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Analysis of Measurement Errors in Passive Sampling of Porewater PCB Concentrations under Static and Periodically Vibrated Conditions

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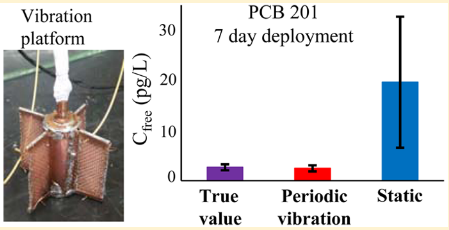
Supporting Information

ABSTRACT: Although the field of passive sampling to measure freely dissolved concentrations in sediment porewater has been sufficiently advanced for organic compounds in the low- to midrange of hydrophobicity, in situ passive sampling of strongly hydrophobic polychlorinated biphenyls (PCBs) is still challenged by slow approach to equilibrium. Periodic vibration of polyethylene (PE) passive samplers during exposure has been previously shown to enhance the mass transfer of polycyclic aromatic hydrocarbons (PAHs) from sediment into PE. Herein, we used a new vibrating platform, developed based on our earlier platform design, to demonstrate the effectiveness of periodic vibration for strongly hydrophobic compounds such as hexa-, hepta-, and octachloro-PCBs. Uptake of PCBs in PE after 7, 14, 28, and 56 days under different vibration modes was compared to that under static and mixed laboratory deployments. All PCBs reached within 95−100% of equilibrium after 56 days of deployment in the system vibrated briefly every 2 min, while none of the congeners achieved more than 50% of equilibrium in static deployment for the same period. Periodic vibration also increased the dissipation rate of four performance reference compounds (PRCs) from passive samplers. Higher fractional loss of PRCs and closer approach to equilibrium in the vibrated deployment resulted in estimation of corrected porewater concentrations that were statistically indistinguishable from the true equilibrium values even after a short 7-day deployment. Porewater concentrations of the strongly hydrophobic PCB congeners were overestimated by up to an order of magnitude in the static passive sampler after the same deployment time.



INTRODUCTION

Reliable bioavailability measurements of hydrophobic organic compounds (HOCs) such as polychlorinated biphenyls (PCBs) and polychorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs) are needed for improved sediment risk assessments, proper selection of remedy, and postremediation monitoring. Several studies have shown that freely dissolved concentrations (C_{free}) of organics in sediment porewater can be related to toxicity and bioaccumulation.[1,2] Passive sampling for the measurement of C_{free} of organic pollutants in sediment porewater has emerged as a very promising approach, but in situ measurements are challenged by slow mass transfer of strongly hydrophobic compounds. The slow mass transfer results in underequilibrated passive sampler measurements that need to be corrected for determining C_{free}. For a passive sampler deployed in stagnant sediment, mass transfer of the contaminants is controlled by transport through the polymer and/or sediment phase, depending on the sediment sorption characteristics and diffusivity of the pollutants in sediment porewater and polymer.[3] For HOCs, the overall kinetics is often controlled by transport through the sediment phase.[3−5] Under this condition, correction for nonequilibrium requires estimation of site specific sorption characteristics (e.g., retarded diffusion). The previously developed methods determined site-specific sorption characteristics from the loss kinetics of selected performance reference compounds (PRCs) and calculated corrected C_{free} from nonequilibrium polymer concentrations.[3,6] However, even with these methods, estimating C_{free} of strongly hydrophobic compounds is prone to errors. Extrapolation based on the loss kinetics of strongly hydrophobic PRCs is challenging, since long exposure times are required to measure PRC levels that are statistically different from the initially spiked PRC levels.[6] For example, Choi et al.[4] observed only 20% reduction in concentration of PCB 192 from 17 μm PE after 265 days of deployment in sediment. Also, high imprecisions involved in the measurement of fractional loss of PCB 192 caused a wide confidence interval for the estimated sediment sorption characteristics for this congener. In addition to the mentioned challenges with using the PRC-correction methods, it is not clear yet whether the retardation factor for HOCs that diffuse from sediment into the passive sampler is identical to the retardation factor for the PRCs that diffuse out of the passive sampler and into the sediment. Apell and Gschwend[5] argued that PCBs exhibit the same retardation factor through the sediment when diffusing into and out of PE

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passive samplers. However, anisotropic exchange kinetics of PCBs and DDTs has been observed for PE and PDMS passive samplers in more recent studies.[4,7] The mechanisms involved in anisotropic exchange kinetics are not well understood but possibly depend on the sediment properties.[4] Enhancing the overall kinetics by reducing the mass transfer resistance in sediment overcomes the mentioned shortcomings of PRC-correction methods. This assumption is tested further in the present study.

In our previous work,[8] we addressed the challenge of mass transfer limitation by using a vibrating platform for the deployment of passive sampling devices in sediments. We demonstrated through laboratory measurements and numerical modeling that the platform can greatly enhance the rate of mass transfer of 16 PAHs ($3.4 < \log k_{ow} < 6.1$) into PE passive samplers by disrupting the formation of a depletion layer in the vicinity of the polymer. Dissipation amounts of pyrene-d10 and phenanthrene-d10 ($\log k_{ow} \cong 5$) from PE in the vibrating system were high and identical to those in the well-mixed system. Correction for nonequilibrium is expected to become more accurate with higher fractional loss of PRCs.[9] However, not enough data were available to demonstrate the accuracy of this hypothesis. While a numerical model showed that significant improvement over static deployment is possible with very low frequency of vibration of the motors (5 d pause and 5 s pulse), this was not confirmed experimentally.

The objectives of the present study were to 1) evaluate the effectiveness of periodic vibration for passive sampling of strongly hydrophobic PCBs and 2) carefully evaluate the errors associated with PRC corrections for different deployment modes. PCB-impacted sediments from the field were used in laboratory mesocosms in the present study. The uptake rates of PCBs into PE under two differently vibrated passive sampling modes (low and high frequency) were compared to the uptake under static and mixed modes. A numerical model based on Jalalizadeh and Ghosh[8] was used to explain the diffusion process of PCBs from sediment particles into the sediment porewater and from porewater into passive samplers. In addition, PRC-corrected equilibrium aqueous concentrations using static and vibrating passive samplers were compared to the true equilibrium concentrations, determined from mixed sampler deployments.

