

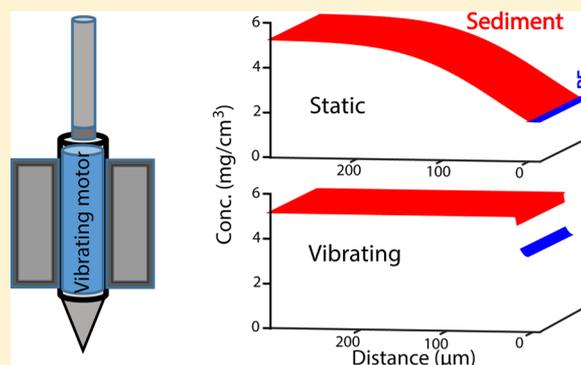
In Situ Passive Sampling of Sediment Porewater Enhanced by Periodic Vibration

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S Supporting Information

ABSTRACT: Passive sampling for the measurement of freely dissolved concentrations of organic pollutants in sediment porewater has emerged as a promising approach, but in situ measurements are complicated by slow mass transfer of strongly hydrophobic compounds. The primary resistance to mass transfer arises in the sediment side where a concentration depletion layer develops in the vicinity of the polymeric passive sampling material. The slow mass transfer results in underequibrated passive sampler measurements that need to be corrected for equilibrium, typically by extrapolation of the loss kinetics of performance reference compounds. Such corrections are prone to large errors, especially when deviation from equilibrium is large. In this research we address the challenge of slow mass transfer by disrupting the external depletion layer around an in situ passive sampler. We report an engineering innovation of adapting low-cost vibration motors for periodically disrupting the depletion layer in a passive sampler deployed in sediments. The uptake of 16 polycyclic aromatic hydrocarbons into polyethylene passive samplers was measured after 7, 14, 28, and 56 days of exposure to sediment under static, vibrating, and fully mixed modes. We demonstrate through laboratory experiments and numerical mass transfer modeling that short periodic shaking of a passive sampler deployed in static sediment enhances the rate of mass transfer and reduces the difference in the extent of equilibrium achieved compared to a well-mixed laboratory equilibrium. The improvement over static sediment deployment is especially evident for the high molecular weight compounds such as benzo(a)pyrene.



INTRODUCTION

The freely dissolved concentration of hydrophobic pollutants in sediment porewater is a critical measurement that is useful in assessing fate, transport, and bioavailability of these compounds.¹ Accurate measurement of low aqueous concentrations of hydrophobic compounds is challenging due to the association with colloidal and dissolved organic matter in porewater. This has led to the development of passive sampling approaches using well-characterized polymeric materials. When the polymeric material is able to reach equilibrium with the sediment porewater, such as in a well-stirred laboratory measurement, the estimation of freely dissolved porewater concentration (C_{free}) becomes a trivial exercise based on the measured partition constant of the polymer.^{2,3} However, in several situations, an in situ measurement in sediment is desired. Such measurements have been challenged by the difficulty in reaching equilibrium between porewater and the passive sampler as mass transfer through the depletion layer outside the commonly used polymers (with commonly used thicknesses) becomes limiting in the absence of active mixing.⁴ It has been shown that for strongly hydrophobic compounds equilibrium may not be achieved in the field even after one year in 51 μm polyethylene (PE).⁵ Several researchers have adopted the use of performance reference compounds (PRCs) dosed in

the polymer to assess the kinetics of mass transfer and correct for nonequilibrium.^{6–14} While corrections based on PRC loss work reasonably well for compounds with low to midrange hydrophobicity, the corrections become increasingly erroneous for strongly hydrophobic compounds when the departure from equilibrium increases.¹⁴ Several approaches for calibration using PRC data have been suggested.^{6–10} In all of these approaches, the uncertainties introduced by the PRC correction are larger when the extent of equilibrium is low, which is the case for strongly hydrophobic compounds in the field.

A primary uncertainty in the PRC correction arises from the fact that nearly always it is the sediment side mass transfer in the immediate vicinity of the passive sampler that controls overall kinetics.⁴ The retarded diffusion in the sediment side is impacted by the site-specific sorption characteristics of the sediment, which can vary across orders of magnitude. For example, Hawthorne et al.¹⁵ reported a 3–4 orders of magnitude range for site-specific K_{oc} values for polycyclic aromatic hydrocarbons (PAHs). Thus, to be able to correct for

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nonequilibrium and estimate in situ porewater concentrations, we need to first have an estimate of site-specific partitioning of the analytes of interest. The loss kinetics of a few PRC compounds into sediment is used to infer the desorption behavior of a large range of analyte compounds from sediment.⁸

Thinner polymeric materials can be used to increase the surface area to volume ratio, reduce the depletion per unit area,⁶ and reduce deployment time. However, even with some of the thinnest polymers practically deployable in the field (e.g., 25 μm thick PE), sediment-side mass transfer limitation can be significant.⁴ Making the polymers too thin makes them prone to damage during deployment in sediment, reduces the total mass of polymer sampling material (impacting detection limits), and also poses a physical challenge of insertion in sediments if the polymer surface area is very large.

To address these challenges, we take a very different approach of manipulating the external depletion layer in the sediment side of a passive sampler. We demonstrate for the first time a novel approach of in situ passive sampling that overcomes the slow approach to equilibrium for hydrophobic organic compounds in static sediments. Our approach involves mechanical disruption of the depletion layer outside the polymer surface using periodic vibration performed in situ. We adapted small vibration motors, used for haptic feedback in cell phones and other electronic devices, to periodically vibrate in situ passive sampling frames. The concept of passive sampling still applies to the vibrated deployment because the disruptions introduced by the periodic vibration is not unlike natural sediment processes induced by burying and sediment ingesting worms that also achieve chemical equilibrium through small-scale physical disruptions in sediments. Laboratory experiments were performed using PAH-impacted field sediments to compare the approach to equilibrium under static, well-mixed, and differently shaken passive sampling modes. We also performed numerical modeling of the mass transfer process to mechanistically explain our observations and optimize the duration and periodicity of the vibrations in order to minimize the energy requirement to drive the vibration motors.

