

Effects of Physical Chemistry and Bioturbation by Estuarine Macrofauna on the Transport of Hydrophobic Organic Contaminants in the Benthos

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Effects of macrobenthos on hydrophobic organic contaminant (HOC) transport during two seasons characterized by high (summer) and low (winter) bioturbation were studied in the laboratory. HOC burial and loss from microcosms were followed in the presence and absence of macrofauna after the introduction of particle-associated polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) to the sediment–water interface. During summer, HOC burial depths and modeled diffusive losses (D_L) increased with compound relative effective diffusivity (D_{eff}^*), consistent with enhanced fluid transport rates due to macrofauna. Although more than 50% of HOC loss was independent of macrofauna, macrofauna-mediated processes had significant effects on the long-term (56 d) removal of the hydrophobic compounds TCB and BaP. A possible mechanism for this effect is direct particle resuspension by macrofauna, which has been shown to enhance loss of materials from our experimental systems. During winter, macrofauna had little effect on HOC burial but may have enhanced HOC retention. Thus, effects of macrofauna-mediated processes depend on HOC physico-chemistry as well as the temporal phasing and duration of contaminant–biota interactions. Bioturbation has important implications for contaminant fate because macrofauna significantly alter the distributions of HOCs near the sediment–water interface.

Introduction

Benthic macrofauna have the potential to significantly influence the transport and fate of hydrophobic organic contaminants (HOCs) in aquatic environments via processes such as bioturbation and interactions with microbes (1, 2). Communities dominated by large infauna, especially head-down deposit feeders, tend to have high rates of particle bioturbation and create deep sediment mixed layers (3–5). In coastal areas, where physical resuspension and current-induced transport processes act to buffer concentrations of materials at the sediment–water interface, bioturbation processes can increase the total inventory of reactive particles in the sediment (6). High rates of bioturbation have also been correlated with increased resuspension of particles and

associated contaminants (3, 7). Despite limited mixing depths, even small, shallow-dwelling infauna have been shown to alter contaminant flux across the sediment–water interface via bioturbation of particles and fluids (8–10).

Through activities such as feeding, irrigation, and burrowing, macrofauna also influence the flux of oxygen and limiting nutrients across the sediment–water interface; alter the geometry of sediment microenvironments; and directly graze on microbes. As a result, macrofauna interact with microbial consortia to alter sediment biogeochemistry and the diagenesis of reactive organic matter (6). This is significant because microbial processes are known to exert strong controls on contaminant degradation rates in aquatic sediments (11–15). Enhanced microbial heterotrophic activity and HOC degradation rates have been observed in the presence of the macrofauna polychaete *Capitella capitata* (16, 17). Metabolism of HOCs by macrofauna may also play some direct role in pollutant degradation (18).

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are widely distributed in estuaries and other coastal systems and have been identified as 'toxics of concern' for many systems. They tend to be hydrophobic, to associate with sediments in aquatic systems, and to bioconcentrate and may be toxic or carcinogenic. Although the dynamics of HOCs in the environment can be complex, chemical behavior and susceptibility to microbial degradation processes can often be predicted on the basis of molecular structure and related parameters such as degree of water solubility and octanol–water partitioning coefficient (19, 20).

For the present study, macrofauna effects on PAH and PCB transport processes were investigated in laboratory microcosms. Selected HOCs ranged in physicochemical properties to provide a better understanding of the interactions of biological and chemical processes. The major hypotheses guiding the study were as follows: (1) macrofauna significantly alter the transport of HOCs in laboratory microcosms relative to treatments in which macrofauna are removed; (2) the mechanisms and rates of macrofauna effects vary seasonally; and (3) the relative importance of macrofauna-mediated transport processes is related to HOC physicochemical properties.

Methods

Field Site. Sediment cores were collected at a subtidal (12 m), polyhaline (> 18 ppt salinity) site (37°16.09' N, 76°09.79' W) in the lower Chesapeake Bay, described in ref 4. Sediment at the site is a mixture of very fine sand, silt, and clay (≈50:35:15 on a wt % basis, <1% organic carbon). Macrofauna include a diverse array of polychaetes, hemichordates, molluscs, crustaceans, and other taxa. Bioturbation is an important process that is seasonally variable, and the biological mixing depth typically exceeds 20 cm (21–23).