■ MATERIALS AND METHODS

Materials. Low density polyethylene (LDPE) sheets (25 μm thickness), manufactured by Poly-America (Grand Prairie, TX, USA), were purchased from The Home Depot (local store in Baltimore, MD). PCB stock solutions were purchased from Fisher Scientific (Pittsburgh, PA, USA). Cylindrical vibrating motors with a diameter of 24 mm and length of 31 mm were purchased from Precision Microdrives (London, United Kingdom). The motors operated at the rated voltage of 3 V and operation current of 190 mA. Their rated vibrating speed was 5000 rpm, and the normalized amplitude of vibration (measure of acceleration caused on a 100 g object) was 10 G. Pulse-pause timers (model 60H) used to control the vibration motors were purchased from Velleman Inc. (Fort Worth, TX). Prior to use, PE sheets were cleaned by soaking twice in hexane/acetone (50/50 v/v) and leaving on a shaker for 24 h each time. Clean PE sheets were cut into 20 mg (2 cm × 5 cm) strips. PE strips were then soaked in a 80:20 v/v methanol/water solution containing four PRCs (2,4,5-trichlorobiphenyl (PCB 29), 2,3′,4,6-tetrachlorobiphenyl (PCB 69), 2,2′,4,4′,6,6′-hexachlorobiphenyl (PCB 155), and 2,3,3′,4,5,5′,6-heptachlorobiphenyl (PCB 192)). The PRC solution was allowed to equilibrate for 15 days on an orbital shaker. After impregnation with PRCs, the strips were transferred into deionized water and left on an orbital shaker overnight to remove the methanol from PE strips. Upon removal from water, three strips were extracted immediately in hexane to determine the initial PRC concentration.

Source of Sediments. PCB contaminated sediment samples from Site 102 Abraham's Creek were used in this study. The site is located in the Marine Corps Base, Quantico, Virginia, 35 miles south of Washington, DC.

Vibrating Platform. The vibrating platform is an improvement over our earlier design[8] with a larger frame and a more powerful motor that could house enough passive sampler to enable measurement of low levels of porewater PCB concentrations in sediment. The platform consisted of a copper pipe section, inside which the motor was located and was fabricated with assistance from the UMBC machine shop (Figure S2). Four fins made of copper plates and meshes were attached radially to the copper pipe. The copper wire mesh fins were designed as pockets that could hold PE sheets sandwiched within. A 20 mg PE strip (prepared as discussed above) was placed inside each pocket, and the open edge was sewn with copper wire.

In Situ Vibrated Passive Sampler Setup. Two platforms were connected in parallel to a timer and a power supply (2 rechargeable batteries 1.2 V, 700 mAh each). The timers were powered by a 12 V power supply and were programmed to control motor vibration duration and frequency. Two experiments were conducted in the lab in order to measure the uptake rate of PCBs into PE under different deployment modes. In experiment 1, PE sheets were deployed in sediment under static, mixed, and high frequency vibrating modes. In experiment 2, PE sheets were deployed under static and low frequency vibrating modes. The pulse duration of vibrating motors was 5 s, and the pause period was 2 min and 5 d in the high and low frequency vibrating systems, respectively. Details of the experimental setup are as follows:

Experiment 1 - The sediment was mixed with DI water containing 200 mg/L sodium azide to make a slurry with a weight ratio of 1:2 (dry sediment/water). For the mixed exposure, three wide mouth jars with Teflon-lined lids were prepared. The sediment-water slurry (500 mL) and two of the 20 mg PE samplers were transferred into each jar. The ratio of PE to sediment mass in each jar was selected to reduce PCB depletion from sediment to <1% at equilibrium based on the guideline provided in Ghosh et al.[10] The jars were placed on a rotary agitator and tumbled at a speed of 28 rpm. The rest of the sediment slurry was placed in two large glass trays (60 cm × 10 cm × 10 cm). Three motors were placed inside the sediment in the trays (two of the motors were placed in one tray with 10 cm separation to prevent influencing each other). The timer was programmed to vibrate the motors with a pulse period of 5 s and pause period of 2 min. Twelve additional PE samplers with a mass of 40 mg each were enclosed in stainless steel mesh without motors and were placed inside the same trays in a static mode at least 10 cm away from the vibrating motors and 5 cm apart from each other to simulate a static system. The trays were then covered with aluminum foil. PE strips were removed from the mixed, static, and vibrating systems and analyzed for PCBs and PRC compounds after 7, 14, 28, and 56 days. At each