MATERIALS AND METHODS

Materials. Low-density PE sheets (25 μm thickness), manufactured by Poly-America (Grand Prairie, TX) were purchased from the Home Depot. PAH and deuterated PAH stock solutions were purchased from Fisher Scientific (Pittsburgh, PA). Cylindrical vibrating motors with a diameter of 9 mm and length of 25 mm were purchased from Precision Microdrives (London, UK). The motors operated at a rated voltage of 3 V, operating current of 130 mA, and vibrating speed of 13 500 rpm. Pulse-pause timers (model 60H) were purchased from Velleman Inc. (Fort Worth, TX). Prior to use, PE sheets were soaked twice in hexane/acetone (50/50) and left on a shaker for 24 h each time to remove oligomers and any target and nontarget contaminants. Clean PE sheets were then cut into 6 mm \times 2 cm strips (2.8 mg) and were soaked in a PRC solution (80:20 methanol:water with pyrene-d10 and phenanthrene-d10) and allowed to equilibrate for 15 days on an orbital shaker.

After impregnation, all strips were removed from the PRC solution and rinsed with DI water to remove residual methanol on the surface. Two strips were extracted immediately in a 1:1 hexane and acetone mixture (3 \times 24 h) to determine the initial PRC concentration in the PE strips.

In Situ Shaken Passive Sampler Design. Two motors were connected in parallel to a timer and a power supply (2 rechargeable batteries 1.2 V, 700 mAh each) (Figure 1). The

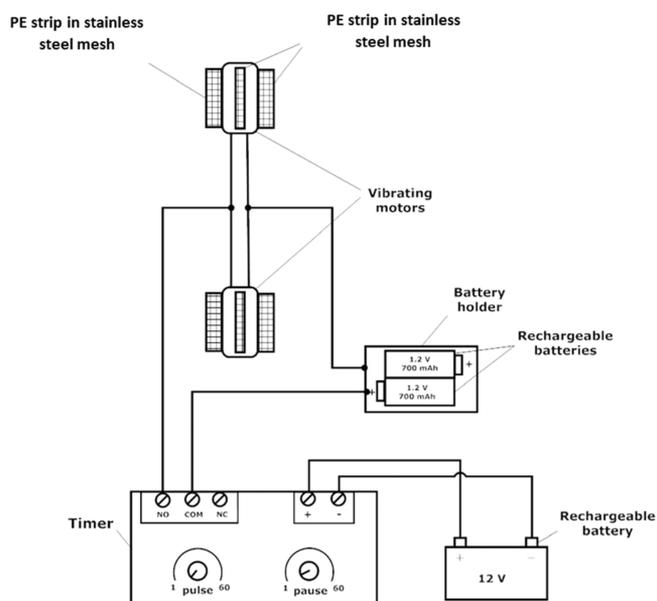


Figure 1. Wire diagram of a vibrating passive sampler. PE samplers, enclosed in stainless steel mesh, were attached to the motors. Two motors were connected in parallel to a timer and a power supply (2 rechargeable batteries 1.2 V each). The timers were powered by a 12 V battery.

timers were powered by a 12 V power supply and were programmed to control motor vibration duration and frequency: 5 s pulse and 2 min pause (high frequency), 2 s pulse and 5 min pause (low frequency). The small PE sheets described above were enclosed in stainless steel mesh (14 mesh from TWP Inc., Berkeley, CA) and were attached like radial fins on cylindrical motors (four fins on each motor) as shown in Figure 1 and Supporting Information Figures S1–3.

PAH contaminated river sediment samples from the vicinity of former manufactured gas plants studied previously (identified as HD-3 and HD-5 in Khalil et al.¹⁶) were used in the present work. The two sediments were combined to obtain a sufficient quantity for the present experiments. The sediment was mixed with DI water containing 200 mg/L sodium azide to make a slurry with weight ratio of 1:2 (dry sediment/water). Water addition was performed to make the sediment more fluid and allow good mixing in the jars.³ For the well-mixed exposure, 250 mL of the sediment–water slurry and eight of the prepared PE samplers were transferred to a wide mouth jar with a Teflon-lined cap. The jar was placed on a rotary agitator and tumbled at 28 rpm. The rest of the sediment slurry was placed in a large glass tray (25 cm \times 35 cm \times 6 cm). Four motors were placed inside the sediment in the tray with 10 cm separation to prevent them from influencing each other. Two motors vibrated at the high-frequency mode and two at the low-frequency mode. Eight additional PE samplers, enclosed in stainless steel mesh without motors, were placed inside the same tray in a static mode at least 10 cm away from any vibrating motor to simulate a static deployment. The tray was then covered with aluminum foil. Two PE strips were removed from the well-mixed, static, and vibrating systems and analyzed

for native PAHs and PRC compounds after 7, 14, 28, and 56 days.