Field Methods. Small cans (10 × 16 × 20 cm) were used to collect intact sediment cores containing fauna and overlying water by subcoring larger box cores. Each subcore, inserted to a sediment depth of ≈14 cm, was sealed at the bottom, placed into an insulated cooler under flowing seawater, and returned to the laboratory within 12 h.

Experimental Design. In the laboratory, sediment cores were placed into glass microcosms, randomly assigned to treatment groups, and then placed into aquaria. Selected groups of microcosms were defaunated as described below. The major treatment effect examined was the presence or absence of macrofauna. Treatment microcosms with macrofauna had intact benthic assemblages and received sediment-associated radiolabeled chemicals. A second group of microcosms were defaunated of macrofauna and also received

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TABLE 1. Physicochemical Properties of Selected Organic Contaminants Utilized in Benthic Microcosm Experiments

compound ^a	log K_{ow}	D_m ($\times 10^{-6}$) ^b (cm ² s ⁻¹)	D_{eff}^* ($\times 10^{-11}$) ^c (cm ² s ⁻¹)
2-chlorobiphenyl	4.52 ^d	4.30	13.0
pyrene	5.00 ^d	4.08	4.08
2,2',5,5'-tetrachlorobiphenyl	5.97 ^e	3.03	0.33
benzo[a]pyrene	6.35 ^d	3.07	0.14

^a HOC pairs used for summer experiment: 2-chlorobiphenyl + pyrene; 2,2',5,5'-tetrachlorobiphenyl + benzo[a]pyrene. HOC pair used for winter experiment: 2-chlorobiphenyl + benzo[a]pyrene. ^b Molecular diffusivity, estimated by method of ref 24 using a seawater viscosity of 1.001 cp (25) at 22 °C and 20 ppt salinity. ^c Relative effective diffusivity (D_m/K_{ow}), see ref 26. ^d See ref 27. ^e Average value from refs 28 and 29.

radiolabeled sediment (controls). A dual-label (³H, ¹⁴C) design was used, and chemicals were added to microcosms in pairs (Table 1). The point of addition of the labeled sediment to the surface of each microcosm began the experimental phase. An additional set of microcosms received only unlabeled sediment (blanks). On selected days, replicate microcosms were removed from aquaria and subsampled as described below.

During the summer experiment, the total number of microcosms sampled for the macrofauna treatments was 3 replicates \times 6 sampling days \times 2 chemical pairs = 36 microcosms. For controls, the total number of sampled microcosms was 2 replicates \times 3 sampling days \times 2 chemical pairs = 12 microcosms. The number of microcosms sampled for each treatment type (with or without macrofauna) in winter was 3 replicates \times 4 sampling days \times 1 chemical pair = 12, for a total of 24 microcosms sampled. Blank microcosms (2 replicates) were sampled on the same days as the treatments with macrofauna. A block design was used to allocate microcosms to aquaria so that replicates for each sampling day were in different aquaria. Inverted microcosms without sediment were replaced in the aquaria after sampling to maintain water residence time.

Procedures for Defaunating Microcosms. N₂ gas was bubbled through the overlying water column in each aquarium for 5 (summer) or 8 (winter) days while the water temperature was maintained at 30 °C using aquaria heaters. Anoxic conditions forced macrofauna to the sediment surface, and visibly dead individuals were removed daily. This procedure was highly effective in killing greater than 99.5% of the macrofauna in the microcosms and resulted in no obvious disruption of the sediment physical structure as occurs when sediments are sieved or frozen to remove resident biota (30). Although estuarine microbes that degrade PAHs are able to withstand extended periods of low oxygen tension (17, 31), we further introduced a slurry (\approx 20 mL) of aerated, macrofauna-free surface sediment from the field site to every microcosm immediately after the defaunation period. Microcosms were then exposed to ambient flow-through conditions for 3 days prior to the initiation of experiments.