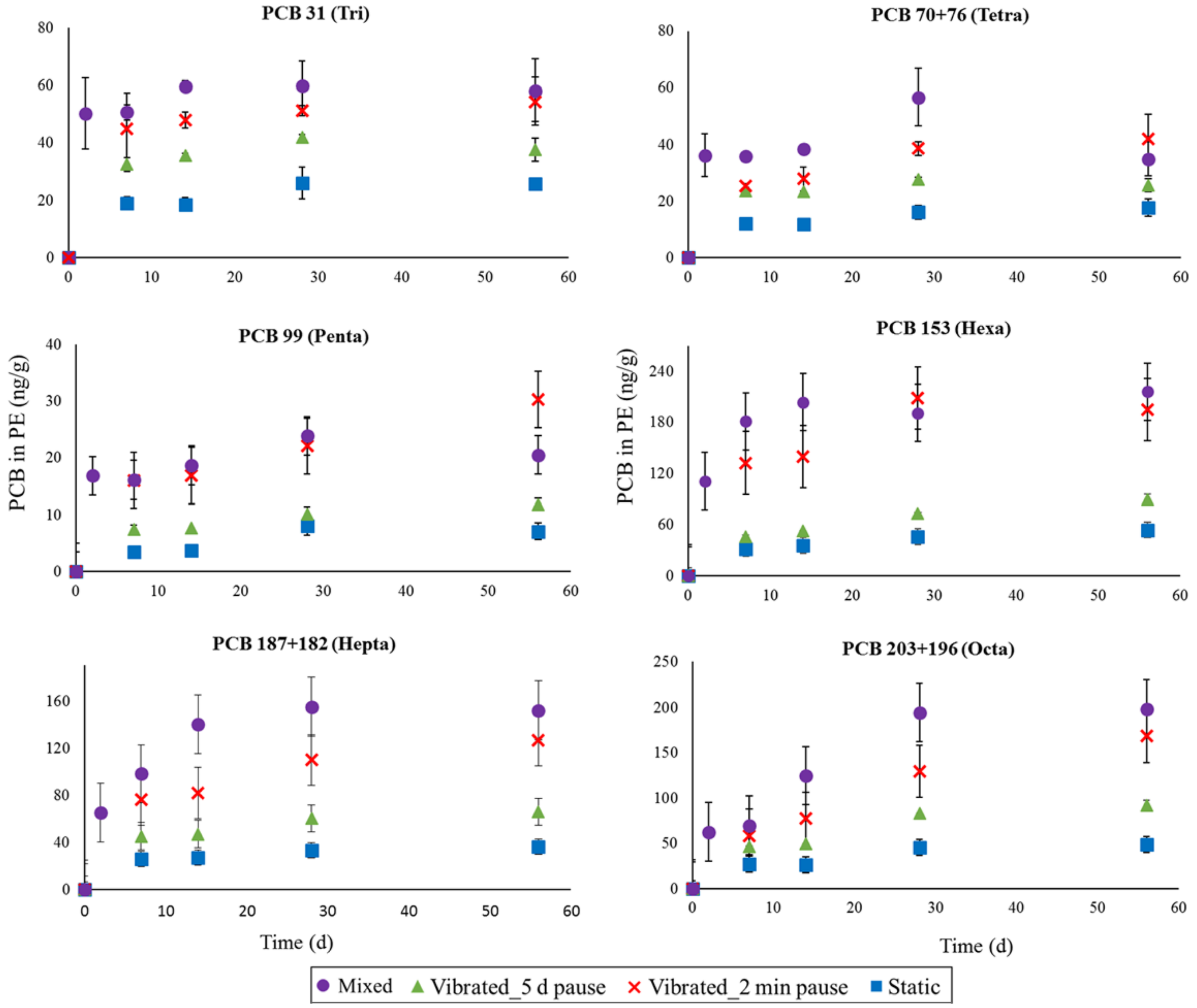

Figure 1. Comparison of uptake profile of PCBs into PE in static, vibrated, and mixed systems. Error bars represent the mean ± one standard deviation ($n = 3$).

time point, triplicate strips were collected from each system for extraction and analysis.

Experiment 2 - PE deployment under static and vibrating modes was repeated in a slurry made with a fresh portion from the same sediment as discussed. This time the motors vibrated with a low frequency of 5 s pulse every 5 days. PE strips were collected in triplicates from static and vibrating systems and analyzed for PCBs after 7, 14, 28, and 56 days.

PCB Extraction and Analysis. Upon removal from the sediment, PE strips were rinsed with water and wiped with laboratory tissue to remove water and adhering particles. Prior to extraction, PCB congeners 14 and 65 were added as surrogate standards to assess the effectiveness of sample processing, and results with lower than 80% surrogate recoveries were discarded. Samplers were extracted in 30 mL of hexane (3 × 24 h, with sequential extracts pooled). The final extraction volumes were blown down to 1 mL using a stream of nitrogen gas. Sediment PCBs were extracted by sonication (EPA method 3550B). Final extracts from passive samplers and sediment were cleaned using deactivated silica gel (EPA method 3630C). Two internal standards were added to the final extracts before analysis (PCB congeners 30 and 204). PCBs were analyzed in an Agilent 6890N gas chromatograph with an electron capture detector (ECD) based on an analytical method described in Beckingham and Ghosh.[11] The analyzed PCB congeners are shown in Supporting Information Table S1.

PCB Desorption Study. The desorption rates of PCBs from sediment into water were measured based on procedures in Ghosh et al.[11] Briefly, Tenax beads (0.5 g) and a sediment sample (5 g) were added to 12 mL glass vials. DI water (10 mL) containing sodium azide (1 g/L) was added to each vial. The vials were placed on a rotary agitator and tumbled at 28 rpm. At sampling times of 2, 4, 8, 12, and 48 h the sediment was allowed to settle and Tenax beads to float up. Tenax beads were scooped out from each vial, and a fresh portion was added. The Tenax beads were dried with anhydrous sodium sulfate, spiked with surrogate standards, and extracted by adding three volumes of 15 mL of 50/50 (v/v) hexane-acetone in a 20 mL vial and shaking horizontally on a rotary shaker for 24 h. The final extraction volumes were blown down to 1 mL using a stream of nitrogen gas and were cleaned using deactivated silica gel (EPA method 3630C). The extracts were

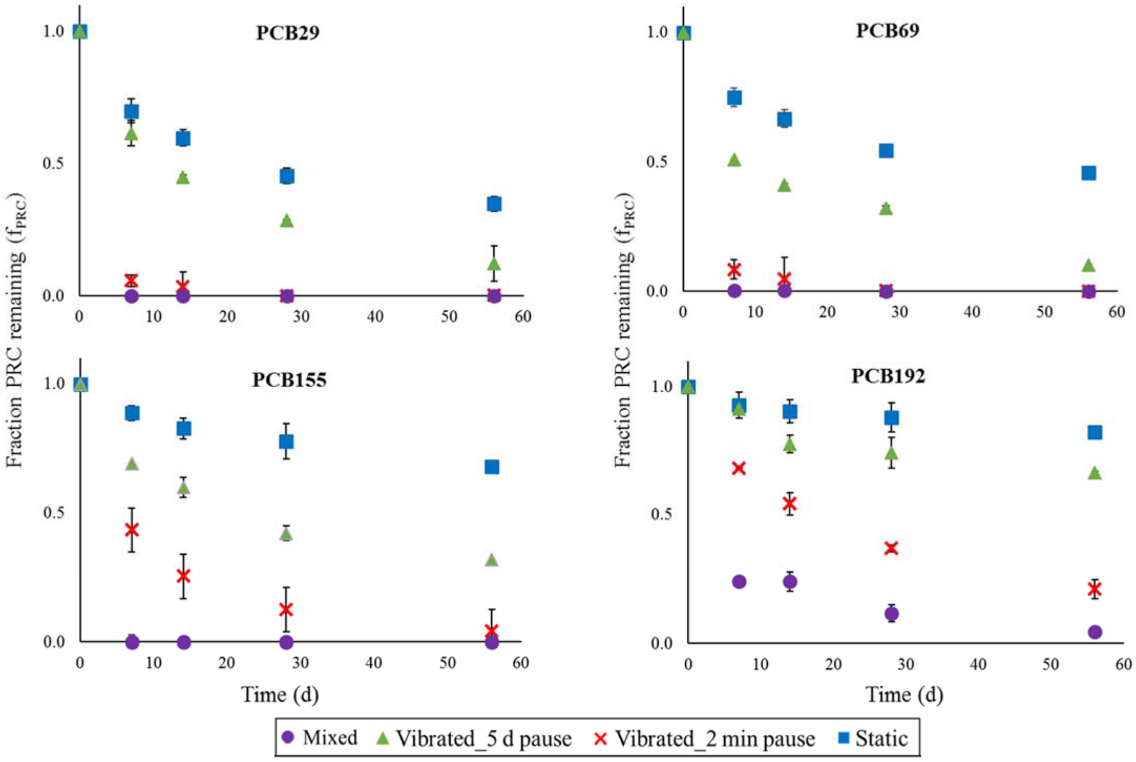

Figure 2. Comparison of remaining PRC fractions in PE (f_{PRC}) in static, vibrated, and mixed systems. Error bars represent the mean ± one standard deviation ($n = 3$).

then analyzed for PCBs using GC-ECD as described above. A two-compartment model[12] was used to describe the desorption kinetics of PCBs from sediment particles into porewater. This model estimates the desorption kinetics of HOCs out of sediment particles based on the assumption that the contaminants are associated with fast and slow desorbing pools in sediment (see the Supporting Information for more details). The model was fitted to the normalized desorption data for PCB 128, 183, and 194 in order to find the desorption rate constants (Supporting Information Figure S3).

