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Quantitative thermodynamic exposure assessment of PCBs available to sandworms (*Alitta virens*) in activated carbon remediated sediment during ongoing sediment deposition†

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Marine mesoscale studies with sandworms (*Alitta virens*) were conducted to isolate important processes governing the exposure and bioaccumulation of polychlorinated biphenyls (PCBs) at contaminated sediment sites. *Ex situ* equilibrium sampling with silicone-coated jars, and *in situ* passive sampling with low-density polyethylene (LDPE) were used to determine the performance of an activated carbon (AC) amendment remedy applied to the bed sediment. A quantitative thermodynamic exposure assessment ('QTEA') was performed, showing that PCB concentrations in polymers at equilibrium with the surficial sediment were suited to measure and assess the remedy effectiveness with regard to PCB bioaccumulation in worms. In practice, monitoring the performance of sediment remedies should utilize a consistent and predictive form of polymeric sampling of the sediment. The present study found that *ex situ* equilibrium sampling of the surficial sediment was the most useful for understanding changes in bioaccumulation potential as a result of the applied remedy, during bioturbation and ongoing sediment and contaminant influx processes. The ultrathin silicone coatings of the *ex situ* sampling provided fast equilibration of PCBs between the sediment interstitial water and the polymer, and the multiple coating thicknesses were applied to confirm equilibrium and the absence of surface sorption artifacts. Overall, *ex situ* equilibrium sampling of surficial sediment could fit into existing frameworks as a robust and cost-effective tool for contaminated sediment site assessment.

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Environmental significance

Critical processes governing the exposure of polychlorinated biphenyls (PCBs) at contaminated sediment sites were isolated in the laboratory. Processes affecting bioaccumulation of PCBs in sediment dwelling worms could be simplified, for remedy effectiveness monitoring, to the PCB concentration in polymers at equilibrium with the surficial sediment. *Ex situ* equilibrium sampling of the sediment will be a robust tool for determining the bioaccumulation potential at field sites experiencing ongoing influx of sediment, following application of AC amendment as a remedial treatment. Overall, *ex situ* equilibrium sampling of surficial sediment could provide better input data for Biota-Sediment Accumulation Factor (BSAF) models, compared to organic carbon normalized sediment concentrations.

Introduction

Contaminated sediment sites require dedicated environmental monitoring before, during, and after remedial activities to assess remedial efficacy. Of the remedial approaches available, mixing or amending contaminated sediments with activated carbon (AC) is increasingly used for sorbing hydrophobic organic contaminants (HOCs) and thereby lowering their freely dissolved concentrations (C_{free}) and, consequently, their bioavailability in the contaminated sediment.[1–5] Meanwhile, ongoing influx of fresh sediment and associated HOCs is a common occurrence at contaminated sediment sites, which are often located in protected net depositional areas.[6] Ongoing input sources, both dissolved and particulate associated, have challenged remediation and monitoring efforts at many contaminated sediment sites.[7–13] Natural and anthropogenic sediment processes at field sites, include: bioturbation, ongoing sediment influx/deposition, groundwater discharge, propellor wash from ship traffic, nearby maintenance dredging

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activity, sediment erosion and scour from flooding, and tidal and seasonal effects. Because of the complexity created by these processes, field studies of AC amendment remediation are often unable to isolate bioturbation and ongoing influx as the only relevant processes.

Existing frameworks available for monitoring contaminated sediment sites often utilize a combination of measurements in bulk phase sediment and in the water column (*i.e.*, exhaustive extractions to quantify total chemical concentrations), determination of bioaccumulation, and increasingly passive sampling. Passive sampling using various polymers has gained recognition as a useful tool for determining the C_{free} of HOCs in sediment interstitial water at sites undergoing remediation.[14–16] In addition to C_{free}, directly measuring and monitoring polymer concentrations is highly informative, as equilibrium concentrations of HOCs in polymers can be directly related to the "thermodynamic potential for bioaccumulation".[17–20] In addition, polymers are being explored as a tool to predict bioaccumulation, as HOC concentrations in polymer and HOC concentrations in biota lipid are highly correlated.[21–23] Consequently, the most immediate implementation of the polymeric sampling techniques, into existing risk assessment and monitoring frameworks, might be to replace organic carbon normalized bulk-phase sediment measurements in the Biota-Sediment Accumulation Factor (BSAF)[24–31] with polymeric sampling of the sediment.[17,18,20–22] While the need for this type of assessment has been known for two decades,[32,33] the practical implementation of polymers and BSAFs at contaminated sediment sites, undergoing remediation with AC, is still an area of scientific inquiry and debate. In this study, two polymeric sampling approaches were explored for establishing thermodynamic reference levels of polychlorinated biphenyls (PCBs) in sediment. The approaches were evaluated for understanding bioaccumulation potential during AC remediation and ongoing influx in a series of mesocosm experiments. The study and results presented in this article are part of a larger investigation (ESI, Fig. S1†).[34,35]