Chemicals. Two ³H-labeled PAHs and two ¹⁴C-labeled PCBs were used in our studies (Table 1). Uniformly labeled 2-chlorobiphenyl (2CB) and 2,2',5,5'-tetrachlorobiphenyl (TCB) were obtained from Sigma Chemical Co. (St. Louis, MO). Crude pyrene was obtained from Amersham International (Cardiff, Wales, U.K.) and purified prior to use with silica column chromatography (32). Benzo[a]pyrene (BaP) [1,3,6-³H] was obtained from NEN Research Products (Wilmington, DE). Contaminant specific activities were as follows: 2CB = 19.6 mCi/mmol, pyrene = 12.9 Ci/mmol, TCB = 16.2 mCi/mmol, BaP = 54.5 Ci/mmol. The octanol/water partition coefficient (K_{ow}) of the selected PAHs and PCBs ranges 2 orders of magnitude, whereas molecular diffusivities (D_m) of the chemicals in water vary by only 30–40% (Table 1). Relative effective diffusivities (D_{eff}^*), which are directly related to the desorption rate constants of the compounds from sediments (26), vary \approx 100-fold, with 2CB predicted to be more rapidly released from sediments than pyrene, TCB, or BaP (Table 1).

Preparation of Labeled Sediment. Radiolabeled HOCs were added to sediments in aqueous slurries. Briefly, 0.75–

2.5 mL of organic compound stock solutions in methanol was added to 800 mL of artificial seawater vigorously stirring in 1-L glass jars. One [³H]PAH and one [¹⁴C]PCB, were added such that specific activities were $\approx 2 \times 10^6$ dpm/mL ³H and 2×10^5 dpm/mL ¹⁴C. Immediately following addition of the chemical spikes, 35 mL of sieved (500 μ m) wet sediment was added to the jars. The aqueous sediment slurries were mixed for 4 h and allowed to settle for at least 24 h while stored at 6 °C. Subsequently, the overlying water was decanted, and replicate sediment slurries were homogenized. The sediment was allowed to age 3–5 days prior to dosing the microcosms. All preparative procedures were carried out under yellow fluorescent lights to minimize PAH photodegradation.

Procedures for Dosing Microcosms. Aliquots of labeled sediment were divided into small beakers so that each contained 30 mL of wet sediment (\approx 50% water; w/w). An additional 20 mL of filtered seawater was then added to each beaker, and the resultant slurry was transferred to a small foil tray that contained a piece of aluminum screen (10 cm \times 16 cm). Wet sediment was distributed over the screen in the tray to a thickness of \approx 1 mm and then frozen at –10 °C overnight. Each aquarium was then drained, and a frozen sediment sheet was placed onto each microcosm. After screens were removed (<5 min), water flow to aquaria was resumed and was maintained at six turnovers per day. Sampling was initiated when microcosms were covered by 2–3 cm of water; the elapsed time from initial dosing to sampling varied from \approx 1 up to 3 h.

The mean temperature for the summer experiment was 22 °C (SE = 0.07, n = 2538), but the temperature decreased gradually through the experiment (maximum 28 °C in early September; minimum 15 °C at end of October). Mean water column dissolved oxygen was 4.4 mg/L (SE = 0.02, n = 2538), and the salinity was 20 ppt (SE = 0.01, n = 2538). A bloom of 'red tide' dinoflagellates (species not determined) occurred in the river beginning on day 17, and it was necessary to discontinue flow-through conditions and aerate each aquarium for 5 days during this period. The mean temperature for the winter experiment was 12 °C (SE = 0.04, n = 1100), mean salinity was 17 ppt (SE = 0.06, n = 1100), and water column dissolved oxygen remained above 10 mg/L.

Microcosm Sampling Procedures. Subcores (7.6 cm i.d.) inserted into the center of each microcosm were sectioned into vertical intervals (0–1, 1–2, 2–4, 4–6, 6–10, and 10–14 cm) and used to determine HOC depth profiles and sediment water content (in treatment microcosms) or sediment water content and bulk density (in blank microcosms). A 5-mm ring of sediment was removed from the outer perimeter of each section to avoid possible contamination at the edges during extrusion. After sample removal, the remaining sediment was sieved on 500- μ m mesh screen, and retained organisms were sorted to species, counted, and weighed (blotted wet weight) for verification of community composition.