PAH 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 anthracene-d10 surrogate was added to assess the effectiveness of sample processing, and extracts with lower than 80% surrogate recoveries were discarded. Samplers were extracted with a 1:1 hexane and acetone mixture (3×24 h, with sequential extracts pooled). The final extraction volumes were blown down to 1 mL using a stream of nitrogen gas. PAHs from sediment were extracted by sonication (EPA method 3550B) and cleaned using activated silica gel (EPA method 3630C). Four internal standards were added to the final extracts before analysis (1-fluoronaphthalene, *p*-terphenyl-d14, benzo(a)pyrene-d12, and dibenz(a,h)anthracene-d14). The 16 USEPA priority pollutant PAHs were analyzed in an Agilent 6890 gas chromatograph coupled to an Agilent 5973N MS detector as described in Khalil et al.¹⁶

Modeling Uptake of Analytes from Sediment Porewater. A numerical modeling approach was used to describe the mass transfer process involved in the static, vibrating, and well-mixed deployments of passive samplers. The modeling structures for static and vibrating deployments are similar and are described first with respective boundary conditions. Finally the well-mixed model is described where mass transfer limitation is only in the polymer side.

Static System. Two modeling approaches were implemented to simulate mass transfer of PAHs from sediment particles into porewater, and from porewater into polymer during static deployment. The first approach is based on the one-dimensional diffusion model presented by Fernandez et al.⁸ but solved numerically. In this model, mass transfer within the sediment particle is assumed to be fast, and instantaneous equilibrium between sediment particles and porewater is assumed (local equilibrium model). Mass transfer within the polymer and in porewater is described by Fick's second law of diffusion. Instantaneous equilibrium is assumed at the polymer surface boundary with porewater as done in previous work.^{4,8} This model is explained in more detail in the [Supporting Information](#).

The second approach is based on the assumption that mass transfer from sediment particles into porewater is described by first-order kinetics.^{4,18} The model was solved using two different hypotheses: (1) All PAHs are associated with the slow desorbing pool in sediment, and desorption is characterized by the slow desorption rate constant. (2) All PAHs are associated with the fast desorbing pool in sediment, and desorption is characterized by the fast desorption rate constant. First-order desorption rate constants were obtained from a study by Ghosh et al.,¹⁷ where sediment from a similar manufactured gas plant impacted site was used (see [Supporting Information](#)).

In a system containing a PE strip with the thickness of $2l_p$ and sediment/porewater with thickness of l_w on both sides, sediment concentration (S) changes following first-order kinetics^{4,18}

$$\frac{\partial S}{\partial t} = k(K_d C_w - S) \quad l_p < x < l_p + l_w \text{ and } -l_p < x < -l_p - l_w \quad (1)$$

where t is time (s), S is chemical concentration in sediment (ng/g), K_d is sediment–water partition coefficient (cm^3/g), k is first-order desorption rate constant (s^{-1}), and C_w is chemical concentration in water (ng/cm^3)

For a PE strip with concentration C_{PE} and at point x and time t

$$\frac{\partial C_{PE}}{\partial t} = D_{PE} \frac{\partial^2 C_{PE}}{\partial x^2} \quad -l_p < x < l_p \quad (2)$$

where C_{PE} is chemical concentration in PE (ng/cm^3) and D_{PE} is chemical diffusivity in PE (cm^2/s)

The transport equation in porewater with concentration of C_w at point x and time t will be as follows

$$\frac{\partial C_w}{\partial t} = D \frac{\partial^2 C_w}{\partial x^2} - \left(\frac{\rho}{\varepsilon} \right) \frac{\partial S}{\partial t} \quad l_p < x < l_p + l_w \text{ and } -l_p < x < -l_p - l_w \quad (3)$$

where ρ is sediment bulk density (g/cm^3) and ε is porosity (cm^3/cm^3).

D is the diffusivity in water (D_w) after correction for tortuosity:

$$D = \frac{D_w}{1 - \ln \varepsilon^2} \quad (4)$$

Substituting eq 1 in eq 3, the transport equation in porewater can be rewritten as

$$\frac{\partial C_w}{\partial t} = D \frac{\partial^2 C_w}{\partial x^2} - \left(\frac{\rho}{\varepsilon} \right) k(K_d C_w - S) \quad (5)$$

Initial Conditions. The polymer was initially clean, and porewater was assumed to be in equilibrium with sediment.

$$C_{PE} = 0 \quad -l_p \leq x \leq l_p \quad (6)$$

$$C_{w0} = S_0/K_d \quad l_p < x < l_p + l_w \text{ and } -l_p < x < -l_p - l_w \quad (7)$$

where S_0 is initial chemical concentration in sediment (ng/g) and C_{w0} is initial chemical concentration in water (ng/cm^3)

Boundary Conditions. Continuity of flux and equilibrium condition was assumed at the PE–water boundary as done in previous work.⁸

$$D_{PE} \frac{\partial C_{PE}}{\partial x_{PE}} = D \frac{\partial C_w}{\partial x_w} \quad x = l_p \text{ and } x = -l_p, \quad t > 0 \quad (8)$$

$$C_{PE} = K_{PEw} C_w \quad x = l_p \text{ and } x = -l_p \quad (9)$$

where K_{PEw} is the PE–water partition coefficient (cm^3/cm^3)

Due to symmetry, the flux will be zero at the center of the PE sheet. Porewater concentration is equal to the initial concentration far away from the polymer at $x = l_p + l_w$ and does not change over time:

$$\frac{\partial C_{PE}}{\partial x} = 0 \quad x = 0 \quad (10)$$

$$\frac{\partial C_w}{\partial t} = \frac{\partial S}{\partial t} = 0 \quad x = l_p + l_w \text{ and } x = -l_p - l_w \quad (11)$$

