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Lotufo et al.

Inter-laboratory study of sediment polymeric sampling

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

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Abstract: This study evaluated the precision and accuracy of multi-laboratory measurements for determining freely dissolved concentrations (C_{free}) of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in sediment porewater (PW) using polydimethylsiloxane (PDMS) and low-density polyethylene (LDPE) polymeric samplers. Four laboratories exposed performance reference compound (PRC) pre-loaded polymers to actively mixed and static *ex situ* sediment for ~ 1 month; two laboratories had longer exposures (i.e., 2 and 3 months). For C_{free} results, intra-laboratory precision was high for single compounds (CV ≤50%), and for most PAHs and PCBs interlaboratory variability was low (magnitude of difference ≤ factor 2) 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 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. Results showed C_{free} polymer equilibrium was achieved in ~ 1 month during active exposures, suggesting use of PRCs may be avoided for *ex situ* analysis using comparable active exposure; although such *ex situ* testing may not reflect field conditions. Polymer-derived C_{free} concentrations for

most PCBs and PAHs were on average within a factor of 2 compared to concentrations in isolated PW, which were directly measured by one laboratory; difference factors of up to 6 were observed for naphthalene and the most hydrophobic PAHs and PCBs. C_{free} results were similar for academic and private sector laboratories. Demonstrated accuracy and precision for determination of C_{free} using polymer sampling is anticipated to increase regulatory acceptance and confidence in method use.

Keywords: bioavailability, passive sampler, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs)

This article includes online-only Supporting Information.

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INTRODUCTION

Freely-dissolved concentrations of nonionic organic chemicals (C_{free}) in porewater (PW) quantify the driving force for contaminant uptake in benthic organisms and the toxic effects such influxes may cause (DiToro et al. 1991; Lydy et al. 2014; Mayer et al. 2014). C_{free} is a critical exposure metric for benthic organism risk assessments (Mayer et al. 2014; Greenberg et al. 2014; Fernandez and Gschwend 2015), including deposit feeding invertebrates (e.g., 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 polychlorinated biphenyls (PCB) concentrations 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 polycyclic aromatic hydrocarbons (PAH) toxicity to the freshwater amphipod *Hyalella azteca* was accurately predicted by C_{free}, while 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 to bulk sediment analysis (Parkerton and Maruya 2014; Mayer et al. 2014; Booij et al. 2016).

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 PW (Burgess and McKinney 1997; Ghosh et al. 2000, Khalil and Ghosh 2006; Lu et al. 2006). Moreover, C_{free} is generally very low (e.g., tens of pg/L) for strongly hydrophobic compounds (Hawthorne et al. 2011; Cornelissen et al. 2008; Jahnke et al. 2012) and typically below the limits of detection of traditional analytical methods for water. Traditional methods to predict C_{free} in PW use solvent-extractable concentrations of sediment-associated HOC normalized to sediment organic carbon (OC) content (Di Toro et al. 1991; Park and Ersfeld 1999). This approach is still used (e.g., Finkelstein et al. 2017) although more complex models to estimate bioavailability were proposed (Cornelissen and Gustafsson 2005). However, these approaches are generally considered unsuitable by the environmental scientific community for realistic assessments of actual risks at contaminated field sites as they often have not yielded accurate predictions of C_{free} (Gschwend et al. 2011; Parkerton and Maruya 2014). The development of partitioning-based, non-depletive polymer sampling methods has allowed for the accurate determination of C_{free} values in sediment PW (Mayer et al. 2000; Booij et al. 2003;

Lohmann et al. 2004; Cornelissen et al. 2008; Tomaszewsky et al 2008; Fernandez et al. 2009).

Polymer-based sampling methods for determining C_{free} of HOCs in sediment PW 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 sediment. The *in situ* sampling approach involves placing a polymer sampler within the sediment in the field (Fernandez et al. 2009; Apell and Gschwend 2016; Schmidt et al. 2017; Apell et al. 2018; Borelli et al. 2018; Yan et al. 2020; Reininghaus et al. 2020). Equilibrium concentrations are inferred during *in situ* sampling through use of performance reference compounds (PRCs) or time series measurements (Apell et al. 2014; Joyce and 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 PW exchange processes (Apell et al. 2018). However, bioaccumulation in deposit feeding organisms may be less sensitive to these PW processes (Bridges et al. 2017; Yan et al. 2020). Vertical placement of polymer samplers into the sampling media *in situ* enables quantitative determination of C_{free} in surface water and depth-specific profile sediment PW (Lampert et al. 2013; Fernandez et al 2014; Apell et al, 2018).

Polymers that are commonly applied in different forms (e.g., thickness and geometries) for sampling sediment PW 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 non-ionized organic chemicals of concern with octanol–water partition coefficients (K_{ow} values) larger than ~10^3. Polymer sampling has been successfully used and thus recommended for use in assessing risks at contaminated sediment sites within the United States Environmental Protection Agency (USEPA) Superfund Program (USEPA 2012; Fernandez et al. 2014; Apell et al. 2016; Burgess et al. 2015; Burkhard et al. 2017) and is 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 and acceptance in the risk assessment and regulatory community (Greenberg et al. 2014; Parkerton & Maruya 2014, Jonker et al. 2018). Small-scale method comparisons were previously performed either by comparing two polymer sampling methods using the same deployment system (Schmidt et al. 2017; Endo 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 (i.e., PDMS, POM and 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 (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 use of polymer samplers as viable tools for laboratories that provide analytical services and increasing the application of this methodology to assess long-term remediation success and inform 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 laboratories, 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 to measure PW PAHs directly at low detection limits (ng/L) from water extracted from sediment via centrifugation is available (ASTM 2013). However, the research community is 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 this 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). This 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 Data) 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 non-equilibrium. Four combinations (LDPE and PDMS with both actively mixed and static exposures) were assessed for interlaboratory variability. One participating laboratory analyzed isolated sediment PW directly to obtain PAHs and PCBs C_{free} for comparison with polymer-derived $C_{free.}$ 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 C_{free} PAHs and PCBs in sediment PW.

MATERIAL AND METHODS

Participating laboratories

Participating laboratories included: 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), and the commercial laboratories Analytical Resources, Inc. (Tukwila, WA., USA), AXYS Enviro (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).

Study description

First, intra- and interlaboratory analytical variability was first checked using a reference "calibration check standard" of containing known PAH and PCB concentrations (method described in Supporting Information). Next, variability associated with the extraction and analysis of PRC-preloaded polymers containing known PRC concentrations was checked (method described in Supporting Information). Finally, methodological variability was checked as all participating laboratories followed unified SOPs to load PRCs into SPME fibers coated with PDMS and into LDPE thin sheets (henceforth simply PDMS and LDPE polymers), extract the polymers, then 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 steps; (1) preparation and loading with PRCs; (2) sediment exposure; and (3) polymer extraction and analysis. C_{free} results obtained via actively mixed and static exposures were then compared against C_{free} results obtained from direct analysis of PW isolated from the sediment.