The present study compared PCB polymeric sampling to sandworm bioaccumulation in 90 days mesocosm experiments containing New Bedford Harbor sediment, which can be considered highly contaminated.[22] The New Bedford Harbor site and sediment have been a focus of past and present contaminated sediment research.[1,2,21,34–38] The mesocosms included ongoing influx of 'fresh' clean or contaminated sediment and bioturbation as processes driving contaminant transport between AC remediated bed sediments and the water column. The objectives of this research were to perform a quantitative thermodynamic exposure assessment ('QTEA') of native bedded PCBs in mesocosms and sandworms (*Alitta virens*), with regard to: (1) the presence or absence of AC mixed into the bed sediment, (2) the presence or absence of spiked PCBs on the input sediment (*i.e.*, sediment introduced periodically to simulate ongoing deposition), and (3) the polymeric sampling method: *in situ* passive (pre-equilibrium) sampling with low density polyethylene (LDPE) (passive sampling devices, PSDs) or *ex situ* equilibrium sampling with silicone coated jars (equilibrium sampling devices, ESDs). Equilibrium concentrations in polymers were converted to concentrations in lipid at equilibrium with the sediment, which then served as a thermodynamic reference level to assess and compare with lipid-normalized tissue concentrations determined in worms.

The type(s) of biota used in mesocosm studies are an important feature allowing experiments to resemble critical aspects of the natural environment.[6,39] The use of sandworms (*A. virens*; formerly *Nereis virens*), has implications on the bioturbation, fate, and transport of HOCs like PCBs.[6,36,40,41] Large marine sandworms make U-shaped galleries or burrows[39,41] approximately 8–10 cm in depth,[27,28,40] with maximum depths of 45 cm in the field.[42] The sandworms irrigate the burrows, and the burrow walls provide for more contaminant transport than uncolonized bed sediment.[40,43] The walls remain well oxidized,[40,41,43] and the burrows effectively increase the surface area of the sediment–water interface.[44] Along with their role in enhancing geochemical processes, sandworms are ecologically significant, forming the base of the food chain in some habitats, as prey for lobsters, fish, and birds.[26,42]

Sandworms have a variety of behaviors influencing their exposure to PCBs; for example, sandworms feed by extending a portion of their bodies from their burrow to deposit feed.[29,40] In addition, they have been reported to process large volumes of sediment or settled detritus, and sediment ingestion is considered a major route of contaminant uptake.[29,45,46] Uptake *via* direct exposure to sediment interstitial water is also a portion of total uptake,[45] and sandworms can take up dissolved organic matter through absorption mechanisms.[40] Further, PCBs in surface water contribute to sandworm bioaccumulation, as sandworms irrigate their burrows with the overlying water.[39,45]

Sandworms have a long history of use in bioaccumulation testing of dredged material and contaminated sediment.[24,25,27,28,31,45,47] The time necessary for PCBs to reach steady-state in sandworms depends on many factors (*e.g.*, PCB concentrations, organism lipid content, sediment organic carbon), but under routine testing conditions, steady-state should be reached within 90 days.[24,26,27,29,45,48] Klosterhaus *et al.*[29] reported that HOCs with $\log K_{OW} > 6.7$ would require >28 days to reach steady-state. This would apply to the more hydrophobic PCBs included in the present study.

While bioaccumulation is often regarded as the "true" indicator of bioavailability – biology is highly complex. The complex biology of the sandworm, and other potential living surrogates for bioaccumulation, make polymers a desirable alternative to assess the bioavailability of HOCs in sediment systems. The use of polymeric sampling to monitor the progress of sediment remedial activities is of great interest, not only in research, but also in practice by environmental managers.[14,16]

Methods and materials

Experimental design

The general layout of the 90 day marine mesocosm experiments have been described previously.[1,2,37] and is presented in the ESI (Fig. S1†). This study examined two different polymeric sampling approaches for a 'QTEA' of PCBs in mesocosms

containing sandworms, *A. virens* (hereafter simply denoted "worm" or "worms"). The mesocosms also included bivalves (*Mercenaria mercenaria*, hereafter, "clams") and fish (*Cyprinodon variegatus*) – however, only the worms will be discussed in detail in this article (Fig. S1†). Animal testing was conducted using methods and protocols approved by the US Army, Engineer Research and Development Center's Institutional Animal Care and Use Committee (IACUC Protocol # EL-6009-2014-6). The mesocosms were comprised of 52 L glass aquaria, measuring 51 × 25 × 41 cm^3 (length × width × height), with bed sediment (∼6 cm depth) that was AC amended or a control with no amendment, a surface water layer (∼32 cm depth), and biota ("E2" and "E3" in Fig. S1†). A control with no amendment or biota ("E1" in Fig. S1†) was also monitored by polymeric sampling, but was not the primary focus of the present study. Results from this no biota control treatment (E1) are presented later in this article. The AC was a coal-based Taste Odor Grade (TOG) type from Calgon Carbon Corporation (80 × 325 mesh, ∼32 to 184 μm) applied at a dose of 4.3% by dry weight (∼native total organic carbon (TOC) level of the sediment). The AC was pre-mixed into the bed sediment for 1 month of active mixing to advance the sediment-to-AC mass transfer of PCBs. In addition to the AC amendment treatment, E3 (denoted "AC mix"), ongoing sediment influxes were added three days a week to every mesocosm to produce a well-dispersed plume, which settled on the bed sediment as a thin accumulating layer. This study focused on the PCB congeners originating from field-collected bed sediment (referred to as "native bedded congeners" or "bedded PCBs"). However, of the six replicate mesocosms used for the controls and AC mix (a total of 18 mesocosms for E1, E2, and E3, Fig. S1†), three replicate mesocosms for each experimental set-up were used to introduce sediment spiked with PCB marker congeners 13, 54, and 173 (for a total of 9 mesocosms from E1, E2, and E3, Fig. S1†). PCB 54 and 173 were not detected in the bed sediment, but PCB 13 was present at lower concentrations in the bed sediment. The remaining nine mesocosms received clean sediment inputs without marker PCBs. The present study focused only on the uptake of native bedded PCB congeners. Uptake of the three ongoing input marker congeners have been examined previously.[1,2,37]