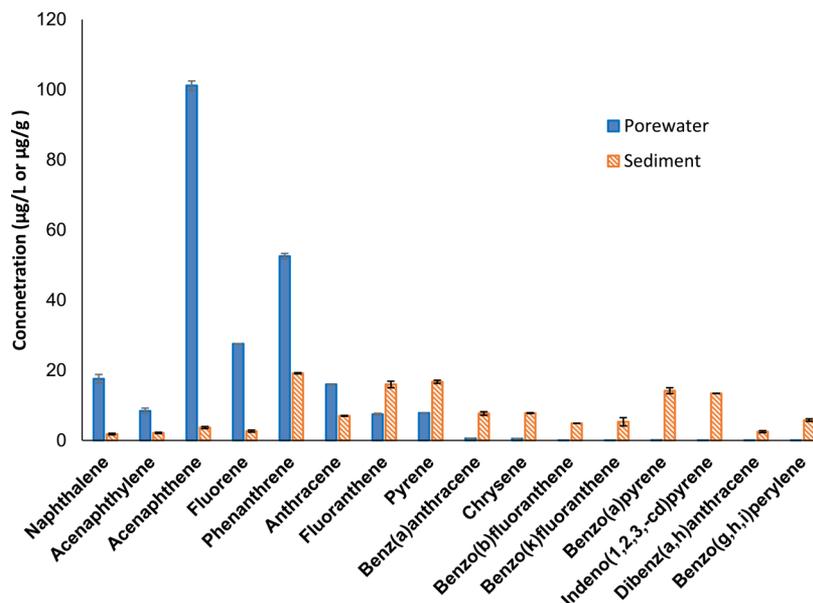


Figure 2. PAH concentration in porewater ($\mu\text{g/L}$) and sediment ($\mu\text{g/g}$). Sediment concentrations are mean values from triplicate measurements. Porewater concentrations were obtained using eq 9 and $C_{\text{PE,eq}}$ which are mean values from duplicate measurements of PE concentration after 56 days of exposure in the fully mixed system.

Vibrating System. In the vibrating system, when the motor is in pause mode, the mass transfer is similar to the static mode, and sediment and porewater concentration in the vicinity of the polymer depletes with time. Every time the motor vibrates, the sediment and porewater in the vicinity of the polymer are mixed up. Our visual observation of the vibration system indicated that the extent of fluidized mixing was at least 1 cm from the surface of the device with pressure waves from the vibration extending to 2–3 cm from the device (Supporting Information Figure S3). We assumed that this mixing is enough to increase sediment concentration to the initial concentration in sediment (S_0). Porewater concentration right after each vibration pulse will also increase to the initial concentration:

$$C_w = C_{w0}; S = S_0 \quad l_p < x < l_p + l_w \text{ and } -l_p < x < -l_p - l_w \quad (12)$$

Fully Mixed System. Diffusion in a polymer with thickness of $2l_p$ follows Fick's second law:

$$\frac{\partial C_{\text{PE}}}{\partial t} = D_{\text{PE}} \frac{\partial^2 C_{\text{PE}}}{\partial x^2} \quad -l_p < x < l_p \quad (13)$$

The passive sampler was assumed to be initially clean. Since the system is perfectly mixed, the porewater concentration remains constant and equal to the initial value (S_0/K_d) during the deployment time. The boundary condition is defined as

$$C_{\text{PE}} = K_{\text{PEw}} C_{w0} \quad x = l_p \text{ and } x = -l_p \quad (14)$$

The model equations were solved in Matlab using an explicit, finite-difference numerical modeling technique.¹⁹ To check the numerical model, the fractional uptake of chrysene into PE was simulated, and the solution was found to be identical to the analytical solution based on Fernandez et al.⁸ Details of parameter estimation, numerical solutions, and Matlab codes are provided in the Supporting Information.

RESULTS AND DISCUSSION

Equilibrium PAH Concentration in Sediment and Porewater.

The concentrations of the 16 EPA priority pollutant PAHs in sediment are shown in Figure 2. The four most abundant PAHs were phenanthrene, fluoranthene, pyrene, and benzo(a)pyrene. The total concentration of PAHs in the sediment was $128 \mu\text{g/g}$. The 2–4 ring PAHs comprised 60% of the total in sediment. The equilibrium concentrations in PE ($C_{\text{PE,eq}}$) were determined by extracting the PE samplers after 56 days of deployment in the fully mixed PE–sediment system. Another time point measurement of PE concentration after 77 days of deployment confirmed that equilibrium had reached in PE for all PAHs in 56 days (Supporting Information Table S3). Both PRCs (pyrene-d10 and phenanthrene-d10) were depleted completely in the fully mixed exposure in 30 days (Supporting Information Figure S5). The freely dissolved porewater concentrations were calculated from equilibrium concentration of PAHs in PE and reported values for K_{PEw} ⁵ (eq 9).

As shown in Figure 2, acenaphthene and phenanthrene are the dominant PAHs in porewater. PAHs up to chrysene contributed to 99% of the total porewater concentration at equilibrium. Toxic units were estimated for each PAH by dividing porewater concentrations by final chronic values (FCVs).²⁰ The total toxic unit of 16 PAHs measured in the sediment porewater was approximately 9.33 indicating that PAHs in this sediment likely pose narcosis toxicity to benthic invertebrates.²⁰

PAH Uptake in Static Deployment. As expected, the uptake of all PAHs was slowest in the static exposure. In fact, none of the PAHs from fluoranthene to indeno(1,2,3-cd)pyrene reached equilibrium in 56 days of contact. The fractional uptakes of benz(a)anthracene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene were only 35%, 11%, and 8%, respectively, after 28 days. Previous studies have reported similar slow uptake in a static exposure,^{11–13} especially for larger molecular weight compounds. For example, Fernandez et al.¹¹ calculated the fractional equilibration of PCBs into 25 μm

PE by measuring the fractional loss of ^{13}C -labeled PCBs after 44 days of field deployment. The average fractional equilibration of penta- and hexachlorobiphenyls from different locations in the field were only 37% and 33%, respectively.