Loading of PRCs to polymeric samplers and revision of SOP

Each participating laboratory cut, cleaned, and loaded polymers with PRCs following SOPs supplied by the academic labs. 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 concentration 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 duration are provided in 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 PW and the polymer. Active exposure accelerates progress toward equilibrium compared to static exposure. Static exposure involved inserting the polymer into the sediment without agitation, thus mimicking some *in situ* field conditions with no PW flow. The protocol for this sampling approach (Supporting Information) 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 non-depletive sampling, and expected analytical detection limits. Participating laboratories removed IH sediment from refrigerated storage, allowed sediment to reach room temperature (22 ± 5^{o}C), opened and mixed sediment jar contents, 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 d for four laboratories, but for

unintended longer periods (i.e., 63 and 90 d) for two laboratories (Table S3) due to COVID-19 Pandemic effects on laboratory access. Constant agitation was achieved using either a roller or 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 unified SOP in Supporting Information), then analyzed the polymer extracts for USEPA 16 Priority PAHs and NOAA's 18 PCB congeners. For static exposure, the procedure was identical to that described above for active exposure except without agitation. Laboratory-specific exposure duration and exposure conditions are detailed in Table S3.

Evaluation of steady state concentrations with performance reference compounds

The fractional approaches to equilibrium (f_{eq}) were modeled using measured losses (i.e., 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}, for target analytes in each polymeric sampler were determined according to the procedures described in the Supplemental Data 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 they 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 to Ghosh et al. (2014) for PDMS (see unified SOP in Supplemental Data) were used to convert these equilibrium polymer concentrations to C_{free} results using

the following equation:.

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

$C_{\text{Polymer}\infty}$ 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

C_{free} results obtained via active and static exposures were compared against C_{free} results obtained from direct analysis of PW isolated from the sediment as described in Supporting Information.

Materials

Polymer samplers. SPME fiber with a 35 μm PDMS coating (nominal) was purchased from Polymicro Technologies™ (Phoenix, AZ). The PDMS fibers cut from this source were cleaned with hexane and acetonitrile, then rinsed with MilliQ water several times and then dried (see unified SOP, Supporting Information). LDPE sheets (drop cloth or plastic tarp material) with thickness of 25 μm (1 mil) was obtained from Husky (Bolton, Ontario). 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 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 unified SOPs, Supporting Information).

Performance reference compounds. PRCs were isotopically labeled versions of the contaminants of interest, which were loaded into the polymer samplers prior to sediment

exposure. PRCs were $^{13}C_6$-labeled phenanthrene, fluoranthene, and chrysene, 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 (Andover, MA, USA).

Sediment. PAHs and PCBs-contaminated Indiana Harbor (IH) sediment was collected in 15, 19-L (5-gallon) buckets in September 2018 and stored at 4°C at the U.S. Army Engineer Research Development Center (ERDC) Environmental Laboratory in Vicksburg, MS. The IH sediment was homogenized in 2, 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, 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 (Table S1). PAHs and PCB congeners were measured in sediment from retained buckets (Table S2) using methods USEPA 8270C and USEPA 8082, respectively. The coefficients of variation (CV) in sediment concentrations were ≤ 11% for all PCB congeners and ≤ 15% for all PAHs except acenaphthene and fluorene, for which the CV was 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 participating laboratories. The sediment was stored at 2-6 °C until use.

Analytical Methods

PCBs were quantified using high-resolution or low-resolution mass spectrometry methods. The high-resolution gas chromatography - high resolution mass spectrometry (HRGC/HRMS) USEPA method 1668C (USEPA 2010) was used to determine target PCB congeners by AXYS-SGS, TestAmerica, and Vista. The twelve World Health Organization designated PCBs (van den Berg et al. 2008) 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 high-resolution gas chromatography - low resolution mass spectrometry (HRGC/LSMS) methodology modified from USEPA Method 8270D (USEPA 1998) was used to determine target PCB congeners by ALS, ARI, UMBC, MIT, and Battelle. TTU quantified PCB congeners by both Method 8270D and 1668C using an internal standard quantification technique, and the data for both methods were employed for calculation of averages and statistical comparisons.

PAHs were analyzed by ALS, ARI, TTU, UMBC, MIT and Battelle with GC/MS methodology modified from USEPA Method 8270D with selective ion monitoring (SIM) mode to achieve lower detection limits. AXYs-SGS and TestAmerica chose to use the isotope dilution technique for analyte quantitation, rather than internal standard technique as stated in USEPA Method 8270D. AXYs-SGS and Vista chose to combine USEPA Method 8270D and USEPA Method 1625B (USEPA 1984) where a HRGC coupled with mass spectrometry (MS) is used for sample analysis, and isotope dilution technique is applied for analyte quantitation. The TOC content of the IH 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 PAHs and PCBs 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 this interlaboratory method validation study. Data submitted by academic laboratories was not validated.

For analysis of calibration checks and polymeric samplers pre-loaded with PRCs, data variability was assessed using the coefficient of variation (expressed as a percentage) and data accuracy was assessed by comparing the result to a reference value. Statistical comparisons of PAHs and PCB congeners C_{free} across laboratories were performed using SigmaStat v3.5 software (SSPS, Chicago, IL, USA). 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 was log-transformed. One-way ANOVA 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 ±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_{free} during their study.

Participating laboratory analysis of polymeric samplers pre-loaded with PRCs

For polymers pre-loaded 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 ^{13}C-labelled congeners PCB-111, PCB-141, and PCB-182 for one laboratory and PCB-138 and PCB-178 for a different laboratory (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 to 3.5, with most values below 2) (Table S5). ^{13}C-labelled PCB PRCs were within ±50% of reference concentrations for most laboratories (Figure S1). A single laboratory reported an exceedance for a single PAH PRC (^{13}C6-indeno(1,2,3-cd)pyrene) in PDMS. A single laboratory also reported concentrations for ^{13}C-labelled congeners PCB-111, PCB-138, and PCB-178 in LDPE samplers lower than the actual concentration by over a factor of two (Figure S1). These deviations for PCBs were attributed to variations in the pre-loaded LDPE samplers. Upon review, it was discovered that laboratory 86 in Figure S1 may have mistakenly received LDPE sheets that were pre-loaded 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) was problematic. 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 per 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., CV ≤20% and average deviating 50% or less from target concentrations) except for an exceedingly low average concentration of PCBs 138 and 178 for one laboratory (Figure S2).