Polymeric sampling approaches

In one approach, LDPE was used as *in situ* (in the mesocosm) PSDs with performance reference compounds (PRCs) to predict PCB concentrations in polymer in equilibrium with the sediment[1] or surface water.[37] In another approach, silicone was used to coat the inner vertical walls of glass jars, which were filled with the study sediment and used as *ex situ* ESDs, where PCB equilibrium was confirmed between the sediment and the polymer after extraction and analysis. Equilibrium was confirmed by using three silicone coating thicknesses.[1] A previous cross validation study demonstrated good agreement between these two polymeric sampling approaches of the surficial sediment on the basis of C_{free}.[1] For this investigation, the focus was on comparing the two polymeric sampling approaches to the lipid-normalized native bedded PCB concentrations in worms. Conversions from polymer to lipid utilized eqn (1):

$$K_{PL} = \frac{C_{polymer \rightleftharpoons media}}{C_{lipid \rightleftharpoons polymer \rightleftharpoons media}} \quad (1)$$

where K_{PL} is the polymer-lipid partition coefficient for the specific PCB congener[49,50] (Table S1†), $C_{polymer \rightleftharpoons media}$ is the concentration in the polymer at equilibrium (confirmed or calculated) with some media (*e.g.*, sediment, water, *etc.*), and $C_{lipid \rightleftharpoons polymer \rightleftharpoons media}$ is the concentration in lipid at equilibrium with that media (often notation is simplified to $C_{lipid \rightleftharpoons media}$). The conversion used in the present study is the same as the "third approach" applied in Burgess *et al.*,[38] and is the approach of Jahnke *et al.*[18] and Schäfer *et al.*[20]

Chemical analyses

The chemical analyses are described in detail in Schmidt *et al.*[1] and Gidley *et al.*[2,37] In brief, sediments were extracted by pressurized fluid extraction using hexane/acetone (USEPA SW-846 Method 3545A) and the extracts were treated with sulfuric acid following a modified EPA Method 3665A to remove interfering organic compounds. Tissues were extracted with hexane in a sonic bath overnight (modified EPA Method 3550) and lipids and other interfering compounds were removed by sulfuric acid based on a modified EPA method 3665. LDPE and silicone were extracted with hexane. Extracts were analyzed by dual column gas chromatography with electron capture detection (GC-ECD) following EPA method 8082A. A total of 133 PCB congeners were analyzed in the sediments, tissues and polymeric samplers, with 34 congeners being the focus of the present study (Table S1†). A microcolorimetric method[51] was used to measure lipids from a separate aliquot of sample. The TOC of the sediment was measured using the Lloyd Kahn method.

Statistical analyses

JMP® 7.0 (SAS® Institute Inc.) was used to perform nonparametric Wilcoxon Signed-Rank tests. Here, the data was paired by congener and treatment, and a p-value less than 0.05 was considered statistically significant (α for 95% confidence). If the data were not paired, the nonparametric Wilcoxon test (also known as the Mann–Whitney U-statistic) was applied, where "Prob > $|Z|$" ≤ 0.05 was considered evidence that the means of the two treatments being compared were significantly different.

Results and discussion

Bed sediments had bulk-phase total PCB concentrations of approximately 30 mg kg^{-1} dry weight (excluding input marker congeners) and a TOC of 4.5%. Table 1 provides basic measurements of tissue mass and lipid content for the worms in the experimental treatments. There were no major differences in biomass across treatments, unlike other studies where the presence of AC may have affected worm nutrition and mass.[39] Though no effect of AC on biomass was detected, AC

Table 1 Mean and standard deviation of sandworm (*Alitta virens*) individual mass and lipid content. Individual mass at experiment initiation (actual) and experiment end (calculated from total tissue and number of individuals from each mesocosm)[a]

	Control		AC mix	
	Clean influx	Spiked influx	Clean influx	Spiked influx
Whole mass (initial), g, $n = 15$	2.8 ± 0.8	3.1 ± 0.9	3.8 ± 0.8	4.4 ± 1.7
Whole mass calculated (end), g, $n = 3$	3.1 ± 0.1	3.3 ± 0.4	4.1 ± 0.2	4.1 ± 0.4
Lipid content, %, $n = 3$	1.8 ± 0.2	1.9 ± 0.3	1.8 ± 0.2	1.7 ± 0.2

[a] Error = one standard deviation of the mean.

may have influenced the activity of the worms and potentially reduced bioturbation (this processes has been documented by Koelmans and Jonker[52]). Sandworms of this general size range have been used in previous studies.[25,27,29,53,54] The lipid content of the organisms was also similar to previous studies of sandworms.[27,29,39,48,54,55] The worms were added to the mesocosms as adults, so significant growth was not expected during the 3 month experiments. Sandworms have been reported to grow slowly.[56] Janssen and Beckingham[57] reviewed the "secondary effects" of AC amendment on benthic organisms, such as changes in: growth, lipid content, behavior, and survival. Secondary effects on growth, lipid content, and survival were minimal in the present study. The present study did not include detailed monitoring of worm activity or bioturbation.

