

POLLUTANT FLUXES TO AQUATIC SYSTEMS VIA BED-SEDIMENT PROCESSES

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INTRODUCTION

Hydrophobic organic contaminants (HOCs) sorb strongly to sediments and partition weakly into the porewater and overlying water. This leads to the detection of HOCs in sediments long after their original introduction to the environment. Water bodies with active sediment processes have larger fluxes of HOCs to overlying water. In the absence of sediment resuspension by erosive processes, the normal life cycle activities of benthic organisms will predominate in the transport of particles from within the sediment bed to the sediment-water interface. As a result the HOCs associated with the particles are released to the water column. This process is called *bioturbation* and is the focus of this paper. There are a number of species that act as bioturbators. The most prevalent ones, especially in contaminated sediments across many sites in the U.S. are the Tubificidae species that burrow within the sediment and defecate at the surface.

Capping with clean sediment is a possible remediation measure for isolating the aquatic system from contaminated sediments (Thoma *et al.*, 1993). The placement of the cap will effectively increase the pathlength for contaminant transport by diffusion and advection and, will also decrease pollutant release by direct bioturbation of contaminated particles. This paper describes our experiments on contrasting the flux of HOCs from bioturbated capped and uncapped sediments in small laboratory microcosms with those of control microcosms (capped and uncapped) without bioturbators.

METHODOLOGY

The experiments were conducted in laboratory microcosms which have been described in detail elsewhere (Reible *et al.*, 1994). They were designed to simulate the flow of water over a sediment surface. Each microcosm was 15 cm x 5 cm x 4.5 cm in dimension and was constructed out of 0.64 cm thick plexiglass. Two flat overflow slots were located on both ends of the microcosms to make water flow more uniformly over the sediment surface. Fifteen such microcosms were used. The total sediment thickness in each was 3.5 cm that included the clean sediment used as cap in some of the microcosms. Seven of them were control microcosms that contained no organisms. Of the seven, three were uncapped and four were capped with clean sediment to a thickness of 0.5 cm. The remaining eight microcosms contained 200 organisms each. Of the eight, four were uncapped and four were capped with clean sediment to a thickness of 0.5 cm. The sediment used was obtained from a local area (Bayou Manchac, Baton Rouge, LA). It had an organic carbon content of 2.8% and a porosity of 0.67. The sediment was processed and inoculated with a mixture of three polyaromatic hydrocarbons (pyrene, phenanthrene and dibenzofuran). In this paper we report our results only for pyrene. The pyrene concentration in the sediment was 31.9±1.1 mg/kg. The sediment inoculation procedure was described in an earlier publication (Reible *et al.*, 1994). The bioturbators used were *Limnodrilus hoffmeisteri*, head-down feeders often found in many freshwater estuarine environments (Stimpson *et al.*, 1985).

In the experiments reported here, the average flow rate of water over the sediment was 500 ml/h. This high flow rate ensured that water-side mass transfer resistance was negligible in the transport of pyrene from sediment to water. The effluent water was collected periodically to estimate the contaminant concentration on an HPLC by an EPA standard method (Reible *et al.*, 1994). The flux of contaminant was determined from $N = C \Delta V / \Delta t$, where ΔV is the volume collected in time Δt . The experiments were run for sixty days and then the sediment was cored into 4 mm thin sections and analyzed for pyrene.