PRC Correction for Nonequilibrium. We used the graphical user interface (GUI) by Tcaciuc et al.[13] to calculate the extent of equilibrium of target PCBs from PRC losses. This GUI is developed based on the mass transfer model presented in Fernandez et al.[6] PRC losses in static and vibrating systems were used to determine the extent of equilibrium of target PCBs in the corresponding systems. PCB and PRC concentrations were measured in triplicates, and PRC losses from each PE strip were used to correct for nonequilibrium in the same strip.

Modeling Uptake of Analytes from Sediment Porewater. Mass transfer models described in Jalalizadeh and Ghosh, 2016[8] were employed to describe PCB diffusion from sediment particles into porewater and from porewater into the polymer under static, vibrated, and mixed modes. Briefly, for static deployment mass transfer within the polymer and in porewater was described by Fick's second law of diffusion. Instantaneous equilibrium was assumed at the polymer surface boundary with porewater. PCB desorption from sediment particles into porewater was assumed to follow first-order kinetics, and all PCBs are associated with the fast desorbing pool in sediment. The diffusion model with the assumption of instantaneous equilibrium between sediment particles and porewater (local equilibrium model) adequately predicted the uptake in PE in a static system in some previous work.[6] However, local equilibrium cannot be assumed in a vibrating system[8] because mass transfer from sediment becomes limiting due to disruption of the depletion layer by vibration. For example, we showed that the overall kinetics of PAHs for the vibrating system was driven by the fast desorption kinetics and not the slow desorption, likely because the sediments are not depleted enough to reach the slow regime. The fast desorption rate constants determined from PCB desorption study were used for model simulation in the present study.

For the mixed system, mass transfer was assumed to be limited by the polymer side. Since sediment is perfectly mixed, porewater concentration remains constant and equal to the initial value during deployment time. In addition, local equilibrium was assumed between sediment particles and porewater as continuous mixing brings a large volume of sediment to the vicinity of the polymer and kinetics is fast enough to appear close to instantaneous equilibrium.

Model equations were solved in Matlab using an explicit, finite-difference numerical modeling technique.[14] The equations and the details of parameter estimation, numerical solution, and Matlab codes are provided in the Supporting Information.

RESULTS AND DISCUSSION

PCB Concentration in Sediment. As shown in Figure S1, hexa-, hepta-, and octachloro- PCBs were the most abundant homologues in the sediment. Mono- and dichloro-PCBs were not detected, and the total PCB concentration was 88 ng/g in dry sediment. The sediment had a total organic carbon content of 2.7%. This sediment was found to be suitable for the present study because our target homologues (hexa- to octachloro-

PCBs) were dominant. The concentrations of individual PCBs in sediment are reported in Supporting Information Table S1.

True Equilibrium Concentration. In the mixed system, no change in concentration in the PE was observed for any of the congeners after 28 days (PE concentrations after 28 and 56 days of exposure were not significantly different as shown in Supporting Information Table S4). Thus, PCB concentrations in PE from the mixed system after 56 days of exposure were taken as the true equilibrium concentrations for all PCB congeners and used to calculate fraction equilibrium for other modes of deployment.

Effect of High Frequency Vibration on PCB Uptake into PE. The uptake profiles of six PCB congeners are compared in static, vibrated, and mixed systems in Figure 1. The congeners shown in Figure 1 were chosen to represent the dominant congener within each homologue group with three to eight chlorine atoms. The remaining detectable congeners are shown in Supporting Information Figures S4−S6. Since measurements of PCB uptake into PE in the static system from experiments 1 and 2 were not significantly different for all PCBs (Supporting Information Tables S2 and S3), only the results from experiment 1 are shown for the static deployment. PCBs had very slow uptake rates into PE in the static exposure system especially for penta and higher chlorinated PCBs. Periodic vibration of the PE sampler every 2 min enhanced the fractional uptake of all congeners compared to the static deployment. For example, after 28 days of deployment, the fractional uptake (concentration in PE (C_{PE}) at a specific time, divided by the true equilibrium C_{PE}) of PCB 99 (penta), PCB 153 (hexa), PCB 187 + 182 (hepta), and PCB 203 + 196 (octa) were 37%, 24%, 23%, and 22%, respectively, in the static system compared to 100%, 100%, 73%, and 65% in the 2 min-paused vibrating system. All PCBs reached greater than 95% of equilibrium after 56 days of deployment in the 2 min-paused vibrating system, while none of the congeners reached more than 50% of equilibrium in static deployment for the same period. For example, the uptake of PCB 201 after 56 days was only 30% of equilibrium in static exposure compared to 100% in the vibrating system. Even after 7 days of exposure, the vibrating system reaches 35% of equilibrium for PCB 201 compared to 16% in the static system. Thus, with vibration it is apparent that in situ measurements of the full range of PCB congeners in sediments would approach high fraction equilibrium.

Effect of Vibration with Low Frequency on PCB Uptake into PE. The fractional uptake of all PCBs in the 5 d-paused vibrating system improved by a factor of 1.5 to 2 over the static system after 28 days (Figure 1 and Supporting Information Figures S4−S6). However, PCBs reached only 30% to 60% of equilibrium in the 5 d-paused vibrating system, except for PCB 31, PCB 70 + 76, and PCB 185 that reached approximately 70%. These results indicate that the pause time between vibrations needs to be less than 5 days in order to improve the uptake of larger molecular weight PCBs (hexa-, hepta-, and octachloro-congeners) to more than 60% in 28 days.