Fig. 1 can be considered a 'QTEA' of PCBs in the surficial bedded sediment relative to the worms. Following eqn (1), equilibrium concentrations in polymer were converted to concentrations in lipid at equilibrium with the sediment (*i.e.*, the thermodynamic potential for bioaccumulation, $C_{\text{lipid}\rightleftharpoons\text{sediment}}$) by using congener specific polymer-lipid partition coefficients[49,50] (Table S1†). The $C_{\text{lipid}\rightleftharpoons\text{sediment}}$ values then served as a basis to assess worm tissue concentrations measured and then lipid-normalized (*i.e.*, "actual measured" in worm lipid by solvent extraction, $C_{\text{lipid(worms)}}$). In-tissue polymer sampling[17] was not conducted in the present study. The data was paired by each mesocosm, so three replicates appear as three separate data points in Fig. 1. A plot of PCB congeners measured in worm lipid and "predicted" in lipids based on ESDs, all *versus* $\log K_{\text{OW}}$, is provided in the ESI (Fig. S2†).

The worms were exposed to PCBs primarily *via* the sediment and had sufficient time to reach steady-state with their environment.[24,26,27,29,45,48] However, lipid normalized concentrations were generally below the equilibrium partitioning level, as indicated by data points below the 1 : 1 line in Fig. 1. The off-set ratio, of $C_{\text{lipid(worms)}}$ to $C_{\text{lipid}\rightleftharpoons\text{sediment}}$, was calculated for each data point in Fig. 1, where $C_{\text{lipid}\rightleftharpoons\text{sediment}}$ is the thermodynamic potential for bioaccumulation (or 'QTEA') from the sediment determined using polymers. For ESDs the average (±standard deviation) ratio was 0.08 ± 0.04 for clean influx, and 0.07 ± 0.03 for spiked influx. For the PSDs, the ratios were 0.26 ± 0.13 and 0.21 ± 0.15 for the clean and spiked influx mesocosms, respectively. Both ratios are utilizing the same $C_{\text{lipid(worms)}}$, and therefore, the smaller ratios for ESDs indicates higher $C_{\text{lipid}\rightleftharpoons\text{sediment}}$ values relative to PSDs. This is consistent with the findings of Apell and Gschwend[58] and Yan *et al.*,[3] who observed *ex situ* C_{free} measurements to be greater than *in situ* measurements. For most congeners with both ESDs and PSDs, the data were well below the 1 : 1 line (ratio < 1), indicating PCB concentrations in the worms below the thermodynamic potential for bioaccumulation from the surficial bed sediment. This assumes sufficient accuracy of the partition coefficients[49,50] (Table S1†). Previous researchers have also found biota to be under-equilibrated relative to sediments.[17–20] Recently, Burgess *et al.*[38] performed a similar analysis at New Bedford Harbor under field conditions. In that study, bioaccumulation of PCBs by mussels (*Mytilus edulis*) deployed in the water column was compared to accumulation by co-deployed LDPE passive samplers. They observed the same type and magnitude off-set from the 1 : 1 line when actual bioaccumulation was compared with polymer predicted accumulation. The off-set presented in Jahnke *et al.*[17,18] were also similar for fish, where polymer was equilibrated with sediment (as in Fig. 1). The degree of under-equilibration, in the present study, was also in the same range as other studies[19,20] depending primarily on the species and system, but perhaps also on the polymer methods and approaches.

In the mesocosm systems of the present study, worms were exposed to influx sediment depositional layers (0.15 cm total theoretical accumulation in 90 days), which also included clean fish feed (unconsumed by fish) and fish feces. The introduction of clean feed and deposits likely reduced the concentration of PCBs in the surficial sediment and reduced the worm's exposure and tissue concentrations in terms of native bedded PCBs. Polymers and biota may have responded to this layering differently in terms of exposure and accumulation. However, relative to clams and fish (not the focus of the present study), the worms were expected to be the experimental species least impacted by the clean feed. The food was sinking through the water column, likely with time to be contaminated with PCBs before the worms consumed these deposits. Also, the worms likely fed on both bed sediment and input sediment. In contrast, caged fish fed exclusively in the water column, and clams fed primarily in the water column of the aquaria.