Procedures for Extracting Sediment and Pore Water. Sediment from the upper two core sections was centrifuged to separate pore water (1000 rpm, 10 min). Water and sediment samples were analyzed for radiolabeled HOCs using

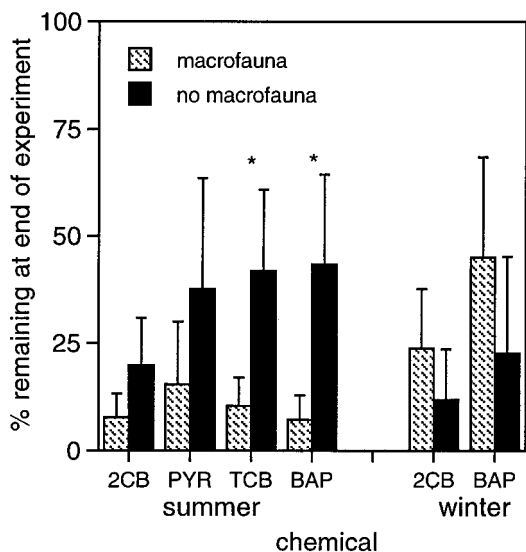


FIGURE 1. Percent contaminant activity remaining at the end of two experiments, conducted in summer (56 d) and winter (21 d), relative to the inventory measured on day 0 of each experiment. One treatment type included macrofauna; the other had macrofauna removed. Bars indicate mean and one standard error. An asterisk (*) above a pair of treatments indicates that the means were significantly different ($p \leq 0.05$) by a *t*-test.

a hexane/methanol extraction procedure modified from ref 33. Samples were first extracted in precleaned centrifuge tubes with 15:3 v/v of hexane/methanol, shaken for 2 min, sonicated for 4 min, and then allowed to settle for 12 h. Milli-Q water was then added such that the solvent ratio was 15:3:6 v/v/v of hexane/methanol/water. The samples were shaken again for 2 min and then centrifuged, resulting in separation into two phases, with the organic phase (hexane) containing the parent compound. Each phase was subsampled, placed into scintillation cocktail, and counted for radioactivity using a Beckman Model LS 5000TD liquid scintillation system. This method was >95% efficient in the hexane phase recovery of parent compounds added to sediment samples. Values reported are based on total radioactivity recovered in the hexane phase, assuming an activity value of zero when the measured activity in a sample was below the detection limit (three times background radioactivity). Aqueous phase radioactivity was <1% of total radioactivity recovered in >99% of the samples measured. Total contaminant activity and depth distributions were determined by correcting for contaminant activity in extracted pore water, sediment bulk density, and porosity (2).

Statistical Methods. For contaminant activity trends, *t*-tests were used to judge significance of treatment effects. Two-way ANOVAs were used to evaluate the integrated effects of time and treatment (presence or absence of macrofauna) on contaminant mean burial depth. Data were transformed when necessary to meet the assumptions of normality and homogeneity of variances. Normality was judged using the Shapiro-Wilk *W*-test. Homogeneity of variances was evaluated using the Bartlett test. Significant main effects were further examined using Tukey-Kramer *a posteriori* comparisons. Preliminary analyses provided no evidence for effects of blocking by aquarium within treatment (tested using ANOVA, no significant *F* statistics), so the effect was dropped from subsequent analyses.

Results and Discussion

In both the presence and absence of macrofauna, contaminant activity was reduced by more than 50% during both experiments (Figure 1). In the absence of macrofauna, 20–43% of the day 0 inventory of each HOC remained after the

56-d summer experiment. Nonetheless, at the conclusion of the summer experiment, contaminant activity in the presence of macrofauna averaged only 7–15% of the inventory introduced at day 0. Differences between treatments were significant at the 95% level for TCB and BaP, but not for 2CB and pyrene. Thus, a major effect of macrofauna during the summer experiment was to significantly enhance loss of TCB and BaP, but macrofauna did not significantly effect the long-term removal of 2CB and pyrene from the benthos. For TCB and BaP, the additional loss associated with macrofauna-mediated processes was of the same order of magnitude as loss in the absence of macrofauna.

For the winter experiment, there were no significant differences between treatments in the percent contaminant activity remaining when the experiment concluded on day 21, although the trend was for contaminant retention in the presence of macrofauna (Figure 1). The lack of macrofauna-enhanced HOC loss during the winter experiment is consistent with the observed seasonal decrease in bioturbation activities (21–23). The difference in macrofauna effects between the two experiments cannot be attributed to changes in community characteristics, because there were no significant differences in macrofauna abundance or biomass measured at the end of the summer versus winter experiments (ANOVA, no significant *F* statistics) and no major shifts in community composition (30).

One surprising result of our studies is the relatively high loss of BaP from winter microcosms in the absence of macrofauna. Higher loss rates in summer versus winter would be expected based on temperature effects on chemical desorption–diffusion and microbial degradation. Thus, we offer a caveat regarding direct comparisons of the percent HOC remaining at the conclusion of each experiment. A variety of environmental factors that were not controlled between experiments, such as the composition of the organic matter in the dosing sediment, salinity, or microbial community composition, could have differentially affected contaminant loss processes.