Effect of Vibration on PRC Loss from PE. The fraction of PRC remaining in PE (f_{PRC}) was measured for the four PRCs in static, vibrating, and mixed systems (Figure 2). The fractional losses (1-f_{PRC}) of lower molecular weight PRCs PCB 29 and PCB 69 in the static system were 55% and 46%, respectively, after 28 days of deployment. However, both PCBs were 100% dissipated from PE after the same exposure time in the high frequency (2 min-paused) vibrating system. The effect of vibration on PRC loss rate was more evident for PCB 155 and PCB 192. For example, the fractional loss was improved over the static deployment from 22% to 87% for PCB 155 (hexachloro-congener) and from 12% to 63% for PCB 192 (heptachloro-congener) after 28 days. As shown in Figure 2, f_{PRC} for PCB 29 and PCB 69 were nearly identical in high frequency vibrating and mixed exposures. In fact, more than 95% of both PRCs were lost in the vibrating system only after 7 days of exposure. The difference in f_{PRC} between high frequency vibrating and mixed systems was larger for more hydrophobic PRCs (PCB 155 and PCB 192). However, the fractional losses of these PRCs were still reasonably large in the high frequency vibrating system (63% after 28 days and 80% after 56 days for PCB 192).

The measured f_{PRC} values in the static system from experiments 1 and 2 were identical for all PRCs as compared in Supporting Information Tables S5 and S6. Thus, only the results from experiment 1 are shown for the static deployment in Figure 2. As indicated in the figure, vibration with low frequency (5 d-paused) was not as effective in improving the dissipation rate of high molecular weight PRCs. For example, the fractional losses of PCB 29 and PCB 69 were increased to approximately 70% after 28 days in the low frequency vibrating system. However, the fractional loss was less than 60% for PCB 155, and the fractional loss was only 25% for PCB 192.

Modeling the Uptake of PCBs. Experimental and modeling results for PCB 128 (hexa), PCB 183 (hepta), and PCB 194 (octa) in static, vibrating, and mixed systems are shown in Figure 3. As described in the modeling section,

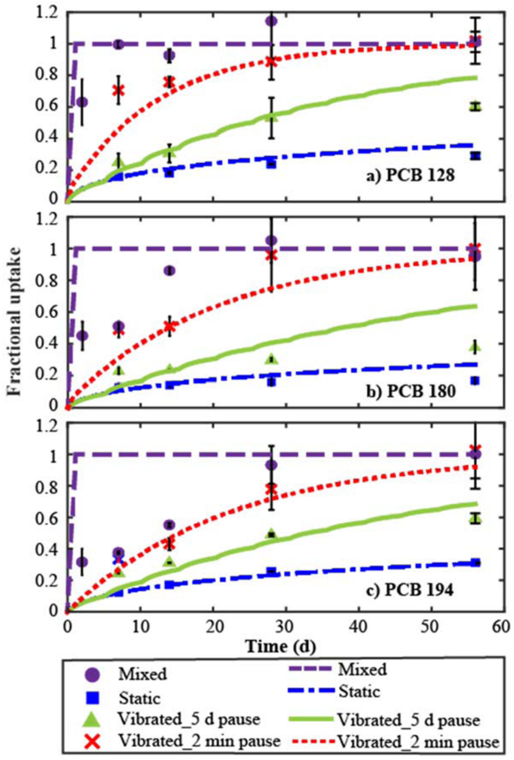

Figure 3. Fractional uptake of PCB 128 (a), PCB 180 (b), and PCB 194 (c) in PE passive samplers in four differently exposed systems. Experimental data are shown by symbols, and fast desorption model simulations are shown by lines. Error bars represent the mean ± one standard deviation (n = 3).

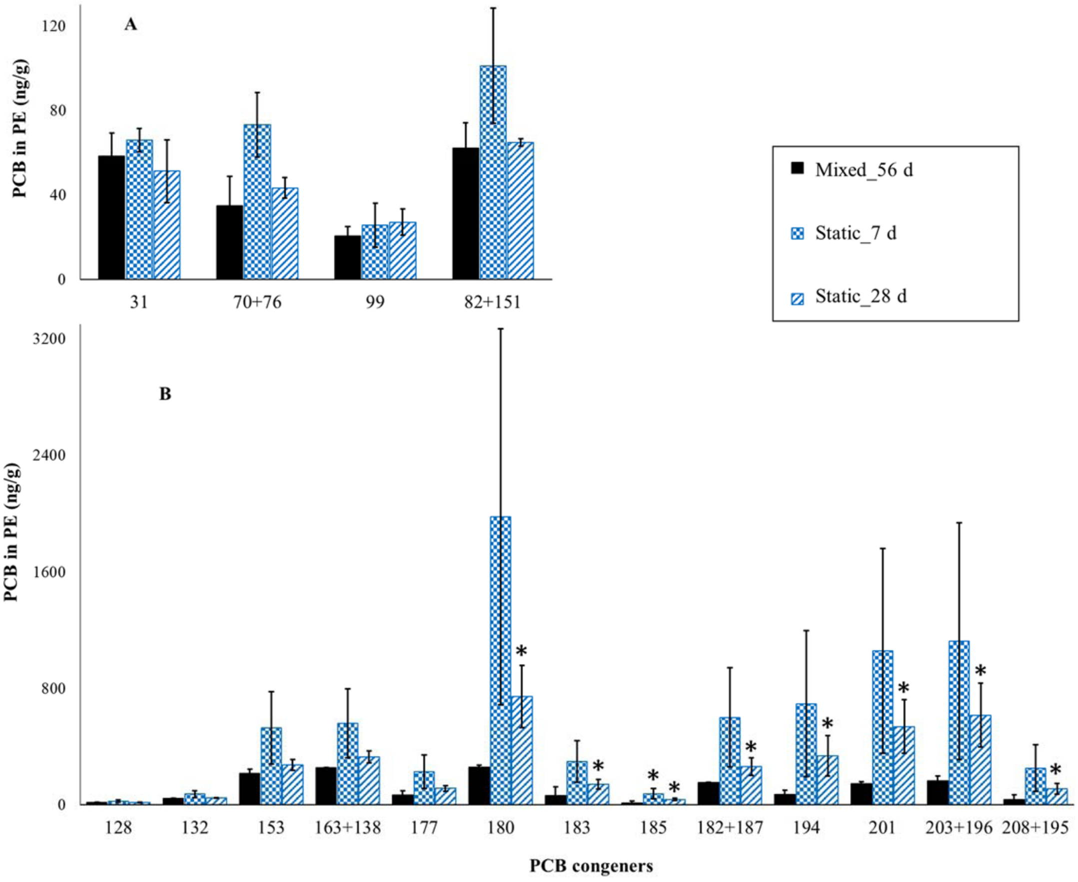

Figure 4. Comparison of 56-day mixed (true) equilibrium concentration in PE with PRC-corrected PE equilibrium concentration measured using 7-day and 28-day static exposures. Plot A shows PCB congeners that belong to pentachloro- and lower molecular weight congeners, and plot B indicates congeners that belong to hexachloro- and higher molecular weight congeners. The corrected concentrations that are statistically different from the 56-day mixed equilibrium concentrations (with alpha level of 5%) are indicated with an asterisk. Error bars represent the mean ± one standard deviation (n = 3).