Precision and accuracy criteria exceedances were more frequent for LDPE (Figure S3). The intra- and interlaboratory variability in the LDPE results were 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 (Figure S4). The LDPE strips remained in the PRC loading solutions for an additional 30 days (minimum) following corrective measures (Table S3). After the additional soaking period, a new set of replicate LDPE segments were 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 (Figure S4). This suggested non-uniform loading of the yellow-colored PRC, indeno(1,2,3-cd)pyrene. Following application of the corrective measures described above to improve exposure uniformity to the PRC loading solution, interlaboratory variability decreased but precision remained low for some analytes, notably those with greater hydrophobicity (Figure S5). The highest CVs, reported for one laboratory, were 68% for indeno(1,2,3-cd)pyrene, and 68-76% for ^{13}C-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 to sediment. If mean concentrations and their associated CV 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 matches the target concentration exactly; rather, it is most important that the PRC loading is measured accurately and is distributed homogeneously throughout the polymer (i.e., high precision on replicate PRC-loaded polymers) since initial PRC concentrations in the polymers is 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 (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 (Table S6). For PDMS active exposure, the fractions remaining ranged from fully depleted (concentrations reported non-detects

after exposure) to 81% and varied widely across laboratories for PAHs (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 to active exposures (Table S6).

For PAHs, the intra-laboratory variability in polymer-determined C_{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% static PDMS exposures (Table 1). High variability (i.e., CV > 50%) was observed for naphthalene (Table 1), which was expected due to its volatility and potential loss from polymers (Thomas and 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, intra-laboratory variability in polymer-determined C_{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% static PDMS exposures (Table 2). High variability (i.e., CV > 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 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. MOD values 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 S7). Interlaboratory variability was higher with the MOD ≥ 6 for naphthalene, benzo(b)fluoranthene, indeno(1,2,3-cd)pyrene, and dibenz(a,h)anthracene for PDMS and naphthalene, acenaphthene, acenaphthylene, and benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, and dibenz(a,h)anthracene for LDPE (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 (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 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 ≥ 6 for PCBs 153, 170, 180, and 187 for LDPE static exposures, for PCBs 44,153, 170, 180, and 187 for PDMS active exposures, and PCBs 44, 66, 153, 170, 180, and 187 for PDMS static exposures (Table S8). Significant differences between laboratories occurred for all PCBs across all polymer sampling methods (Table S8).

The unified SOPs developed here (Supporting Information), included all aspects and steps of polymer exposure and extraction, included some IH sediment-specific content where needed, but was not prescriptive regarding analytical methods used for polymer extracts. The polymer sampling methodology used in this study are 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 Tables S7 and S8), as discussed below.

The only comparable previous large-scale polymer sampler study on interlaboratory variability involved only research laboratories with a proven track record 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, 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; $r^2 = 0.99$) for PAHs and 0.98 (± 0.01; $r^2 = 0.99$) 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, agreement with an average ratio of static and active of 0.87 ± 0.84 for PAHs and 1.35 ± 2.28 for PCBs and the slopes of the log-log regressions for the plots in Figure 4 were 1.08 (± 0.026; $r^2 = 0.95$) for PAHs and 0.950 (± 0.026; $r^2 = 0.94$) for PCBs. For LDPE, highest disagreement between the two methods occurred for many high molecular weight PAHs and

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 PAHs for the active method for some laboratories. In contrast, the intercept for the correlation for PCBs was very low (0.00002 ± 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_{free} averages for one polymer (i.e., LDPE and PDMS) were plotted against those for the other for either active or static exposure methods (Figure 5). For PAHs, results from LDPE and PDMS methods were in overall good agreement with an average ratio of LDPE and PDMS of 1.19 ± 1.41 for active exposure and 0.55 ± 0.37 for static exposure and the slopes of the log-log regression for the plots in Figure 5 were 1.00 (± 0.027; $r^2 = 0.95$) for active exposure and 0.903 (± 0.022; $r^2 = 0.96$) for static exposure. The intercept for the correlations for PAHs (0.16 ± 0.08 and 0.54 ± 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 ± 0.40 for active exposure and 1.05 ± 0.50 for static exposure and the slopes of the log-log regressions for the plots in Figure 5 were 1.03 (± 0.018; $r^2 = 0.98$) for active exposure and 1.03 (± 0.029; $r^2 = 0.96$) for static exposure. The intercepts for the correlations were 0.02 ± 0.02 and 0.05 ± 0.03 log units (not significantly different from zero), indicating very low bias.

To further compare polymer sampling methods, average C_{free} and their respective standard deviations and CVs were determined using all replicates across laboratories for each of the polymer and extraction methods (Table S9; Figures 6, 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 PAHs and PCBs when comparing polymer and exposure methods. For PAHs, the ratio between averages for PDMS active vs. LDPE active exposures exceeded 2 (rounded to the nearest whole number) only for naphthalene and acenaphthylene. For PDMS static vs. 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, 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 vs. LDPE static only for PCBs 170, 180 and 187 (higher for PDMS static). The ratio between averages for PDMS active vs. 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 PW and in the sampler approached equilibrium. For static exposures, both polymeric sampler-based PW 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} (Gschwend et al. 2011; Fernandez et al. 2014; Apell and Gschwend 2016; Schmidt et al. 2017). The present study and Jonker et al. (2018) demonstrated that when laboratories used 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. static) were observed for highly hydrophobic PAHs and PCB congeners (Figure 2 and Tables S7 and S8), which where those associated with large PRC-based corrections, as they were far from attaining sediment-polymer equilibrium. Heterogenous loading of some of the most hydrophobic PRCs to LDPE polymer by some laboratories (Figure S5) likely contributed to higher uncertainty associated with using the initial PRC concentration, with was determined by each laboratory, to calculate equilibrium concentrations. It is well established that using PRCs contribute to the uncertainty of estimating C_{free}, specially for poorly equilibrated PRCs (Joyce et al 2020; Jonker et al. 2018, 2020). Uncertainty associated with the use of poorly equilibrated PRCs (e.g., Jalalizadeh and Ghosh 2017; Sanders et al. 2018) may have contributed to the higher interlaboratory variability for the more hydrophobic compounds observed in this study. When selecting polymer sampler deployment methods, those that result in higher fractional loss of PRCs and closer approach to equilibrium have been shown to result in lower uncertainty (i.e., higher accuracy) (Jalalizadeh and Ghosh 2017) and should be employed whenever feasible.

