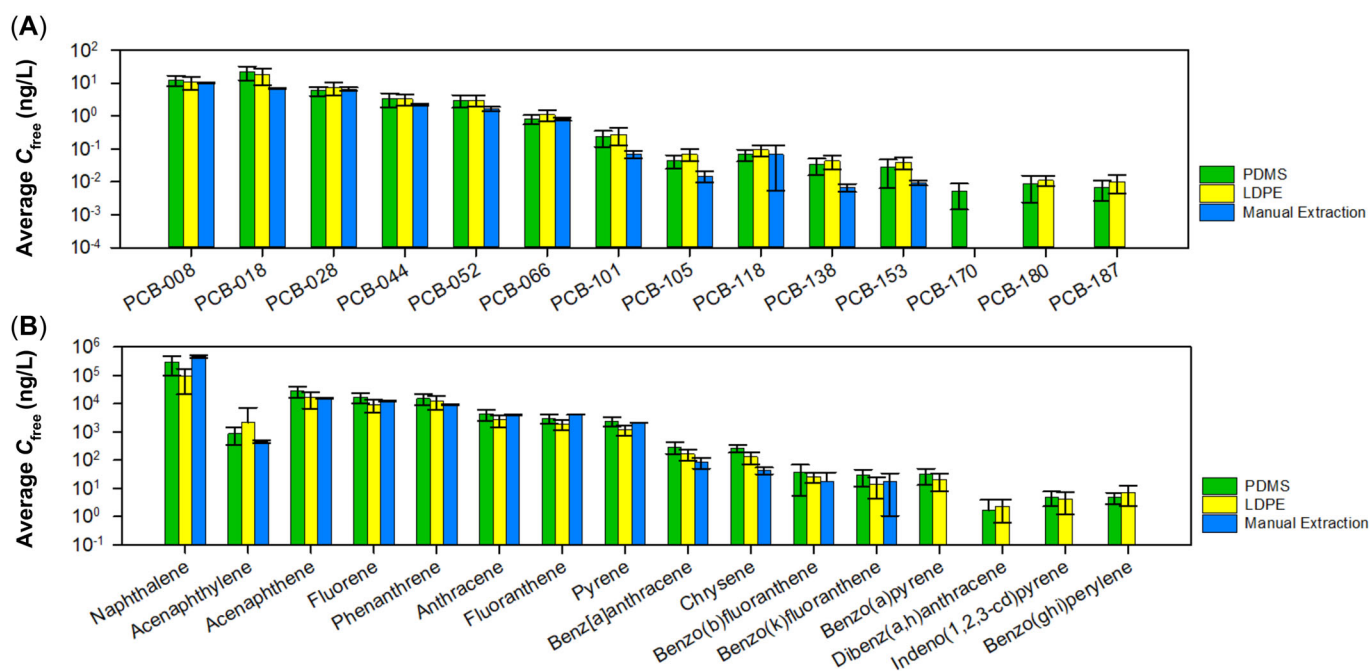
active and static exposures, comparisons focused on  $C_{\text{free}}$  results for active exposures. Figure 7 shows compound-specific comparisons of average  $C_{\text{free}}$  values using all replicate data across participating laboratories for polymer and active exposure combinations and average  $C_{\text{free}}$  values determined directly from isolated porewater laboratories by a single laboratory. Polymer-determined PAH and PCB  $C_{\text{free}}$  values were on average within a factor of 2 of  $C_{\text{free}}$  values obtained from isolated porewater (difference factor of  $2.3 \pm 1.1$ , average  $\pm 1$  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



**FIGURE 6:** Average polymer-sampler-derived freely dissolved porewater concentrations ( $C_{free}$ ) 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).

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  $C_{free}$  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 7:** Comparison of average (and 1 standard deviation) freely dissolved porewater concentrations ( $C_{free}$ ) 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  $\mu\text{g/L}$  levels for smaller PAHs down to  $\text{pg/L}$  for larger PCB congeners. Overall, intralaboratory 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  $\sim 1$  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>.

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**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. **Adesewa 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).

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