The experimental systems used for this study were relatively large and 'open' in order to ensure the viability of the macrofauna. Thus, the ultimate fate of contaminants lost from the microcosms could not be determined practically. Based on previous investigations, we assume that the major loss processes in our systems were diffusive and advective losses of fluid-phase and fine particle associated HOCs (7–9, 34) and microbial degradation (11–15); both may be enhanced by macrofauna activity. For example, the rapid loss of 2CB from experimental microcosms during our experiments, regardless of the presence or absence of macrofauna, is consistent with its relatively low hydrophobicity, high diffusivity (Table 1), and susceptibility to microbial degradation (35). Conversely, our results indicate that macrofauna significantly enhanced the loss of TCB, a HOC that is highly hydrophobic and resistant to microbial degradation (20).

We observed considerable direct resuspension of particulate material by macrofauna during the summer experiment. In a subsequent experiment, we (7) demonstrated that bioturbation and direct sediment resuspension by macrofauna enhanced short-term rates of sediment and BaP loss from microcosms by an order of magnitude or more relative to defaunated controls. Thus, we assume that the enhanced loss of TCB and BaP in the presence of macrofauna at the conclusion of our summer experiment was the result of similar processes. Although particles resuspended by macrofauna within our experimental system have the potential to return to the sediment–water interface, some of the material is lost due to the flow-through design of the system. In the environment, resuspension processes will act to increase the cycling of particle reactive contaminants at the sediment–water interface and, thereby, increase the potential for chemical desorption and microbial degradation of some

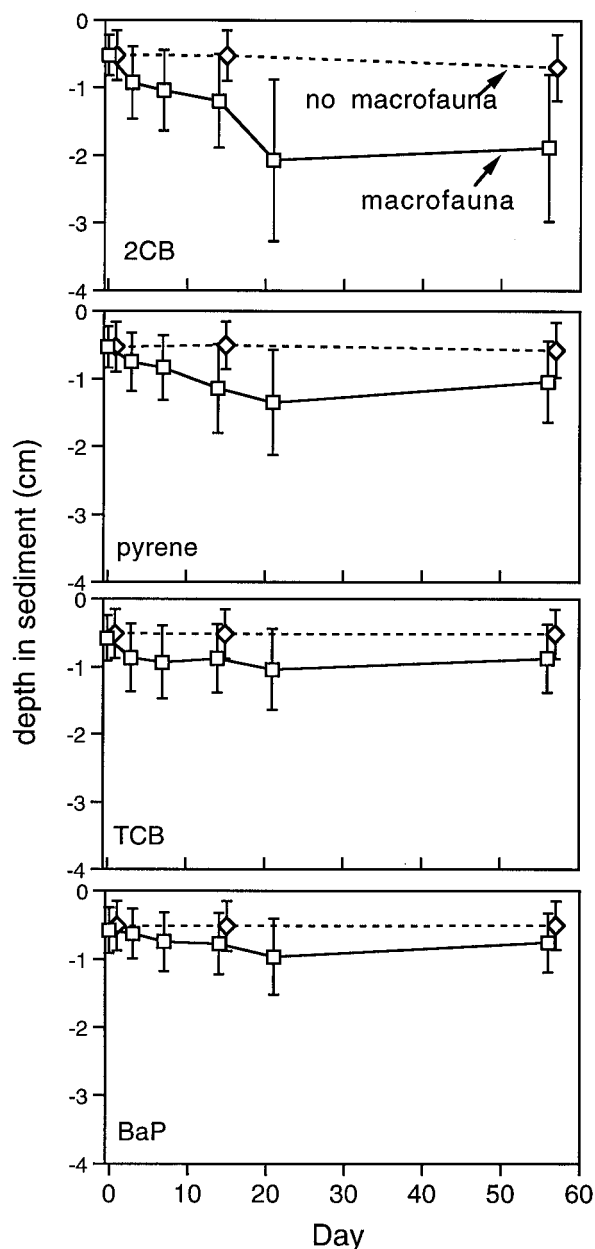


FIGURE 2. Contaminant mean burial depth versus time in the summer experiment. Solid lines indicate treatments that contained macrofauna; dashed lines indicate treatments that lacked macrofauna. Symbols indicate mean and one standard error.