C_{free} determined directly from isolated porewater

To further evaluate the C_{free} results found using polymeric sampling, comparisons were made to results from extractions of isolated PW samples (Tables S7 and S8; Figures S6 and S7). Considering the similarities between C_{free} results for active and static exposures, comparisons focused on C_{free} results for active exposures. Compound-specific comparisons of average C_{free} using all replicate data across participating laboratories for polymer and active exposure combinations and average C_{free} determined directly from isolated PW laboratories by a single laboratory is shown in Figure 7. Polymer-determined PAHs and PCBs C_{free} values were on average within a factor of 2 of C_{free} values obtained from isolated PW directly by a single laboratory (difference factor 2.3 ± 1.1, average ± one standard deviation); difference factors up to 6 were observed for select volatile and hydrophobic PAHs and PCBs such as chrysene, and PCB 138 (Figures 7, S6 and S7). Four PAHs (benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perylene) and three PCBs (PCBs 170, 180 and 187) were below detection in extracted PW 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 PW PCB concentrations with concentrations independently measured using an air-bridge approach and centrifugation and direct water extraction. They reported polymer-inferred PW concentrations and independent PW measures agreeing within a factor of 2. Hence, usage of the polymeric sampling appears to have acceptable accuracy based on comparison with direct measurement methods.

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 PW from the µg/L levels for smaller PAHs down to pg/L for larger PCB congeners. Overall, intra-laboratory variability was low (i.e., precision was high) and interlaboratory variability was also low (< 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_{free} determination Such 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_{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 as 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 PW, 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. C_{free} polymer equilibrium was typically achieved in ~ 1 month during active exposures, suggesting use of PRCs may be avoided

for *ex situ* analysis if sediment is actively sampled; but this is done at the risk of not reflecting field conditions (e.g., effects of bioirrigation; Apel et al. 2018), best assessed using *in situ* polymer sampling corrected based on PRC losses. Overall, average C_{free} polymeric results were similar to average C_{free} directly measured in extracted PW for most PAHs and PCBs. Based on comparison performed in the present study and previously (e.g., Gschwend et al. 2011), 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.

The successful outcome with private sector laboratories producing results similar to those generated by academic laboratories with research expertise in polymer sampling, given the availability of detailed standard protocols (Supporting Information, and also Jonker et al. 2020) 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 and site characterization and management.

Supporting Information—The Supporting information are available on the Wiley Online Library at DOI: 10.1002/etc.xxxx.

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Data availability—Data, associated metadata, and calculation tools are available from the corresponding author (Guilherme.Lotufo@usace.army.mil).

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FIGURE CAPTIONS

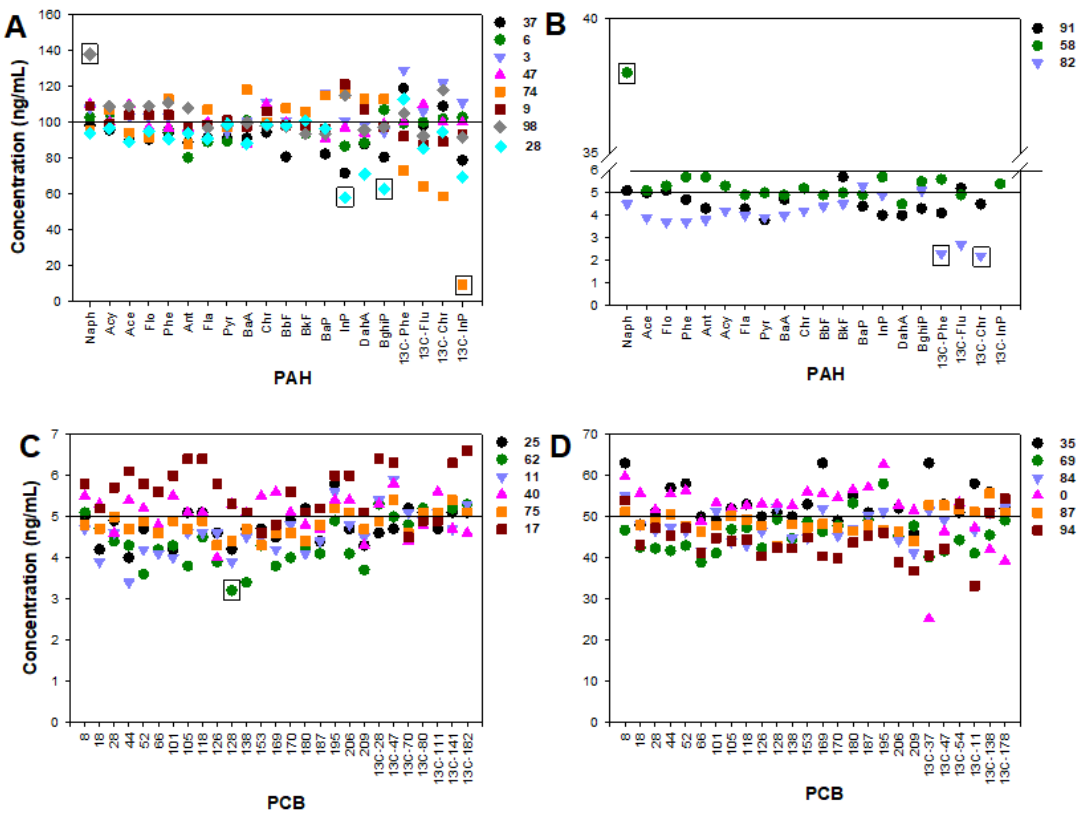

Figure 1. Average concentrations of PAHs and PCB congeners, including labeled compounds selected for use as PRCs, in calibration standards by participating laboratories. A: PAHs, low sensitivity; B: PAHS, high sensitivity; C: PCBs, low sensitivity; D: PCBs, high sensitivity. Colors indicate results from six different laboratories designated by numbers. The horizontal line indicates the reference concentration. Squares around data points indicate exceedance of 2-fold difference criterion. Ace = acenaphthene, Acy = acenaphthylene, Ant = anthracene, BaA = benz(a)anthracene, BaP = benzo(a)pyrene, BbF = benzo(b)fluoranthene, BghiP = benzo(g,h,i)perylene, BkF = benzo(k)fluoranthene, Chr = chrysene, DahA =

dibenz(a,h)anthracene, Fla = fluoranthene, Flo = fluorene, InP = indeno(1,2,3-cd pyrene, Naph = naphthalene, Phe = phenanthrene, Pyr = pyrene.