sediment desorption rate constants are required for the modeling of mass transfer in the vibration system. The measured desorption rate constants (k_f) for the three PCB congeners were in the range of 2.4 to 2.8 d^{-1} (Supporting Information Table S9). The measured k_f values are in the same range as the values reported by Cornelissen et al.[15] for sediments from Lake Oostvaardersplassen (Netherlands). However, our measured rates are approximately 1 order of magnitude larger compared to the reported rates by Zimmerman et al.[16] for sediments from Hunters Point (CA) and those reported by Sun and Ghosh[17] for sediments from Grasse River (NY). As shown in Figure 3, modeled uptake in PE generally had good agreement with the measured uptake of all three PCBs in static and vibrating systems with low and high frequency of vibration. This is especially noteworthy because the model uses parameters that have been independently measured or obtained from the literature (Supporting Information Table S7).

The mixed model overpredicted the earlier time point measurements (Figure 3), likely due to incomplete mixing of the sediment. While it is often assumed that a slurry of sediment in a tumbled jar is well-mixed, depending on the fluidity of the slurry, it is possible to have less than required relative movement between the passive sampler and sediment. This could cause inefficient breakup of the depletion layer[8] that forms around the polymer. Deviations between the model simulation and experimental data for the mixed deployment were more obvious for more hydrophobic PCBs (PCB 183 and PCB 194), as mass transfer of these compounds is mostly controlled by the sediment side.[8] Arp et al.[18] also observed slow diffusion of higher molecular weight PCBs from mixed sediment slurry into POM. The authors argue that the reason for slow mass transfer of the larger molecular weight PCBs in their study could be slower desorption from the less available subdomains of the sediment.

Prediction of Equilibrium Concentration Based on Static vs Shaken Deployment. Measured PCB concentrations in PE using the static and vibration deployments were corrected for nonequilibrium based on the fractional losses of PRCs. Since four PRCs were available for use in correction, the method by Fernandez et al.[6] was used as described in the Materials and Methods section. PE equilibrium concentrations were also determined from the 56-day mixed deployment. To compare the accuracy of the equilibrium estimations, the estimated C_{PE} values based on PRC-corrected concentrations in PE were compared to the true equilibrium concentrations from the mixed system. In the laboratory mesocosms with static overlying water, we expect that PCBs in porewater approach thermodynamic equilibrium with the sediment. Thus, porewater concentrations measured in the "mixed equilibrium exposures" should closely represent the true equilibrium porewater concentration to be expected in the static and

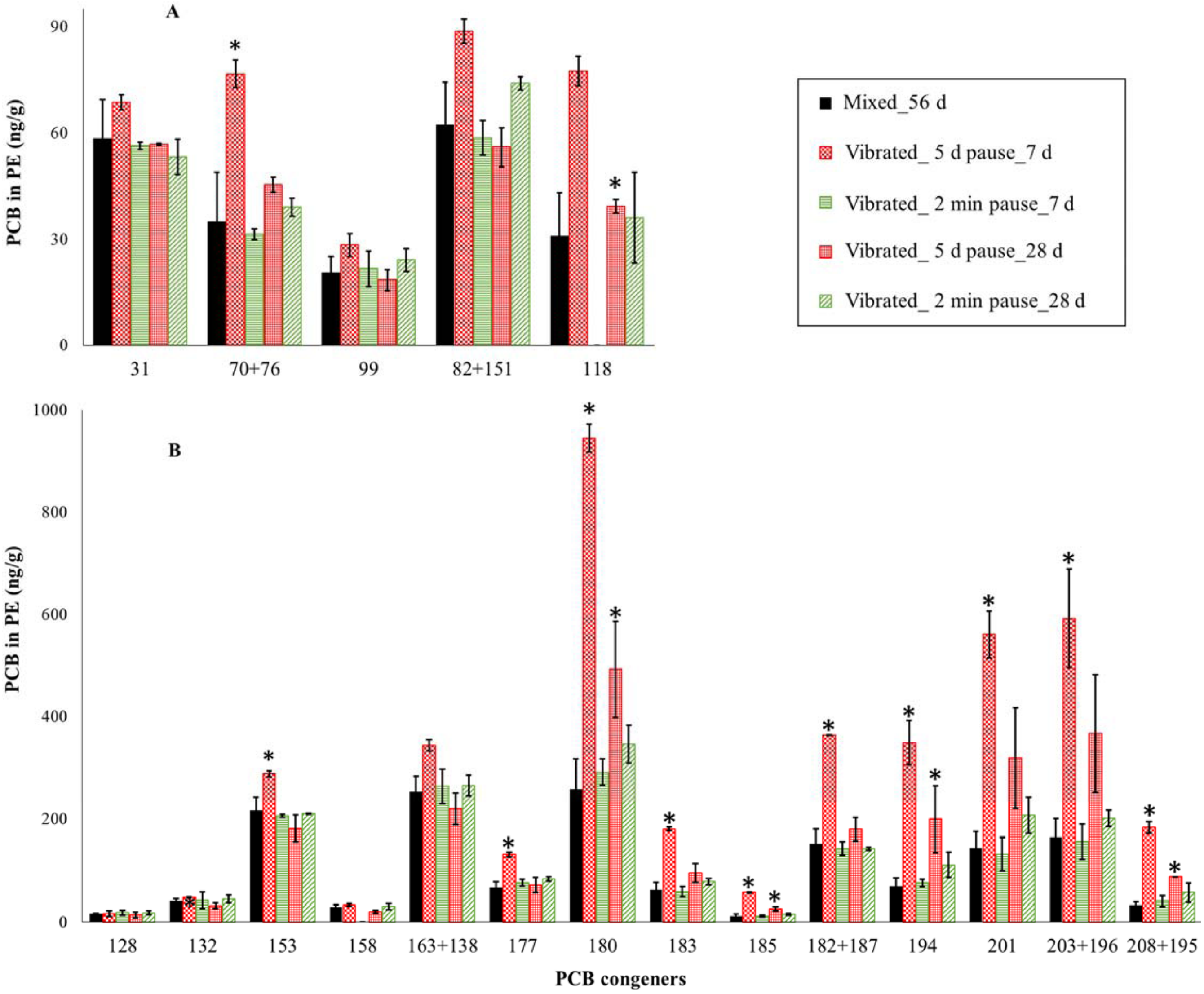

Figure 5. Comparison of 56-day mixed equilibrium concentration in PE with PRC-corrected PE equilibrium concentration measured using 7-day and 28-day vibrated passive samplers. Plot A shows PCB congeners that belong to pentachloro- and lower molecular weight congeners, and plot B shows congeners that belong to hexachloro- and higher molecular weight congeners. The corrected concentrations that are statistically different from the 56-day mixed equilibrium concentrations values (with alpha level of 5%) are indicated with an asterisk. Error bars represent the mean ± one standard deviation ($n = 3$).