HOCs. Thus, our results demonstrate that macrofauna can have significant effects on contaminant transport at the sediment–water interface, but further studies will be necessary to identify the relative importance of various mechanisms and their seasonal variability in estuarine benthic systems.

Contaminant Burial

Macrofauna had major effects on contaminant burial in the experimental systems during the summer period of active bioturbation. Mean HOC burial depths increased with time through at least the first 21 days in the presence of macrofauna (Figure 2). Little transport into the sediment was observed in the absence of macrofauna, except for the most diffusive compound, 2CB. ANOVA reveals that there were significant effects ($p \leq 0.05$) of time on contaminant burial depth (log transformed data) for 2CB ($F_{2,9} = 7.41$, $p = 0.013$) and significant treatment effects for 2CB ($F_{1,9} = 8.72$, $p = 0.016$), TCB ($F_{1,9} = 10.65$, $p = 0.0098$), and BaP ($F_{1,9} = 6.81$, $p = 0.028$) during the summer experiment. No significant time by

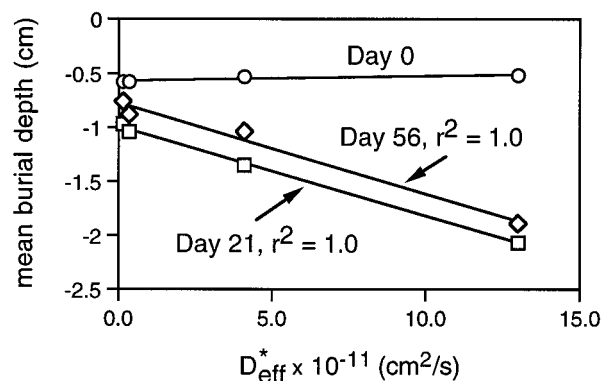


FIGURE 3. Contaminant mean burial depth in microcosms containing macrofauna versus effective diffusivity (D_{eff}^*) during the summer experiment.

treatment interactions for any contaminant were observed. Treatment effects for pyrene in the summer experiment were consistent with those for the other contaminants, but were not significant at the 95% level ($F_{1,9} = 3.85$, $p = 0.081$). There were no significant effects of time or treatment on contaminant burial in the winter experiment (not shown).

A diverse community of organisms interacted to transport contaminants in these experiments via a variety of feeding, burrowing, and irrigation activities. Localized mixing processes are the likely cause of relatively high within-treatment variability apparent in the data (Figure 2). Nonetheless, we found a clear relationship between contaminant mean burial depth and relative effective diffusivity (D_{eff}^*) for treatments with macrofauna (Figure 3). The relationship was significant for day 21 ($t = 28.2$, $p < 0.01$) and day 56 ($t = 10.8$, $p < 0.01$). Macrofauna-mediated fluid transport provides a mechanism for dissolved constituents to be rapidly transported into the sediment (θ), as was observed in our study for the most hydrophilic compounds (e.g., those with the highest D_{eff}^*).

Our results contrast with those of Karickhoff and Morris (8), who found that pollutant transport within a biologically reworked layer was worm-mediated and largely independent of pollutant fugacity. In their laboratory systems, sediment pelletization and rapid bioturbation by dense assemblages of head-down deposit feeding oligochaete worms limited pellet residence time at the sediment–water interface and may have reduced contaminant exposure to the overlying water column. Our experimental design more closely approximates an environmental setting common in the high salinity regions of estuaries or open coastal settings where benthic communities and their effects on sediment processes are diverse (21–23). Our finding of the dependence of contaminant mean burial depth on contaminant effective diffusivity in the presence of macrofauna demonstrates that biological and physicochemical processes interact to determine the extent of transport of HOCs in the benthic boundary layer of some aquatic environments. Contaminant burial by macrofauna has important implications for contaminant fate in the environment because microbially-mediated degradation rates for many HOCs are redox sensitive (11–15).

Modeling Contaminant Loss

Rates of contaminant loss from the microcosms were modeled as both first-order and diffusive processes to account for the various mechanisms that may contribute to loss. First-order loss is modeled as

$$\frac{dA}{dt} = -k_L A \quad (1)$$

where A is the total contaminant activity (dpm) in the microcosm, t is time (d), and k_L is the first-order loss rate coefficient (d^{-1}). Integration of eq 1 yields

$$\ln A = -k_L t + \ln A_0 \quad (2)$$

where A_0 is the initial contaminant activity, indicating that k_L can be derived from the natural log-transformed data versus time using linear regression.