Effect of Vibration on Polymer Uptake Rate. Periodic vibration of the PE sampler resulted in faster uptake compared to static deployment for all PAHs measured. As shown in Figure 3, the uptake of chrysene after 56 days was only 40% of

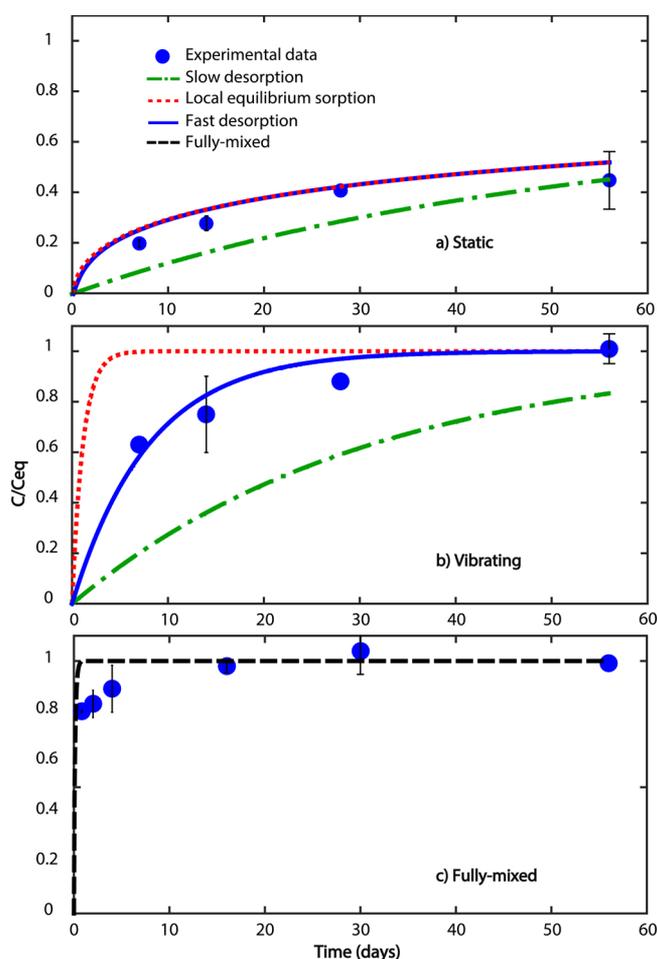


Figure 3. Fractional uptake of chrysene in PE passive sampler in static (a), vibrating (b), and fully mixed (c) systems. Experimental data have been shown by circles, and model simulations have been shown by lines. Note that for the static system the local equilibrium and fast desorption models overlap.

equilibrium in static exposure compared to 100% for the vibrating system. Even after 7 days of exposure, the vibrating system reaches 63% of equilibrium for chrysene compared to 20% in the static system. Comparison between the static and vibrating system for several other PAH compounds is shown in Figure 4 and Supporting Information Figure S4. Both PRCs were lost more than 90% at the first time point of measurement for the vibrating systems and fully mixed systems (Supporting Information Figure S5), which generally agreed with the uptake of the analogous PAHs. As PRC performance was not the focus of this study, using a full range of high molecular weight PRCs and performing shorter duration measurements of PRC loss are recommended in future work in order to provide a more robust analysis of PRC performance in the vibrating system.

For PAH compounds less hydrophobic than chrysene (e.g., fluoranthene and pyrene), the static system showed reasonable uptake of close to 70% in 56 days while the vibrating system reached equilibrium during that exposure. When the passive sampler is close to equilibrium, the correction for non-equilibrium is relatively accurate. However, as the kinetics slow down and only a small fraction of equilibrium is achieved in the sampler, the correction for nonequilibrium becomes error-prone.⁹ This is the case for the PAH compounds that are more hydrophobic than chrysene. The improvement over static system was more evident for larger molecular weight PAHs. For example, the measured fractional uptake of benzo(a)pyrene was improved from 6% to 55% in 7 days and from 23% to 90% after 56 days. The fact that vibration was more effective on uptake rate of heavier PAHs can be explained based on the nature of the overall mass transfer resistance in a passive sampler⁶

$$\frac{1}{k_0} = \frac{\delta}{D_w} + \frac{1}{K_{PEW}D_{PE}} \quad (15)$$

where k_0 is the overall mass transfer rate constant and δ is the diffusion distance.

The first term on the right-hand side of eq 15 describes the sediment-side mass transfer resistance. The large K_{PEW} values of the more hydrophobic compounds make the second term smaller than the first, thereby making the first term or the water-side mass transfer more dominant. The ratio of diffusivities in water and polymer (D_w/D_{PE}) also increases as the compound becomes more hydrophobic. However, K_{PEW} tends to be the dominant factor influencing which side controls mass transfer since K_{PEW} changes over a wider range of values compared to the range where the diffusivity ratios vary for different compounds.²¹ As a result, disrupting the depletion layer (decreasing apparent δ) by means of vibration will be more effective on the overall mass transfer rate of larger molecular weight PAHs. Our experimental data indicated that concentration of larger molecular weight PAHs ($\log K_{ow} > 5.5$) reached more than 50% of their equilibrium concentration in PE within 14 days of deployment in the vibrating system (Supporting Information Figure S4). Thus, field deployment of passive samplers with periodic vibration will encounter less challenges of nonequilibrium correction for larger molecular weight compounds.

Results from the vibration work demonstrated a great improvement of PE uptake after short exposure times (1–2 weeks). The faster exchange will also allow the use of high molecular weight PRCs to accurately correct for the remaining nonequilibrium in a vibrating system without the need for long exposure times.