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RESULTS

The measured fluxes of pyrene from the experimental microcosms are shown in Figure 1. The open symbols represent the chemical flux from the bioturbated systems while the solid symbols represent the flux from the non-bioturbated control microcosms. All fluxes represent the average of four replicate microcosms (except the controls which represent three microcosms); the error bars indicate the standard deviation in the measured fluxes. The standard deviation among the replicate microcosms was typically about 20%, indicating the variability associated with the worm biological activity, liquid extraction and concentration procedures for HPLC analysis. In figure 1 are shown the pyrene flux from both the capped and uncapped Bayou Manchac sediments populated with 200 worms. For comparison the pyrene flux from the control channels are also presented. Pyrene flux in uncapped control channels decreased gradually from ~ 250 ng/cm²/d at the start of the experiment to about 10 ng/cm²/d after 25 days. The flux remained stable at the lower value for approximately 30 days. In the capped control channels the pyrene flux observed in the outlet water was zero indicating the effectiveness of the cap in retarding the movement of a hydrophobic compound from the underlying sediment. The data is in agreement with the observed trend in earlier experiments on capping (Thoma *et al*, 1993). The organisms were added after six days of the experiment, the influence of which is obvious in the flux of pyrene. Whereas the pyrene flux in the control channels was about 60 to 70 ng/cm²/d at the time of worm incorporation into the sediment, the bioturbated microcosms showed a flux of 140 ng/cm²/d. Even towards the end of the experiment the flux in the bioturbated microcosms remained about 60 ng/cm²/d. In the capped microcosms populated by the worms, the flux was quite stable during the course of the experiment and varied between 30 to 40 ng/cm²/d. Towards the end of the experiment, the fluxes from both the capped and uncapped sediments with worms were almost identical.

Figure 2 represents the sediment concentration profile for pyrene in uncapped control without worms, capped control without worms, uncapped sediment with worms and capped sediment with worms. The profiles in the uncapped controls without worms showed the expected exponential profile over the first 4 mm of the contaminated layer where the sediment concentration decreased from an initial loading of 32 mg/kg to 7 to 12 mg/kg. In the uncapped microcosms with worms the depletion of pyrene was larger at the surface. In the capped control without worms, the expected effect of decreased movement of pyrene at the surface was apparent; in fact, there was only minimal amount of pyrene that migrated into the clean cap. In the microcosm with cap and worms, there was a clear indication of the worm transporting pyrene through the cap. It was observed that the worm fecal pellets collected at the surface contained about 5 mg/kg of pyrene, while the underlying 3 mm of the cap contained no pyrene. The depletion layer in this case was ~ 10 mm.

The above results clearly indicate that bioturbation significantly increased the contaminant flux from the sediment over control capped and uncapped microcosms. The total contaminant flux from the sediment can be regarded as the sum of the diffusive flux from the porewater and the bioturbation flux. The latter is a combination of the sediment particle transport and water pumping during feeding activities by worms. Initially the diffusion from the sediment surface will be large; however, with time the effective depletion of the surface sediment will lead to a decrease in the rate of molecular diffusion. As the diffusive flux decreases with time relative significance of bioturbation will increase. The bioturbation flux from the sediment can be determined by subtracting the flux in the controls without worms from those of the microcosms with worms. For pyrene the average bioturbation related fluxes estimated thus were: 55±14 ng/cm²/d in the uncapped microcosms, and 33±6 ng/cm²/d in the capped microcosms. Therefore the decrease in pyrene flux as a result of the cap was only 40% in the presence of the worms. The flux due to bioturbation as obtained above was observed to remain relatively constant for pyrene during the course of the experiment.

An effective bioturbation mass transfer coefficient can be defined as the ratio of the flux due to bioturbation to the contaminant concentration in the sediment:

$$K_b = \frac{(N_{obs} - N_{cont})}{(\rho_b \cdot W_{sed})} \quad (1)$$

The numerator represents the bioturbation flux, viz., the difference in flux between the microcosms with the species (N_{obs}) and the microcosms without the species (N_{cont}). ρ_b is the