Risk assessments at contaminated sites are often driven by fish and shellfish data because of concerns with human consumption of seafood. In the field, many fish species will have a sediment linkage, either food web related or by direct sediment interaction.[6,20,59] Supporting this, Schmidt and Burgess[23] found *ex situ* sediment ESDs predicted fish and shellfish bioaccumulation with greater strength and accuracy than *in situ* water column PSDs. Among the species in the mesocosms, the worm tissue concentrations may be the most similar to fish tissue concentrations at field sites, when considering the

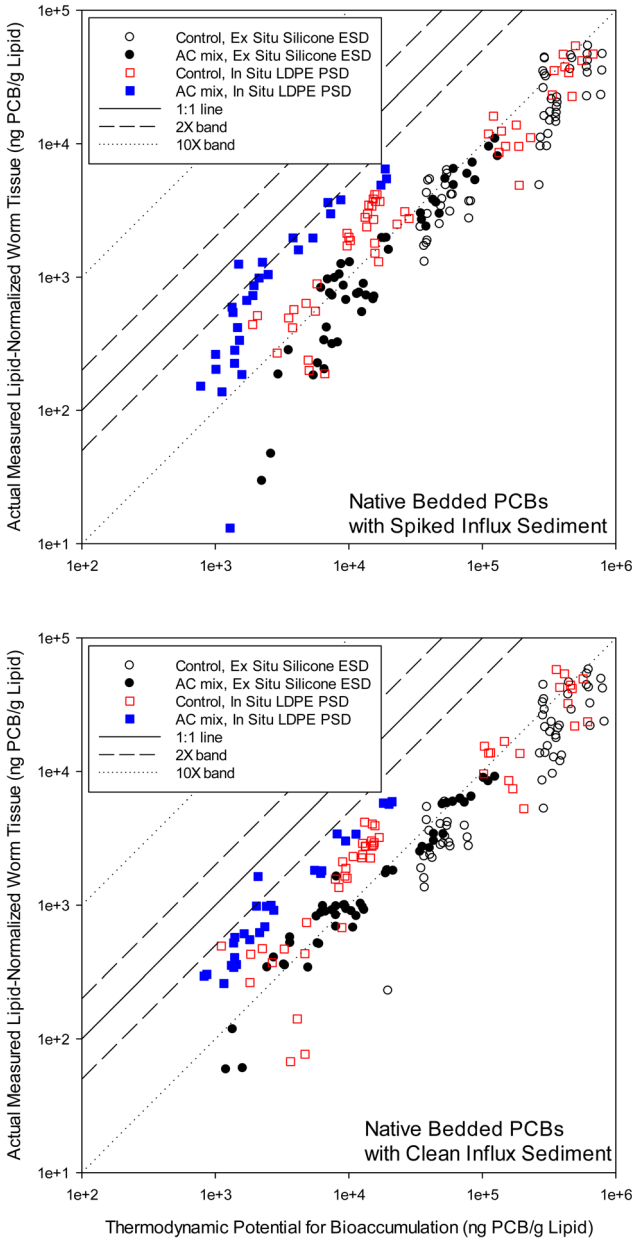

Fig. 1 Measured lipid-normalized PCB concentrations in worm tissue ($C_{lipid(worm)}$, ng PCB/g lipid) *versus* the predicted thermodynamic potential for bioaccumulation ($C_{lipid \rightleftharpoons sediment}$, ng PCB/g lipid) on a PCB congener basis. Circles show *ex situ* silicone equilibrium sampling device (ESD) results for $C_{lipid \rightleftharpoons sediment}$, with hollow circles showing the control, and black filled circles showing the activated carbon (AC) mix treatment. Squares show *in situ* low density polyethylene (LDPE) passive sampling device (PSD) results for $C_{lipid \rightleftharpoons sediment}$, with hollow red squares showing the control, and blue filled squares showing the AC mix treatment. The 1 : 1 line, 2× bands (1 : 1 ± a factor of 2), and 10× bands (1 : 1 ± a factor of 10) are shown.

addition of clean feed. The fish in the mesocosms were confined to the surface water in cages (to reduce sediment resuspension by swimming activity) – disrupting the sediment linkage. Applying clean feed to the mesocosms is a departure from field conditions.[35] Compared to biota in these mesocosm experiments, the resident biota in the field are expected to consume material fully equilibrated with PCBs from their environment. Bridges *et al.*[35] applied C_{free} values and a deconvoluted food web model[60] to these mesocosms. They found that the food web model could represent exposure conditions in these experiments assuming the worm diet consisted of 50% sediment and 50% clean feed, and worm ventilation consisted of 100% overlying water. The strong influence of the surface water is consistent with worms irrigating their burrows.[39,45]

Polymer samplers measured the depositional layer, but this would be in proportion to the depth of sediment measured (*i.e.*, spatial vertical scale sampled) by the polymers. The depth of the depositional layers was theoretically 0.15 cm accumulation in 90 days, or only 5–8% of the sampler depth (sampler depth was approximately the top 2–3 cm). The worms were exposed to depositional layers and sediment at depth, but the proportions could have been different than the vertical scale sampled by the polymers. In addition, the worms have a surface water exposure component. Preferential feeding by the worms around the depositional layer is presumed to have occurred, as it would have been enriched in feed and feces from the fish. Sandworms may metabolize some PCBs, which does not occur in polymers, but the PCBs that metabolize are generally known.[21,25–27,40,54,61] There were no outliers in Fig. 1 that could be explained by PCB metabolism in the worms and not in the polymer. Furthermore, the interaction of physical/chemical processes in the sediment *versus* metabolic alteration in the worms may never have been properly delineated, previously, in systems including sediment.[25,26]