Comparison of Three Modeling Approaches in Static, Vibration, and Fully Mixed Deployments. Figure 3a and 3b demonstrate modeling results for chrysene in static and vibrating systems based on local equilibrium, slow desorption, and fast desorption models. As shown in Figure 3a, in static deployment, overall mass transfer into the polymer is slow and the predictions based on local equilibrium assumption and the fast desorption rate model are indistinguishable. Also, both predictions are close to the observed uptake of chrysene in the static deployment. However, the slow rate of desorption model predicts uptake that is slower than the observed values. Thus, it appears that for modeling static deployments, due to the rate limiting mass transfer through the depletion layer, it is adequate to assume local equilibrium between sediment and water.

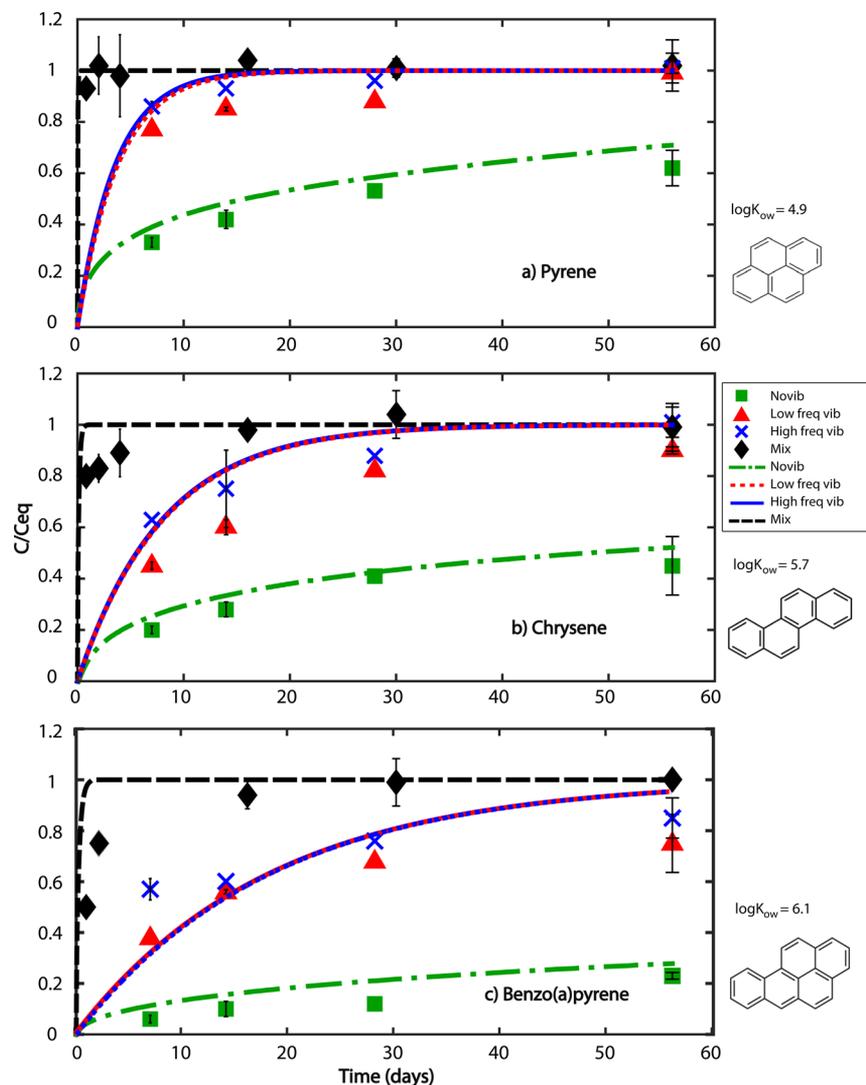


Figure 4. Fractional uptake of pyrene (a), chrysene (b), and benzo(a)pyrene (c) in PE passive sampler in four differently exposed systems. Experimental data have been shown by symbols, and fast desorption model simulations have been shown by lines.

For the vibrating system, assuming that the sediment is effectively mixed after vibration, the model predictions based on local equilibrium and fast rate of desorption deviated as shown in Figure 3b. While the fast rate of desorption model prediction is close to the measured uptake of chrysene, the prediction based on local equilibrium greatly overpredicts uptake. The same results were observed for pyrene as indicated in Supporting Information Figure S6. Thus, it appears that as the depletion layer is disrupted by vibration and mass transfer is enhanced, desorption from sediment becomes limiting and local equilibrium between sediment and water can no longer be assumed. The fast desorption rate adequately predicts uptake while the slow desorption rate still underpredicts uptake in the polymer. Past work has demonstrated that PAH desorption from MGP-impacted sediments is characterized by slow and fast desorbing PAH fractions.¹⁷ However, the overall kinetics for the vibration system appear to be driven by the fast desorption kinetics and not the slow desorption likely because the sediments are not being depleted enough to reach the slow desorption regime.

For the fully mixed system, a local-equilibrium model was implemented. As shown in Figure 3c, the model agrees

reasonably with the observed fast uptake of chrysene and the attainment of equilibrium in the matter of a few days. The fully mixed system brings a large volume of sediment to contribute to the required uptake by the passive sampler, and hence the kinetics are fast enough to appear close to instantaneous equilibrium.