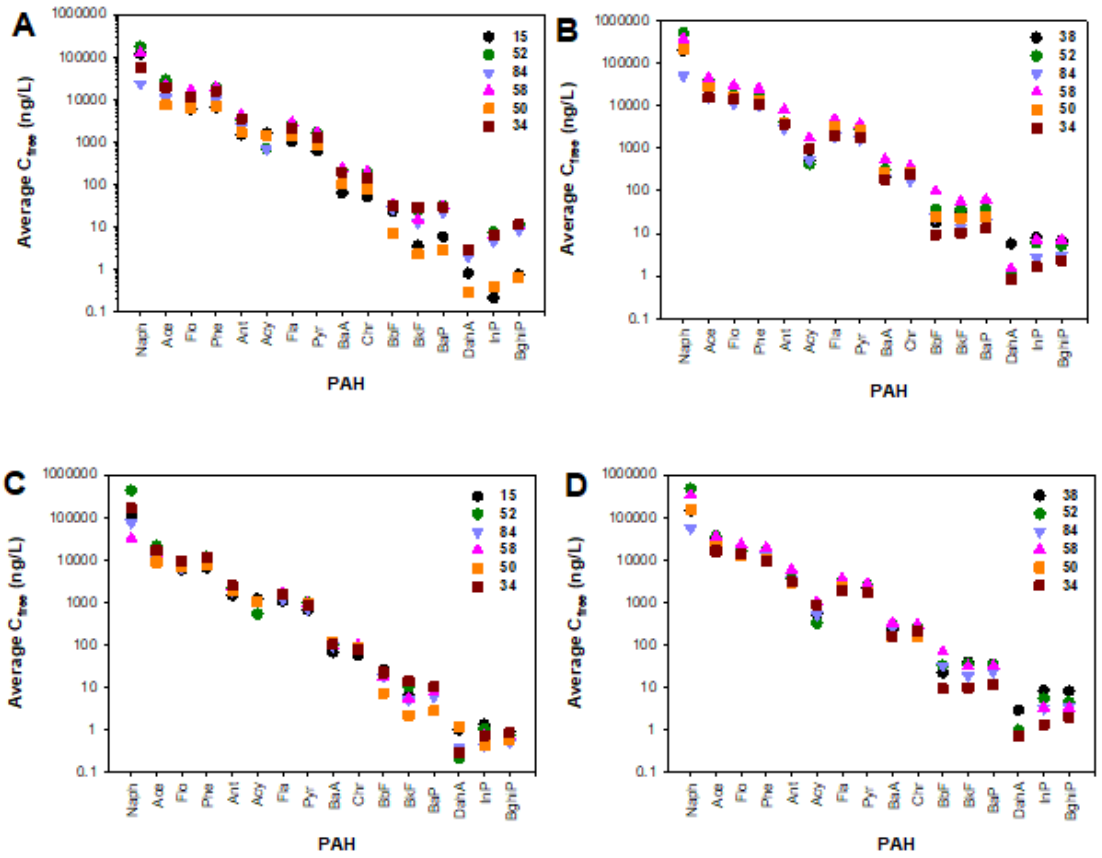

Figure 2. Plots of average freely dissolved porewater concentrations (C_{free}) in porewater from the Indiana Harbor sediment for individual PAHs using active (A and B) or static (C and D) exposures of two polymers to the sediment, with low-density polyethylene (LDPE) (A and C) and polydimethylsiloxane (PDMS) (panels B and D). Colors indicate results from six different laboratories designated by numbers. Ace = acenaphthene, Acy = acenaphthylene, Ant = anthracene, BaA = benz(a)anthracene, BaP = benzo(a)pyrene, BbF = benzo(b)fluoranthene, BghiP = benzo(g,h,i)perylene, BkF = benzo(k)fluoranthene,

Chr = chrysene, DahA = dibenz(a,h)anthracene, Fla = fluoranthene, Flo = fluorene, InP = indeno(1,2,3-cd pyrene, Naph = naphthalene, Phe = phenanthrene, Pyr = pyrene.

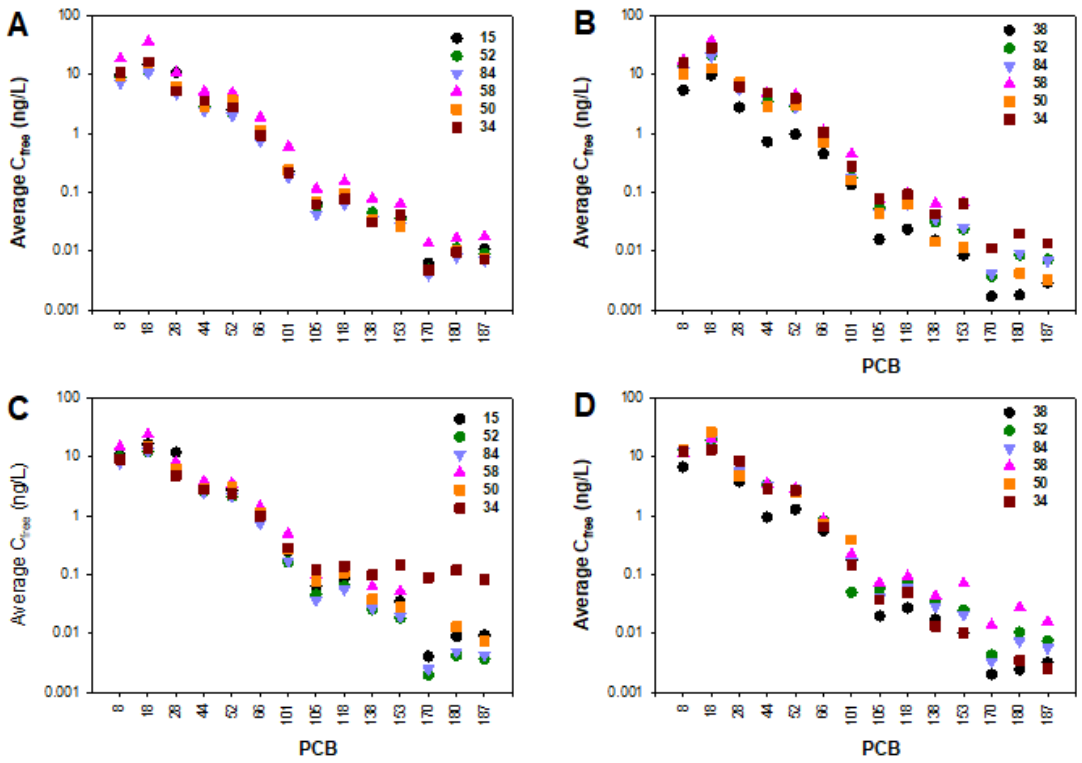

Figure 3. Plots of average freely dissolved porewater concentrations (C_{free}) in porewater from the Indiana Harbor sediment for individual PCB congeners using active (A and B) or static (C and D) exposures of two polymers to the sediment, with low-density polyethylene (LDPE) (panels A and C) and polydimethylsiloxane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