For the summer experiment, the k_L values for all HOCs were significantly greater than zero in the presence of macrofauna and for TCB and BaP in the absence of macrofauna (Table 2). Relative to the values computed for microcosms with macrofauna, the k_L values for controls were significantly reduced ($t \leq 2.66$, $p < 0.025$) by 59 and 66% for TCB and BaP, respectively, illustrating an enhanced rate of HOC loss by macrofauna-mediated processes during the summer experiment. There were no significant relationships between k_L values and contaminant physical chemistry as indexed by the octanol-water partitioning coefficient or relative contaminant effective diffusivity for the summer experiment.

The calculated rate loss coefficients for the treatments with macrofauna in the winter experiment were not significantly different ($t \leq 1.82$, $p > 0.05$) than those derived for the summer experiment, whereas BaP was lost at a significantly ($t = 3.91$, $p < 0.01$) faster rate from the controls during the winter experiment relative to the summer. In part, the lack of differences in k_L values for the 56-d summer experiment versus the 21-d winter experiment may result from modeling contaminant loss from the experimental systems as a first-order process. Note that, for 2CB and pyrene, losses during the experiments appear to be nonlinear when $\ln A$ is plotted versus time (Figure 4). If loss rates were enhanced during the early part of the experiments, calculated first-order rate coefficients decrease with time.

Diffusive loss of a chemical from the sediment is described as

$$\frac{dA}{dt} = D_L \frac{d^2 A}{dz^2} \quad (3)$$

where z (cm) is the linear dimension over which the diffusive change occurs, t is time (h), and D_L is the diffusion coefficient (cm^2/h). For the situation where a finite amount of a diffusing species is initially deposited on the surface of a plane, the solution to eq 3 for one-dimensional diffusion away from the source is (37)

$$A = \frac{A_0}{(\pi D_L t)^{1/2}} \exp\left(-\frac{z-z'}{4D_L t}\right) \quad (4)$$

where $z' = 0$ is the sediment-water interface.

Data from both experiments were modeled using the diffusion equation (eq 4), assuming that (a) the HOC was well-mixed within the top 1-cm layer, the limit of resolution determined by the core subsampling procedures and (b) diffusive loss occurs in one dimension (i.e., diffusive loss is reflected predominantly out of the sediment). Assuming that diffusion occurs in one dimension is justified by considering the diffusional resistances in the reservoirs above and below the sediment-water interface. For example, a HOC desorbed from particles deposited at the sediment-water interface at the start of the experiment will diffuse upward at a rate reflective of the compound's molecular diffusivity in water (Table 1) or faster, dependent upon the degree of turbulence generated by the seawater flow through the aquaria. In contrast, diffusion of a desorbed HOC downward in the sediment will be retarded by sorption-desorption interactions with particles. In this case, the rate of HOC diffusion down core is reflective of its effective diffusivity (Table 1). Thus, for HOCs that can desorb from sediments, downward transport past the top 1-cm layer will be substantially slower than diffusive loss out of the sediments.

TABLE 2. First-Order Loss Rate Coefficients (k_L) Derived from Linear Regression Modeling of Contaminant Activity versus Time during Summer and Winter Experiments

experiment	treatment	chemical	k_L	r^2	t^a	df ^b
summer	w/macro	2CB	0.038	0.58	4.71***	16
		pyrene	0.036	0.51	4.07***	16
		TCB	0.044	0.70	6.07***	16
		BaP	0.051	0.66	5.55***	16
summer	w/o macro	2CB	0.022	0.51	2.03 ^{ns}	4
		pyrene	0.015	0.50	1.98 ^{ns}	4
		TCB	0.018	0.72	3.22*	4
		BaP	0.017	0.75	3.47*	4
winter	w/macro	2CB	0.062	0.53	3.35**	10
		BaP	0.041	0.46	2.92*	10
winter	w/o macro	2CB	0.094	0.77	4.43*	6
		BaP	0.069	0.73	4.08*	6

^a One-tailed t -test, significance as follows: ns, not significant; *, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$. ^b Degrees of freedom.