Modeling Uptake of Pyrene, Chrysene, and Benzo(a)-pyrene. Experimental and modeling results for pyrene ($\log K_{ow} = 4.9$), chrysene ($\log K_{ow} = 5.7$) and benzo(a)pyrene ($\log K_{ow} = 6.1$) in static, vibrating, and fully mixed systems are shown in Figure 4. Based on the discussion above, only the fast desorption model was used for predicting uptake in static and vibrating systems, and a local equilibrium model was used for predicting the fully mixed system. As shown in Figure 4, the model predictions reasonably agreed with the uptake profiles of the three PAHs in all three modes of exposure. For all three PAHs, although there were small differences between the experimental results from 2 and 5 min pause times (not statistically significant except for pyrene at day 14), the model predicted that there should not be a significant difference between the two (see Supporting Information Tables S4, S5, and S6). In the model we assumed that both pulse durations

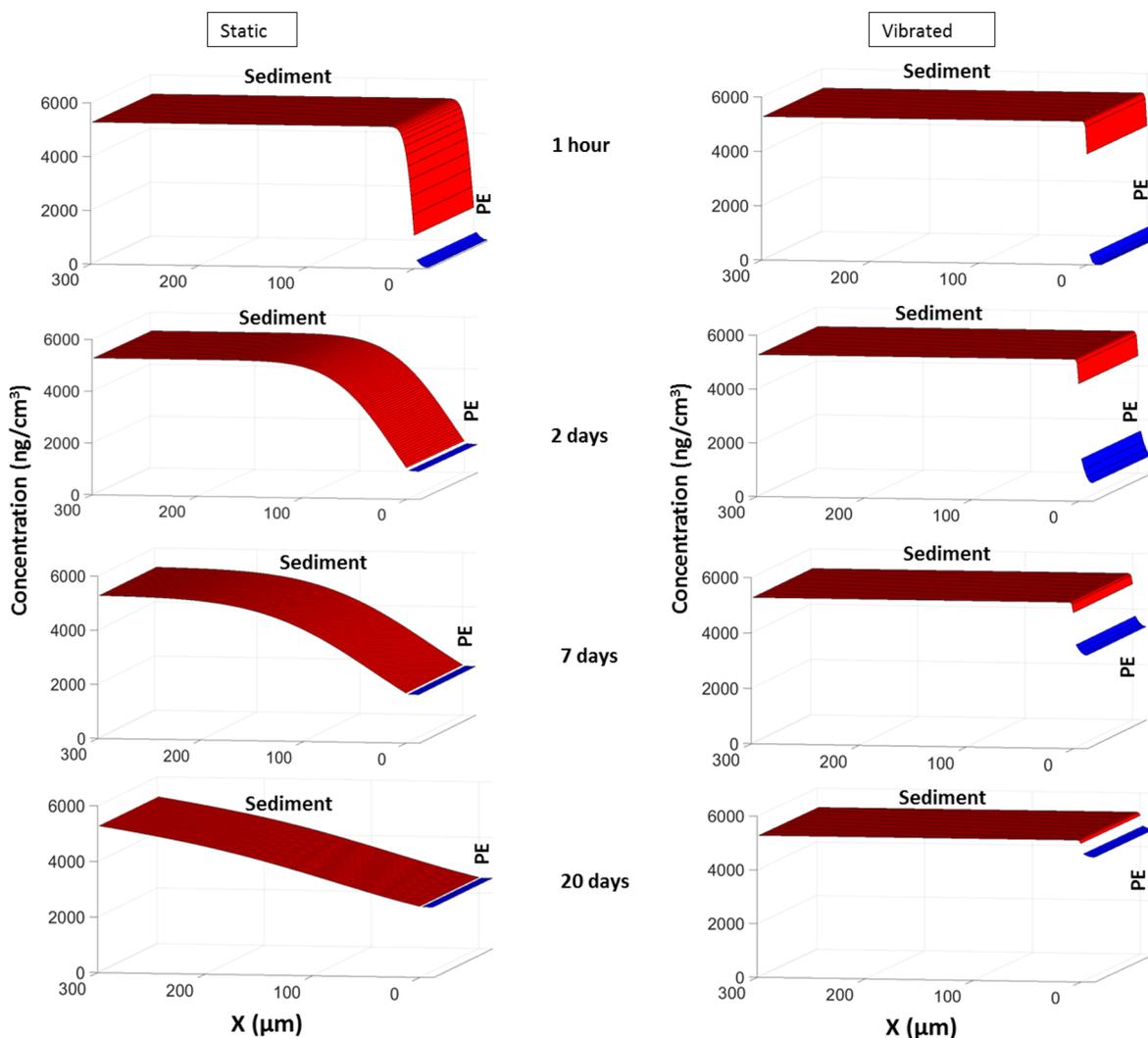


Figure 5. Model simulations of chrysene concentration profile within sediment and PE for static and periodic vibration deployments. The values shown on the Y-axis are chrysene concentration in sediment and concentration in PE multiplied by sediment–PE partition constant ($C_{PE} \times K_{sed-PE}$).

are long enough to mix up the sediment to initial bulk concentration. However, in reality short pulse time (2 s) in the low-frequency system may not be long enough to satisfy the model assumption.

To better illustrate how the periodic vibration impacts development of the sediment-side depletion layer, the concentration profiles in the sediment and half-width of the PE sampler were plotted for chrysene as a function of exposure time. As shown in Figure 5, left panel, for the static deployment, chrysene in the sediment side is depleted well into 300 μm distance from the PE surface after 20 days. The concentration values for PE plotted in Figure 5 have been multiplied with K_{sed-PE} to make the values directly comparable to the sediment concentration. As indicated in Figure 5, left panel, the concentration in PE reaches equilibrium with the depleted concentration in the sediment adjacent to the surface in 2 days or less, and the mass transfer limitation is moved to the sediment-side depleted layer. Also, after the first few hours of exposure, there is no concentration gradient within the polymer indicating all mass transfer resistance is in the sediment side. In stark comparison, for the periodic vibration deployment, since the sediment side is mixed up at frequent intervals, the deep depletion layer in the sediment side is not

able to develop, and the mass transfer resistance is limited to a few microns near the polymer surface. In fact, as seen in the 2-day simulation for the concentration gradient within PE in the vibrating system, the model suggests that there is still some polymer-side resistance. As a result, the concentration in PE rises much more rapidly than in the static case.