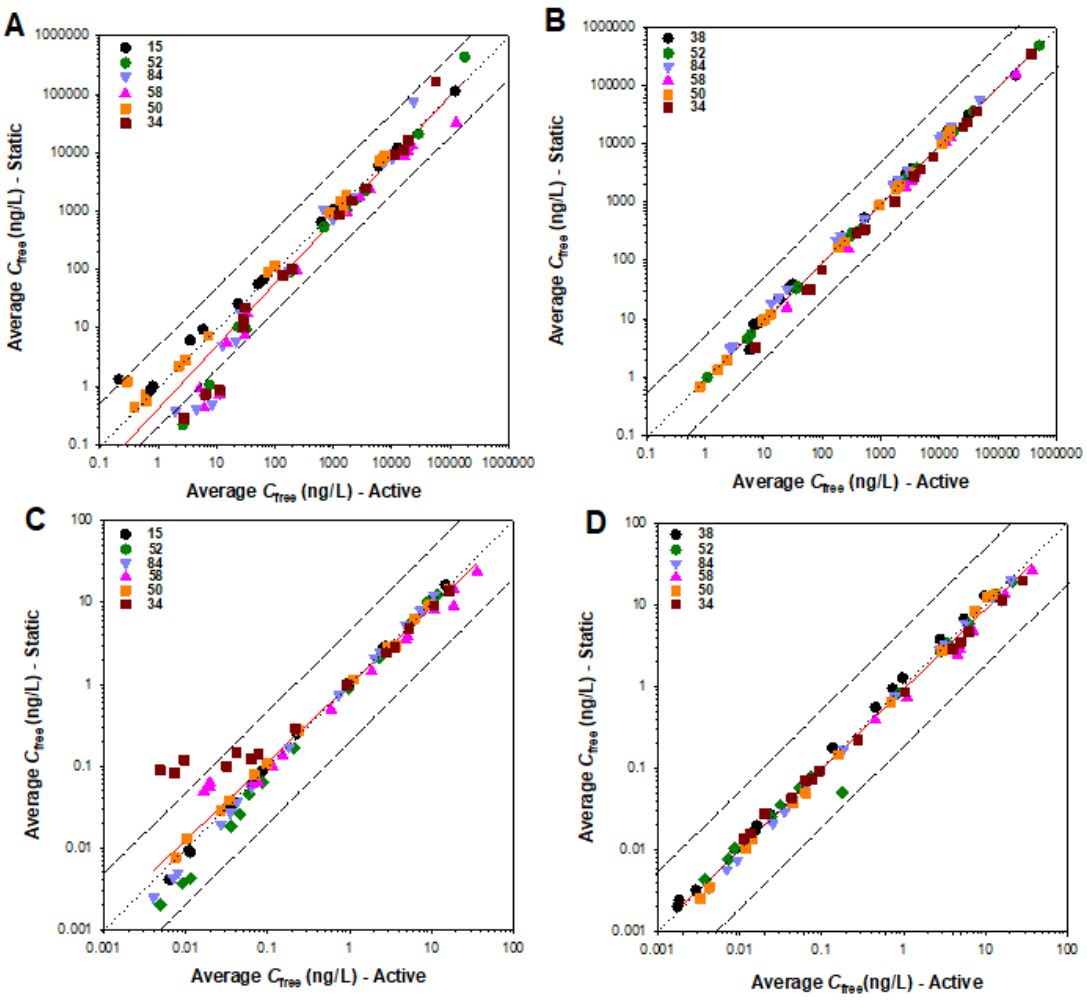

Figure 4. Relation between average polymer-sampler-derived freely-dissolved porewater concentrations (C_{free}) in porewater from the Indiana Harbor sediment measured using static exposure and using active exposure fit to a linear regression model (solid line). Dashed lines indicate a factor of 5 deviation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