vibrating passive sampler deployments. The PRC-corrected C_{PE} values measured with 7- and 28-day static and vibrated passive samplers are plotted in Figures 4 and 5, respectively, and compared against the true equilibrium C_{PE} values. In both figures, the PRC-corrected C_{PE} values that are statistically different from the true values (with alpha level of 5%) are indicated with asterisks.

As shown in Figure 4, the tri-, tetra-, and pentachloro-congeners (PCB 31, 70 + 76, 99, and 82 + 151) are generally well-predicted by the static passive samplers (within a factor of 2) for both 7-day and 28-day deployments. For these moderately hydrophobic congeners, the PRC losses are high in both deployment durations, and correction for non-equilibrium is relatively accurate. The measurements using static deployment start deviating strongly for the higher chlorinated PCBs (hexa and higher). There appears to be a consistent positive bias for the estimation from static deployment. For example, equilibrium C_{PE} for PCB 180 is predicted to be 7.7-fold higher from the 7-day deployment and 2.9-fold higher from the 28-day deployment. As expected, C_{PE} estimations using the 7-day deployment data in the static system were less accurate compared to the estimations using 28-day deployment data, especially for higher molecular weight PCBs. The error bars are also large, indicating poor precision. Many of the equilibrium C_{PE} prediction for the static deployment have large deviation from the true equilibrium C_{PE} (e.g., up to a factor of 10 for 7-day deployment) but often do not show statistically significant difference due to the very large associated error of the estimation. The predictions improve with length of deployment but remain poor with a factor of 5 overprediction for several hepta- and octachloro-PCBs.

As shown in Figure 5, the PRC-corrected C_{PE} values from the 2 min-paused vibration deployment are much more accurate and precise compared to measurements from the static deployment. For example, the estimated equilibrium C_{PE} for

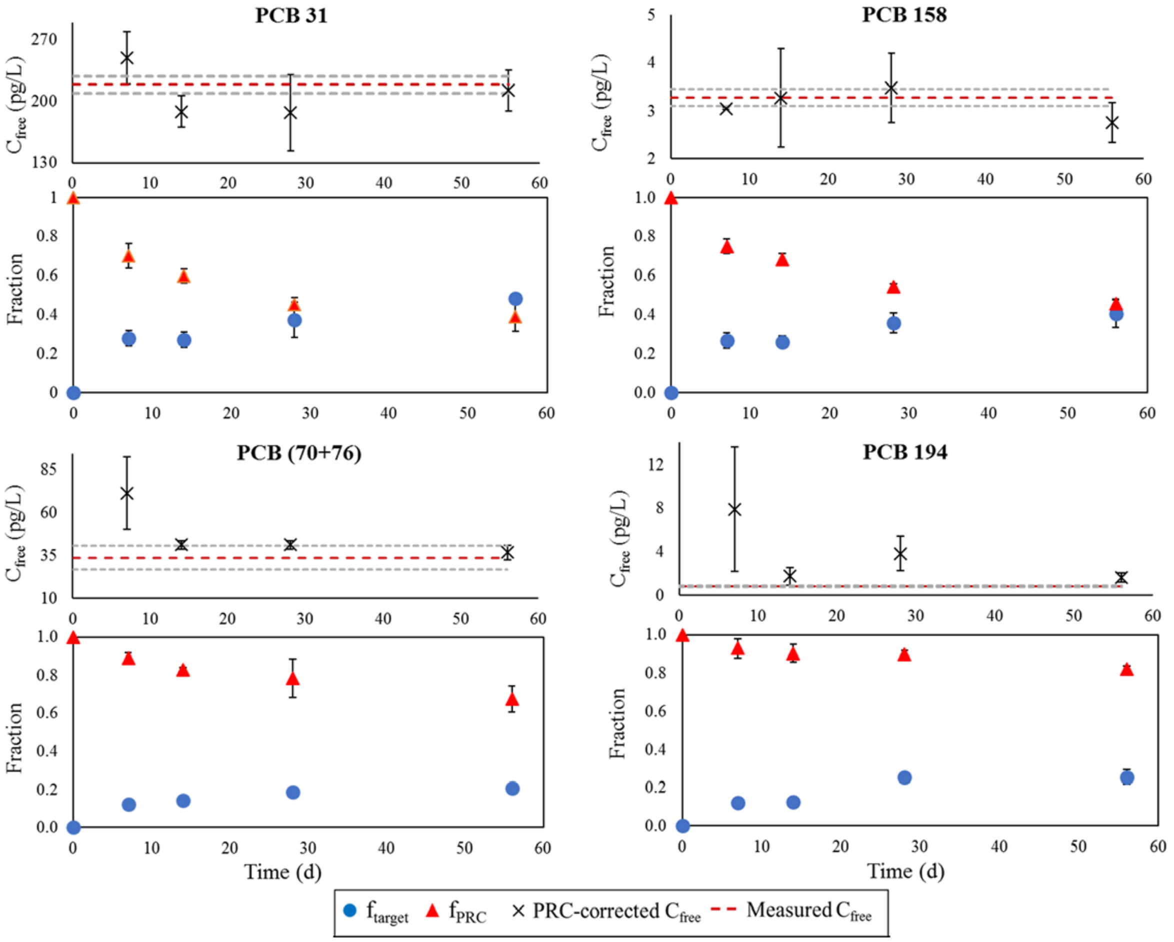

Figure 6. Comparison of estimated C_{free} (cross) with the true equilibrium C_{free} (red dash lines) for four PCBs. The fractional loss of PCB 29, 69, 155, and 192 at each time point measurement was used to estimate the C_{free} for the target PCBs 31, (70 + 76), 158, and 194, respectively. The fractional uptake of the target PCBs into PE (f_{target}) (circles) is also compared with the remaining fraction of their corresponding PRCs in PE (f_{PRC}) (triangles). Error bars and the thin dashed lines represent the mean ± one standard deviation (n = 3).