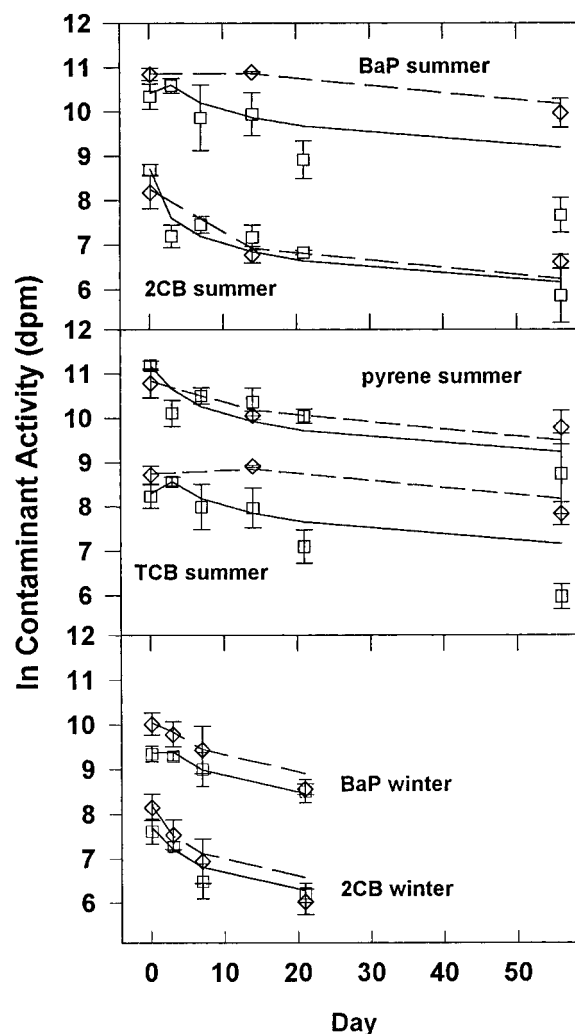


FIGURE 4. Depth-integrated contaminant activity (ln total dpm per core) versus time and treatment in two laboratory microcosm experiments. The modeled diffusive losses (D_L) are shown as solid or dashed lines. Solid lines indicate treatments that contained macrofauna; dashed lines indicate treatments that lacked macrofauna. Symbols indicate means and one standard error.

Modeling contaminant loss as diffusion, rather than as a first-order process, provides a good fit to the observed data, particularly during the first 14–21 d of the experiment (Figure 4). The derived diffusive loss coefficients (D_L) range from 1 to $5 \times 10^{-5} \text{ cm}^2/\text{s}$ and are 2–10 times higher than the HOC molecular diffusivities in water (Table 1). The diffusive loss

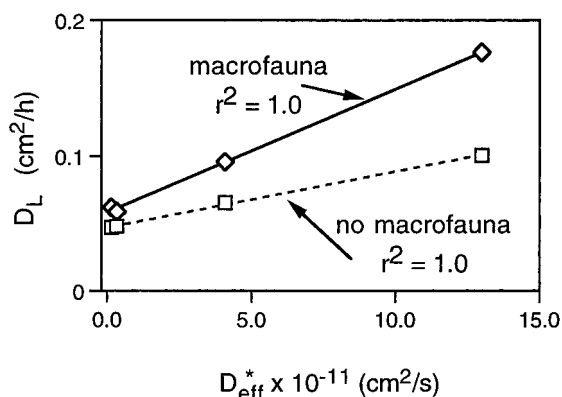


FIGURE 5. Modeled diffusive loss coefficients (D_L) versus contaminant relative effective diffusivities (D_{eff}^*) during the summer experiment.

coefficients are consistent with turbulent diffusion of dissolved or fine particle-associated contaminants, particularly during the first few days to weeks after the initial deposition at the sediment–water interface. Although there were significant ($t \geq 20.5$, $p < 0.001$) positive relationships between the derived D_L values and D_{eff}^* of the contaminants for treatments with macrofauna and controls, the slope is significantly greater ($t = 25$, $p < 0.001$) for the treatments with macrofauna (Figure 5). This indicates that benthic macrofauna enhanced the short-term diffusive loss of HOCs from the sediment and that the effect was amplified for the most hydrophilic compounds. In addition, in the presence of macrofauna the D_L value for 2CB was significantly higher ($t = 2.2$, $p < 0.05$) in the summer as compared with winter. These observations imply an increase of desorptive–diffusive loss of the more soluble HOCs via macrofauna activities such as tube and burrow irrigation, which are expected to be greater in summer relative to winter.

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