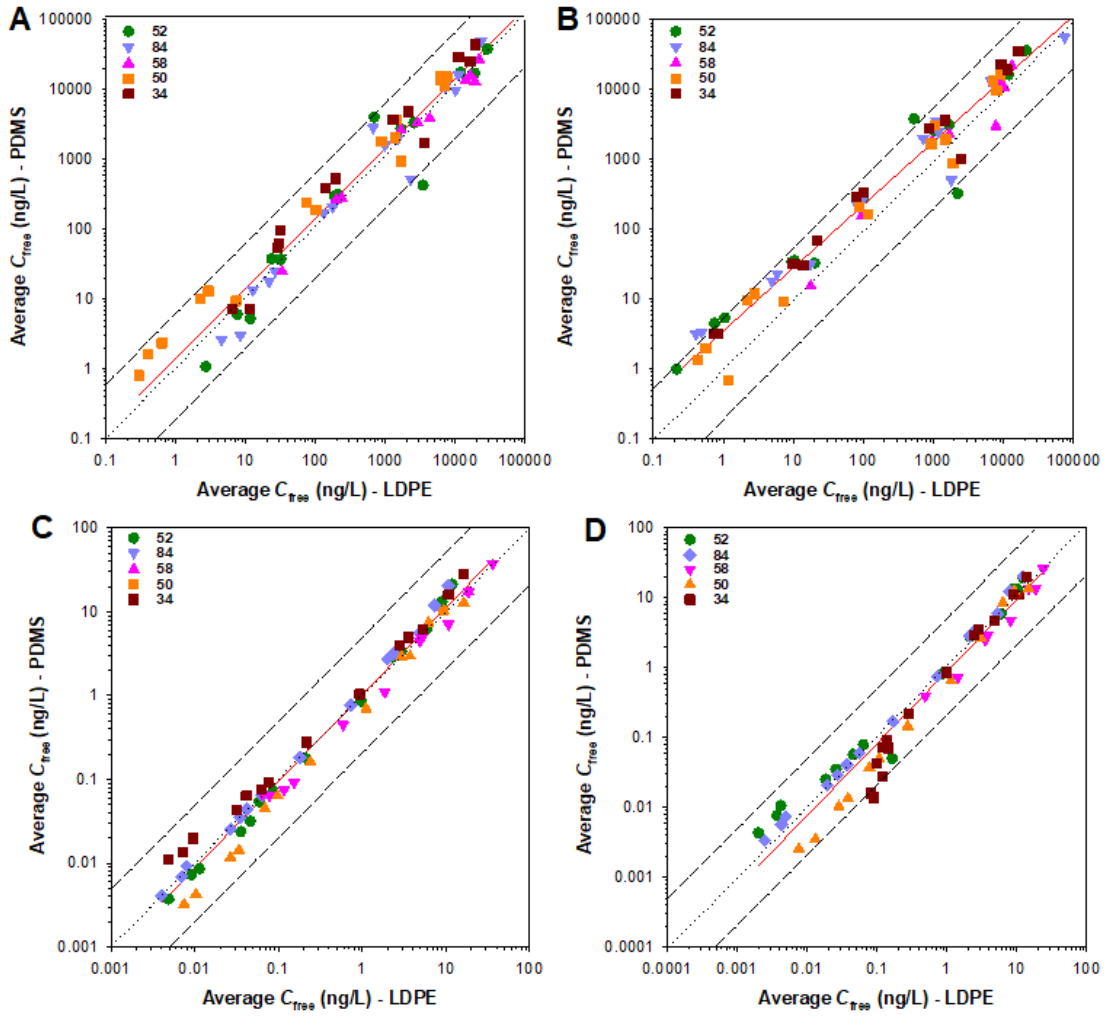

Figure 5. Relation between average polymer-sampler-derived freely-dissolved porewater concentrations (C_{free}) in porewater from the Indiana Harbor sediment measured using polydimethylsiloxane (PDMS) and using low-density polyethylene (LDPE) fit to a linear regression model (solid line). Dashed lines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

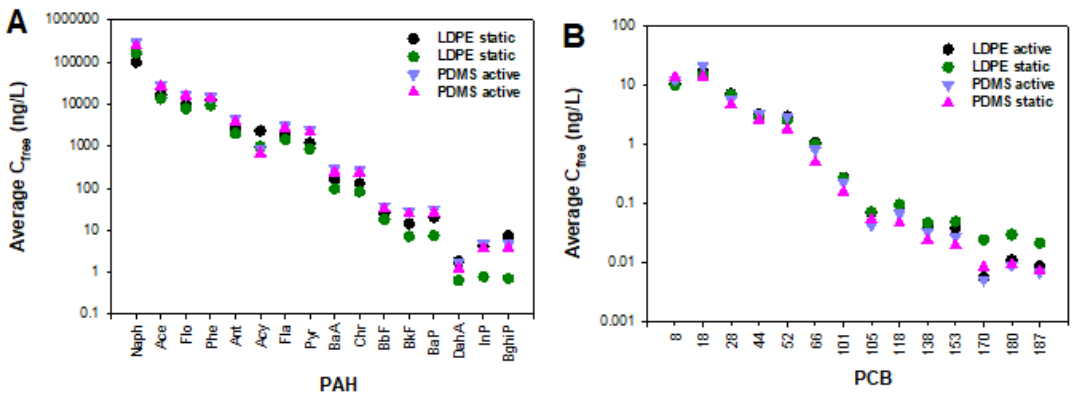

Figure 6. Average polymer-sampler-derived freely-dissolved porewater concentrations (C_{free}) in porewater from the Indiana Harbor sediment derived using all replicate data across all participating laboratories for two polymers, polydimethylsiloxane (PDMS) and low-density polyethylene (LDPE), and two exposure methods combinations. A: PAHs; B: PCBs.

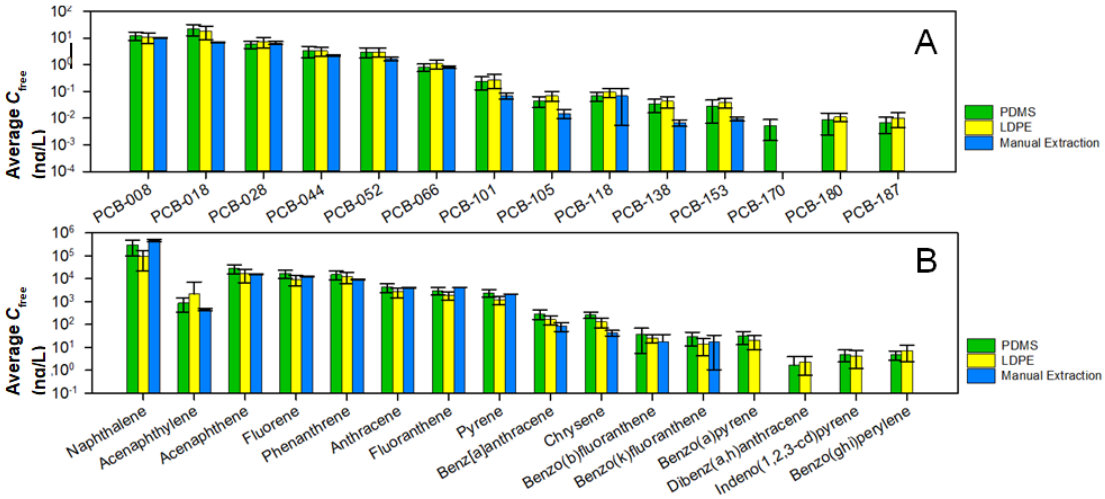

Figure 7. Comparison of average (and one standard deviation) freely-dissolved porewater concentrations (C_{free}) for PAHs (a) and PCBs (b) in actively sampled sediment measured all participating laboratories using polymers (PDMS, green; LDPE, yellow) vs.

measures performed by isolation and direct measurement of porewater from the same sediment by one laboratory (blue).

Table 1. PAH C_{free} coefficients of variation (CV) by participating laboratory and average (AVG) and standard deviation (SD) across laboratories for LDPE and PDMS using active or static exposure methods. Values >50% are highlighted.

PAH	LDPE, active exposure								LDPE, static exposure							
Laboratory	**15**	**52**	**84**	**58**	**50**	**34**	**AVG**	**SD**	**15**	**52**	**84**	**58**	**50**	**34**	**AVG**	**SD**
Naph	45	37	58	70	ND	22	**46**	**19**	48	36	67	56	ND	38	**49**	**13**
Ace	28	29	50	54	27	19	**34**	**14**	44	10	39	13	18	11	**22**	**15**
Flo	30	31	51	12	18	21	**27**	**14**	47	17	39	12	15	11	**23**	**16**
Phe	28	29	49	8	15	20	**25**	**14**	44	10	31	10	8	13	**19**	**15**
Ant	26	31	49	11	15	19	**25**	**14**	43	13	34	10	8	15	**21**	**15**
Acy	13	21	37	ND	11	ND	**21**	**12**	30	14	25	ND	20	ND	**22**	**7**
Fla	23	25	42	8	12	16	**21**	**12**	36	10	21	9	9	11	**16**	**11**
Pyr	22	23	41	4	12	15	**20**	**13**	34	9	18	10	9	11	**15**	**10**
BaA	22	22	41	6	12	17	**20**	**12**	37	11	15	10	9	13	**16**	**11**
Chr	21	22	39	5	12	14	**19**	**11**	35	33	16	11	8	9	**19**	**12**
BbF	17	18	33	9	12	14	**17**	**9**	34	16	15	11	9	22	**18**	**9**
BkF	15	16	34	3	12	12	**15**	**10**	38	21	23	17	10	12	**20**	**10**
BaP	1	1	3	3	11	13	**15**	**10**	4	2	18	16	10	14	**22**	**14**