Fig. 2 presents decreases in $C_{lipid(worms)}$ (*Y*-axis) *versus* decreases in $C_{lipid \rightleftharpoons polymer \rightleftharpoons sediment}$ (*X*-axis, from $C_{polymer \rightleftharpoons sediment}$) in AC treated systems relative to the control system without AC, following eqn (2):

$$\text{fraction remaining} = \frac{C_{lipid(worms),AC\ mix}}{C_{lipid(worms),control}} \text{ and } \frac{C_{lipid \rightleftharpoons polymer \rightleftharpoons sediment,AC\ mix}}{C_{lipid \rightleftharpoons polymer \rightleftharpoons sediment,control}} \quad (2)$$

The "fraction remaining" is similar to the "fraction of initial condition" described by Grundy *et al.*[16] Overall, there was good agreement between decline in thermodynamic potential ($C_{lipid \rightleftharpoons polymer \rightleftharpoons sediment}$) and decline in actual bioaccumulation ($C_{lipid(worms)}$). In terms of total PCBs analyzed, the AC provided 90% reductions in worms, 93% reductions in silicone ESDs, and 97% reductions in LDPE PSDs (not all data shown). Of the congeners presented in Fig. 2, three replicates for each condition were averaged before the fraction remaining was calculated. The fraction of PCB bioaccumulation remaining in the worms resulting from the presence of AC ranged from 1.1 (10% increase) to 0.004 (99.6% reduction) depending on the chlorination of the PCB congeners. The fraction of PCBs remaining in polymers caused by the AC ranged from 0.65 (35% reduction) to zero (non-detect, 100% reduction). Tri-chlorinated congeners were non-detect in the AC mix with the additional mixing of the ESDs, so tri-chlorinated congeners were only shown for the PSDs. In Fig. 2, the differences in the remedy effectiveness based on K_{OW}, reflected by the PCB homologs, has been previously observed and reported for the bioaccumulation data of all

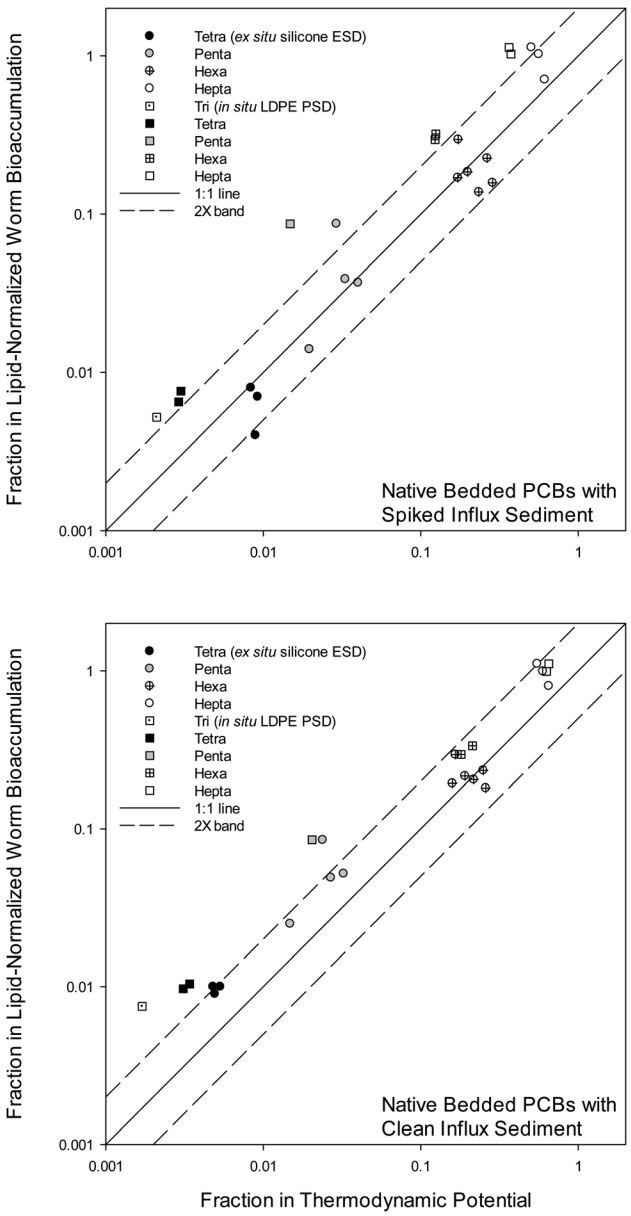

Fig. 2 Fraction remaining in lipid-normalized worm bioaccumulation by the addition of activated carbon (AC) ($C_{lipid(worm),AC\ mix}/C_{lipid(worm),contol}$) *versus* fraction remaining in the "thermodynamic potential for bioaccumulation" from sediment by the addition of AC ($C_{lipid \rightleftharpoons sediment,AC\ mix}/C_{lipid \rightleftharpoons sediment,control}$). Circles show *ex situ* silicone equilibrium sampling device (ESD) results for $C_{lipid \rightleftharpoons sediment}$ separated by PCB chlorination/homolog. Squares show *in situ* low density polyethylene (LDPE) passive sampling device (PSD) results for $C_{lipid \rightleftharpoons sediment}$, also separated by PCB chlorination. The 1 : 1 line and 2× bands (1 : 1 ± a factor of 2) are shown.

mesocosm species.[2] In the current study, highly chlorinated PCBs showed little-to-no exposure reductions.