PCB 180 is 291 and 346 ng/g after 7 and 28 days of deployment in the 2 min-paused vibration system, respectively. That means, equilibrium C_{PE} of PCB 180 is predicted within a factor of 1.1 of the true value of 258 ng/g even after a 7-day deployment. Even PCB 208 + 195, which are the most hydrophobic congeners measured, are predicted within a factor of 1.2 after 7 days deployment despite the fact that only 40% of the equilibrium concentration was reached. Both 7-day and 28-day deployments of the 2 min-paused vibrating system yield close to the true value for all measured PCBs.

Increasing pause time to 5 days made the equilibrium C_{PE} measurements less accurate than the 2 min pause vibration but was better than the static deployments. For example, C_{PE} for PCB 180 was predicted within a factor of 1.9 by the 5-d-paused deployment in 28 days compared to a factor of 2.9 for the same deployment period for the static system. Thus, even a very intermittent vibration can greatly enhance the accuracy of the C_{PE} measurement. Higher precisions in estimation of C_{PE} using the low frequency vibration deployment results in estimated equilibrium concentrations that are statistically different from the true values, yet the absolute values are closer to the true value compared to the static deployment.

Since passive sampling is often used to estimate C_{free}, PCB concentrations in PE were converted to C_{free} using the individual congener PE-water partition constants (K_{PEw}) and are presented in Supporting Information Figures S7 and S8. The K_{PEw} values for PCB congeners were estimated from the correlation provided in Ghosh et al.[10] (Supporting Information Table S8). Conversion to C_{free} values appears to reduce the contribution of the highly chlorinated congeners toward the total PCB C_{free}. However, an important environmental impact of the pollutants in the porewater is the accumulation at the base of the aquatic food web and partitioning into benthic organism lipids. Predicted equilibrium concentrations in organism lipids were also calculated based on the assumption that organism lipids are similar to octanol, and the lipid concentrations at equilibrium are plotted in Supporting Information Figures S9 and S10. In Figures S9 and S10 again, the contribution of the highly chlorinated PCBs in porewater is emphasized because these compounds have a strong partitioning in lipids and, thus, need to be measured with a high degree of accuracy. This exercise illustrates the importance of assessing concentrations in the right matrix or to convert concentrations to chemical activities as suggested in Mayer et al.[1]

Apell and Gschwend[9] using the same PRC-correction method observed that the C_{free} estimates from 30 day and longer deployment times (up to 120 days) in static sediment were not statistically different from the measured concentrations. However, they did not conduct the comparison for deployment times of less than 30 days and for the PCBs larger than heptachloro-congeners. In this study, we did not see significant differences between the PRC-corrected and true equilibrium C_{PE} of hexachloro- and lower molecular weight PCBs for the 28 d-deployment time, which agrees with the observations by Apell and Gschwend.[9] In fact, the differences were significant for high molecular weight PCBs (some of the hepta-, and all octa-, and nonachloro congeners) (Figure 4). Although Apell and Gschwend[6] concluded that uptake kinetics of PCBs into PE is identical to the release kinetics of PRCs out of the PE, more recent studies reported anisotropic exchange kinetics for diffusion of PCBs and DDTs into passive samplers. For example, Choi et al.[4] observed slower uptake kinetics of the target PCBs compared to the release kinetics of the PRCs for PE deployed in stagnant sediment. In contrast, Bao et al.[7] reported faster kinetics of uptake for PCBs and DDTs into PDMS compared to the release kinetics out of PDMS and into the sediment.

Comparison of Exchange Kinetics. To further investigate the difference between the exchange kinetics of PCBs, f_{PRC} of the four PRCs used in this study was compared to the fractional uptake (f_{target}) of four target PCBs with similar K_{ow}s. If the exchange rates are identical, then the sum of f_{target} and f_{PRC} should be equal to one for all the time point measurements. In Figure 6, f_{target} for PCBs 31, (70 + 76), 158, and 194 is compared to f_{PRC} for PCBs 29, 69, 155, and 192, respectively after 7, 14, 28, and 56 days of deployment. The sum of f_{target} and f_{PRC} deviates from one by less than 20% for all the congeners. However, the ratio of fraction PRC lost to fractional uptake (shown in Supporting Information Figure S11) is dramatically different from 1 for the static deployment at early times and is highly variable. The PRC-corrected C_{free} of the four PCB congeners (shown with cross) is also compared to the measured value (shown with dash lines) for all the time point measurements in Figure 6. For all congeners, the accuracy of C_{free} estimation improves at longer deployment times. Thus, reasonably symmetric long-term kinetic profiles for uptake of PCBs and release of their corresponding PRCs were found in this study. Therefore, we suspect that the high variability and positive bias for the estimation of C_{free} (or equilibrium C_{PE}) of highly chlorinated congeners from static deployment is likely due to small fractional losses of the larger PRCs, which cause large PRC correction errors for predicting the equilibrium concentrations. The large variability comes from the fact that at times the direction of error in analyte measurement and PRC measurement cancel each other and at other times they compound the error.

Implications. PRC corrections have allowed extension of passive sampling to compounds that do not achieve equilibrium during a reasonable period of field deployment. However, we showed that the corrections are not reliable for estimating sediment porewater concentrations of strongly hydrophobic PCBs during a typical deployment time. The introduction of periodic vibration greatly enhances the time to equilibrium, increases measurement accuracy, reduces deployment times, and extends the use of passive sampling in conjunction with PRCs to strongly hydrophobic compounds. As demonstrated in the present work, with periodic vibration, even a 7-day deployment is adequate for a reasonably accurate in situ measurement of C_{free} for all PCB compounds. Shorter deployment times reduce the risk of loss, destruction, and vandalism of deployed passive sampler platforms in the field and can reduce costs when deployment and retrieval may be performed in one mobilization to the field. Using periodic vibration for a longer deployment of a month, it may even be possible to reach so close to equilibrium that PRC corrections may not be necessary for many compounds. We expect that using the proposed vibration technique for deployment of the passive samplers would also improve the accuracy of in situ measurements of C_{free} for other strongly hydrophobic compounds such as polychlorinated dibenzo-*p*-dioxins/dibenzofurans since these compounds are in the same range of hydrophobicity as hexa-, hepta-, and octachloro-PCBs. Further work is needed to operationalize the vibrating passive sampler through optimization of the vibration frequency, increased size of the devices to accommodate larger samplers, and field demonstration with HOC contaminated sediments.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b01020.

> Parameter estimation; model equations; details of model simulations; Matlab codes, and additional figures and tables (PDF)

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The authors declare no competing financial interest.

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