	3	8	3						9	4						
DahA	11	13	28	ND	10	13	**15**	**7**	63	30	27	ND	14	51	**37**	**20**
InP	14	10	25	5	9	11	**12**	**7**	79	42	19	18	16	35	**35**	**24**
BghiP	13	13	26	7	9	10	**13**	**7**	57	29	16	20	18	27	**28**	**15**
AVG	**21**	**22**	**40**	**15**	**13**	**16**			**45**	**20**	**27**	**16**	**12**	**19**		
PAH	**PDMS, active exposure**								**PDMS, static exposure**							
Laboratory	**38**	**52**	**84**	**58**	**50**	**34**	**AVG**	**SD**	**38**	**52**	**84**	**58**	**50**	**34**	**AVG**	**SD**
Naph	35	34	73	61		30	**47**	**19**	21	46	31	59	ND	32	**38**	**15**
Ace	8	5	40	44	40	5	**24**	**20**	5	10	10	14	22	6	**11**	**6**
Flo	4	7	38	47	21	6	**21**	**18**	9	6	9	11	21	9	**11**	**5**
Phe	2	4	36	50	12	6	**18**	**20**	5	2	7	9	22	8	**9**	**7**
Ant	3	6	37	46	12	8	**19**	**18**	1	5	9	9	27	7	**10**	**9**
Acy	1	12	22		29	13	**15**	**11**	5	17	11	ND	23	10	**13**	**7**
Fla	9	5	33	22	4	7	**14**	**12**	9	2	6	9	20	9	**9**	**6**
Pyr	11	5	34	19	4	7	**13**	**11**	5	2	5	8	18	11	**8**	**6**
BaA	9	7	36	26	6	9	**16**	**13**	15	2	8	12	26	16	**13**	**8**
Chr	8	7	37	23	6	6	**14**	**13**	8	6	8	12	26	12	**12**	**7**
BbF	12	8	35	26	8	17	**18**	**11**	31	4	10	ND	29	17	**18**	**12**
BkF	8	1	3	12	6	12	**14**	**10**	1	3	18	N	26	17	**15**	**9**

		2	3						0			D				
BaP	17	14	37	16	7	14	**17**	**10**	28	4	7	ND	27	27	**19**	**12**
DahA	80	14		ND	9	31	**34**	**32**	19	11	ND	ND	31	ND	**20**	**10**
InP	15	16	11	ND	8	18	**14**	**4**	20	4	10	ND	31	34	**20**	**13**
BghiP	8	14	9	ND	7	11	**10**	**3**	26	6	10	ND	25	34	**20**	**12**
AVG	**14**	**11**	**34**	**33**	**12**	**13**			**14**	**8**	**11**	**16**	**25**	**17**		

Ace = acenaphthene, Acy = acenaphthylene, Ant = anthracene, BaA = benz(a)anthracene, BaP = benzo(a)pyrene, BbF = benzo(b)fluoranthene, BghiP = benzo(g,h,i)perylene, BkF = benzo(k)fluoranthene, Chr = chrysene, DahA = dibenz(a,h)anthracene, Fla = fluoranthene, Flo = fluorene, InP = indeno(1,2,3-cd pyrene, Naph = naphthalene, Phe = phenanthrene, Pyr = pyrene.

Table 2. PCB C_{free} coefficients of variation (CV) by participating laboratory and average and standard deviation across laboratories for LDPE and PDMS using active or static exposure method. Values >50% are highlighted.

PCB	**LDPE, active exposure**								**LDPE, static exposure**							
Laboratory	**15**	**52**	**84**	**58**	**50**	**34**	**AVG**	**SD**	**15**	**52**	**84**	**58**	**50**	**34**	**AVG**	**SD**
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	**22**	**18**	25	29	17	12	6	9	**16**	**9**
PCB-028	28	59	16	9	8	18	**23**	**19**	27	33	16	5	5	9	**16**	**12**
PCB-044	24	54	13	11	7	17	**21**	**17**	24	27	14	7	11	8	**15**	**8**
PCB-052	26	53	14	10	12	17	**22**	**16**	22	25	14	9	13	8	**15**	**7**
PCB-066	28	53	14	8	6	17	**21**	**17**	22	29	14	7	13	24	**18**	**8**
PCB-101	2	5	1	6	4	1	**18**	**17**	1	27	14	6	18	39	**20**	**11**

	0	0	4			5			8							
PCB-105	29	52	13	9	10	17	**22**	**17**	44	32	16	11	22	69	**32**	**22**
PCB-118	20	51	14	8	7	16	**19**	**16**	21	32	15	9	21	62	**27**	**19**
PCB-138	20	48	12	11	15	20	**21**	**14**	24	27	16	8	23	90	**31**	**30**
PCB-153	22	46	12	10	7	16	**19**	**14**	20	26	18	11	22	95	**32**	**31**
PCB-170	43	46	9	10	ND	16	**25**	**18**	41	28	27	ND	ND	123	**55**	**46**
PCB-180	13	45	11	10	10	17	**18**	**14**	20	29	26	ND	17	118	**42**	**43**
PCB-187	19	45	9	8	6	18	**18**	**15**	21	28	21	ND	34	120	**45**	**42**
AVG	**25**	**51**	**13**	**10**	**8**	**17**			**25**	**29**	**17**	**8**	**16**	**56**		
PCB	**PDMS, active exposure**								**PDMS, static exposure**							
Laboratory	**38**	**52**	**84**	**58**	**50**	**34**	**AVG**	**SD**	**38**	**52**	**84**	**58**	**50**	**34**	**AVG**	**SD**
PCB-008	41	3	15	14	13	14	**17**	**13**	9	5	7	9	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	14	13	13	13	**17**	**15**	8	12	5	6	8	10	**8**	**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	15	6	15	**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	**19**	**9**	29	14	16	ND	14	7	**16**	**8**
PCB-187	33	31	28	13	20	13	**23**	**9**	9	ND	ND	ND	11	13	**11**	**2**
AVG	**44**	**11**	**17**	**12**	**14**	**12**			**13**	**12**	**9**	**10**	**7**	**12**		