For the well-mixed system, pyrene uptake is fast and modeled reasonably well by the fully mixed local equilibrium model (Figure 4a). However, the model is not accurate for early times for the more hydrophobic compounds, especially benzo(a)pyrene (Figure 4c). This could be due to inaccuracy of reported diffusivity in PE, slow desorption from sediment, or inefficient mixing of the system. Inefficient mixing slows the uptake of more hydrophobic compounds since sediment-side mass transfer is dominant for high molecular weight PAHs (as described earlier) and disruption of depletion layer by efficient mixing is more important. Previous studies²² have observed slower uptake of larger PCBs in well-mixed sediment–slurry systems and attributed the slow kinetics to inefficient mixing and slow desorption.

Optimization of Vibration Frequency. Results of the vibration model for PE uptake of chrysene were used to test the effect of different vibration frequencies and to optimize power

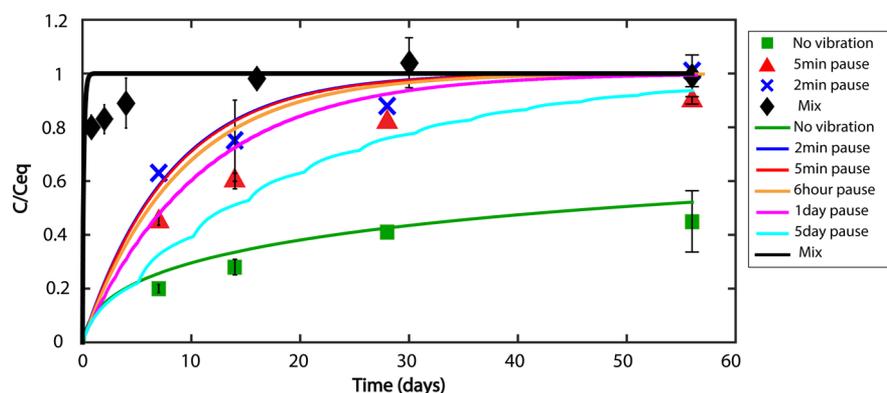


Figure 6. Model simulation of chrysene uptake in vibrating system with different pause times of vibration. Experimental data have been shown by symbols, and fast desorption model simulations have been shown by lines.

requirement. All vibration frequencies had pulse duration of 5 s and varied in pause time. The modeling results were based on the fast desorption model, and pause times were set at 2 min, 5 min, 6 h, 1 day, and 5 days (Figure 6). Small differences (6% or less) were observed between the 2-min and 6-h pause models (see Supporting Information Table S7). Even the 1-day pause model predicted an uptake profile which was not greatly different from the 2-min pause model. The 5-day pause profile tracked the unmixed profile for the first 5 days and then jumped up to a higher uptake profile as mixing altered the boundary condition. Although the 5-day pause model does not show significant improvement over the static system in short deployment times (<7 days), the model still predicts 75% fractional uptake after 28 days. In comparison the fractional uptake of chrysene is only 40% in static system for the same exposure duration. These results indicate that significant improvement over the static system is possible with lower frequencies of vibration (large pause times). Increasing pause time is desirable as there is no energy consumption during the pause time when the motor is not vibrating. In order to optimize pause time, energy consumption was estimated for deploying a vibration system for 15 days and a range of pause times. The fractional uptake of three PAHs (pyrene, chrysene, and benzo(a)pyrene) in PE after 15 days was also determined with the model for each pause time and plotted versus energy consumption (Supporting Information Figure S7). Only 30 mWh is required to enhance the fractional uptake of chrysene to 80% in 15 days of deployment. In comparison, a typical AA size NiMH rechargeable battery can provide about 1000 mWh of energy. However, further enhancement of fractional uptake in PE from 80% to 82% increases the energy requirement to 2340 mWh. This is also evident from Figure 6 where we see little enhancement of uptake when the pause time is reduced below 6 h.

Implications. A recent review article on passive sampling by Booi et al.²³ concluded that options to reduce time for equilibrium are limited to manipulation of area/volume ratio of sampler, choice of sampler material, and flow rate. Past work has led to significant optimization of the physical aspects of the passive samplers, yet attainment of equilibrium remains difficult for strongly hydrophobic compounds especially for in situ sediment porewater measurements. Also, there is little that can be done in the sediment environment to enhance porewater velocity. This study advances the practice of passive sampling by addressing a key bottleneck through the novel introduction of periodic vibration in the sampling platform to disrupt the

depletion layer that develops in the sediment side and slows mass transfer. Through mass transfer modeling, we also provide a mechanistic interpretation of how periodic vibration enhances the approach to equilibrium. While PRC corrections have allowed extension of passive sampling to compounds that do not achieve equilibrium during a reasonable period of deployment, the introduction of vibration greatly enhances approach to equilibrium, reduces deployment times, and extends the use of passive sampling in conjunction with PRCs to strongly hydrophobic compounds as shown for benzo(a)pyrene in this study. Further development is necessary to build robust prototypes and perform tests in the field. The size of the devices and motors may also need to be increased to enable deployment of larger passive samplers to target low concentrations in sediment.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b00531.

- (1) experimental setup; (2) details of the mathematical models used; (3) Matlab code for the numerical solution; (4) additional figures for high molecular weight PAHs, PRC desorption, energy usage, and statistical interpretation of the data (PDF)

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Notes

The authors declare no competing financial interest.

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