For the tri-, tetra-, and penta-chlorinated congeners in the clean influx mesocosms, both polymeric sampling methods showed $C_{lipid \rightleftharpoons sediment}$ reductions greater than actual determined reductions in $C_{lipid(worms)}$ (Fig. 2). It is possible that this is primarily related to the introduction of clean feed (as described above). The signal (*i.e.*, change in PCB uptake due to the addition of AC) from the worm tissue was dampened (or reduced) by the clean feed relative to the signal in the polymers. In other words, it is expected that polymers do not respond as much to the clean feed as do the biota.

Sediment ingesting organisms are expected to align better with *ex situ* passive sampling than *in situ* passive sampling,[3] and the results of the present study appear consistent with this. There is a minor to moderate difference between PSD and ESD derived measurements, which can be seen in both Fig. 1 and 2. ESD measurements seem generally closer to the 1 : 1 line in Fig. 2, thus having higher predictive value of the bioaccumulation response to the remedy, compared to PSD measurements. In Fig. 1 this is seen as better alignment of the ESD data, for both the AC mix and the control, relative to PSDs. For the spiked influx mesocosms (Fig. 2), this difference is significant ($p = 0.02$, paired test; prob > $|Z| = 0.0005$) between the PSDs and the ESDs across all PCB homologs. This result was not necessarily expected at the start of this study, as *ex situ* sampling involves two weeks of additional mixing, which advances the sediment-to-AC mass transfer of PCBs. The 1 month pre-mixing at the start of the mesocosm studies helped the ESDs in this respect.

Additional data is included in Fig. 3 (not shown in Fig. 1 and 2), which shows: fractions of the thermodynamic level from PSDs used to measure the sediment ("LDPE strips"), PSDs used to measure the surface water ("LDPE discs"), and lipid-normalized worm bioaccumulation; all relative to the ESDs used to measure the sediment. The fraction of the thermodynamic potential as defined by silicone ESDs was determined following eqn (3):

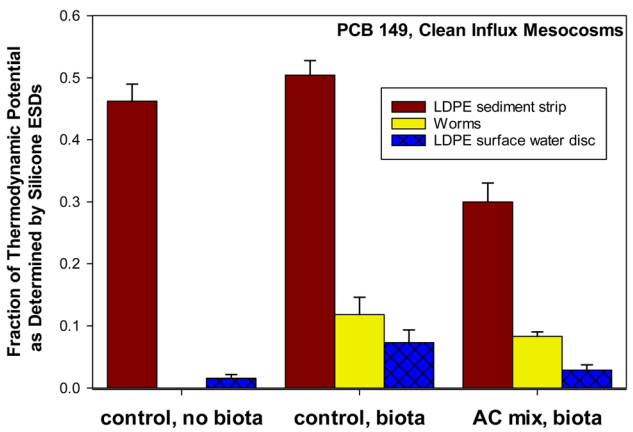

Fig. 3 Fraction of thermodynamic potential as defined by silicone equilibrium sampling devices (ESDs). Silicone ESDs sampled surficial bed sediment. *In situ* low density polyethylene (LDPE) strips sampled surficial bed sediment (0 to 90 days). *In situ* LDPE discs sampled surface water (overlying water) from 45 to 90 days. Controls (with and without biota) and activated carbon (AC) mix treatments are shown. A mean LDPE-lipid partition coefficient of 0.0938 for PCBs was used to convert concentrations of PCB 149 in LDPE to a lipid basis.[50] A congener specific silicone-lipid partition coefficient of 0.0945 was used to convert concentrations of PCB 149 in silicone to a lipid basis.[49] Error bars show one standard deviation of the mean ($n = 3$).

$$\text{Fraction of potential} = \frac{C_{\text{lipid} \rightleftharpoons \text{LDPE} \rightleftharpoons \text{sediment}} \text{ or } C_{\text{lipid(worms)}} \text{ or } C_{\text{lipid} \rightleftharpoons \text{LDPE} \rightleftharpoons \text{surface water}}}{C_{\text{lipid} \rightleftharpoons \text{silicone} \rightleftharpoons \text{sediment}}} \quad (3)$$

Additionally, a set of control mesocosms containing no biota was included in Fig. 3. PCB 149 was selected because it was the only non-coeluting peak on chromatograms that was consistently detected in all replicates above detection limits in the surface water of the AC mix treatment. PCB 149, a hexachlorinated congener with a $\log K_{OW}$ of 6.67,[62] can be considered highly hydrophobic. In order to emphasize the relationship within each mesocosm, rather than the average across mesocosms (as in Fig. 2), the fraction of the ESD measurement was taken within each mesocosm (as in Fig. 1) prior to averaging across three replicate mesocosms receiving clean sediment influx (Fig. 3). PCB 149 shows that for clean influx mesocosms, the worms were at a thermodynamic level closer to the surface water (LDPE disc) than the sediment (LDPE strip) for both the AC mix and control treatments. The sediment (measured by polymer) was at a higher thermodynamic level than the worms and surface water. PCB 149 was the congener in organisms closest to the thermodynamic potential for bioaccumulation from the sediment (in worms at 12.4% of the potential). In the control (no AC), other congeners in the worms were at a level even more comparable to the surface water. Field studies have found polymers equilibrated with surface waters to be at higher thermodynamic levels than biota.[19,38] The spiked influx mesocosms may agree more with field studies in this respect, but this data was not shown (Fig. S3†), as PCB 149 was below detection in the spiked influx AC mix treatment by the surface water PSDs (LDPE discs). In the clean influx mesocosms (Fig. 3), the surface water levels were close to detection limits in the AC mix. If the fish feed (flakes) and clam feed (algae) had been pre-equilibrated with the system (contaminated), the worms may have been at a level closer to the sediment.

In Fig. 3, it can be seen that the relative thermodynamic levels between sediment, worms, and surface water are maintained in the control and AC mix treatments. In other words, the worms remain at about 5 to 10% of the thermodynamic potential of the sediment regardless of whether or not the sediment contains AC. Rather than the traditional BSAF model, Sormunen *et al.*[63] discuss a "refined BSAF" – a term utilized here (eqn (4)), where:

$$\text{refined BSAF} = \frac{C_{\text{lipid(worms)}}}{C_{\text{polymer} \rightleftharpoons \text{sediment}}} \text{ or } \frac{C_{\text{lipid(worms)}}}{C_{\text{lipid} \rightleftharpoons \text{polymer} \rightleftharpoons \text{sediment}}} \quad (4)$$

The ratio of $C_{\text{lipid(bio)}}$ to $C_{\text{lipid} \rightleftharpoons \text{sediment}}$ has been utilized previously.[18–20] The "activity ratio",[20] "partitioning status"[64] or "refined BSAF" between biota and sediment would still vary based on the species-specific traits within a system and perhaps K_{OW}, but not vary based on partitioning to different types of organic matter[30,33] or from AC amendment and associated aging. Fig. S2c† shows the refined BSAFs did not vary much based on K_{OW} in the present study, likely due to the ingestion of sediment by the worms. Diepens *et al.*[30] found traditional BSAFs for similar congeners to range between 7.4 and 19.2 for worms exposed to spiked sediment. Applying these refined BSAFs would not likely narrow this range of BSAFs much, relative to their overall magnitude (these researchers were not investigating different types of organic carbon). However, the refined BSAFs may have removed the confounding factors of organic matter quality changes and sediment-PCB aging over time.

Conclusions

These mesocosm studies were complex relative to routine bioaccumulation tests, but successfully isolated some important processes occurring in the experimental system, which could be representative of processes occurring in the field. This work contributes to a growing number of studies on the use of polymeric samplers to monitor sediment remedy performance (particularly during AC amendment). In the present study, a 'QTEA' was accomplished, showing that complex processes affecting bioaccumulation in worms might be monitored relatively simply by polymeric sampling. Specifically, for remedy effectiveness monitoring, this could be accomplished by measuring the concentration of HOCs in a polymer at equilibrium with the surficial sediment.

In practice, monitoring the performance of remedies in the field should utilize a consistent and predictive form of polymeric sampling of the sediment. Previous researchers have concluded that measuring C_{free} in the interstitial water,[15,58] or polymer concentrations from surface water[37,38] would be best for monitoring remedies. Researchers have also found the *in situ* interstitial C_{free} (from PSDs) may be most useful for understanding sediment-to-water column fluxes.[65] PSDs may be more responsive to conditions in the surficial sediment than the worms and *ex situ* ESDs, but the latter two tracked better through the AC remedy. The present study found that *ex situ* sampling of the surficial sediment may be most useful for tracking the performance of an AC remedy applied to the sediment with ongoing influx. Apell and Gschwend[58] and Yan *et al.*[3] recognized that *ex situ* C_{free} determination might be preferred to *in situ* C_{free}, if *ex situ* shows the highest possible interstitial water concentrations. This was not obvious to the authors of the present study, with regard to AC amended sediments, as *ex situ* methods involve additional mixing. Surficial sediment is often dynamic, being resuspended and redeposited. It is likely that sampling suspended particulate matter,[64] or dredged material in a maintenance dredging operation, could yield similar useful measurements depending on the questions being asked.

Ex situ equilibrium sampling was, in the present study, conducted using silicone coated jars with multiple coating thickness. The ultrathin silicone coatings provided fast equilibration of PCBs in sediment interstitial water, and the multiple silicone coating thicknesses were applied to confirm equilibrium and the absence of surface sorption artifacts. Commercialization of the coated jars would promote uniformity of samplers and incentivize the adoption of this method.[66] Jonker *et al.*[15] recently provided practical guidance on other *ex situ* equilibrium sampling techniques that are simpler to operate and can yield similar concentrations in polymer. Overall, *ex situ*

equilibrium sampling of surficial sediment (or dredged material during maintenance dredging activities) will be a more accurate alternative to conventional, organic carbon normalized, sediment measurements used in the BSAF model[17,18,20–22] and existing risk assessment and monitoring frameworks.

Conflicts of interest

The authors declare no conflict of interest associated with this study. Citation of trade names utilized in this study does not constitute an official endorsement or approval of the use of such commercial products. Any opinions, findings, conclusions, or recommendations expressed in this article are those of the authors, and not necessarily the views of the US Army Corps of Engineers, or the US Environmental Protection Agency.

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