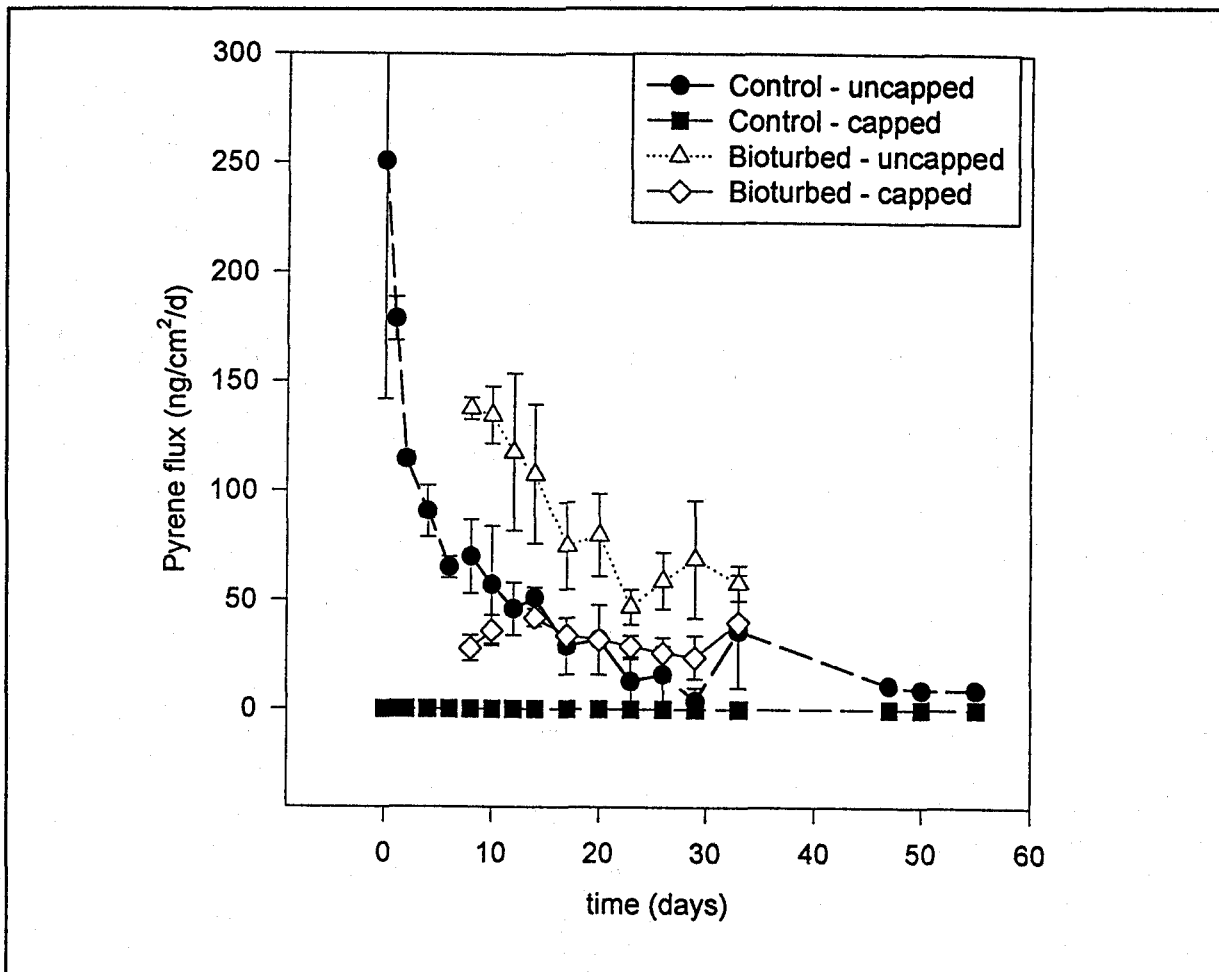


Figure 1. Sediment-to-water flux of pyrene in the various microcosms as a function of time.

sediment bulk density and W_{sed} is the sediment concentration of pyrene. The effective bioturbation mass transfer coefficient for pyrene was 0.7 cm/y. This is comparable to measured values in the field for other compounds which range from 0.1 to 10 cm/y (Reible *et al.*, 1994). Assuming that the effective bioturbation depth is limited to ~ 3 cm, an effective bioturbation diffusion constant can be estimated from $D_{b10} = K_b \cdot (3 \text{ cm})$, which for pyrene would be 2.1 cm²/y.

CONCLUSIONS

The major focus of these experiments was to evaluate the effects of a conveyor-belt worm *Limnodrilus hoffmeisteri* on capping as a control technology for contaminated sediment remediation. The overall approach was to inoculate the sediment with contaminants and then monitor its effluent concentration in small microcosms inhabited by the species. The pyrene flux in uncapped control microcosms decreased gradually from 250 ng/cm²/d at the start of the experiment to about 10 ng/cm²/d after 30 days. The flux then remained constant for the next 30 days. The addition of the worms after six days of the experiment markedly increased the flux of pyrene. The flux due to bioturbation from an uncapped sediment was 55±14 ng/cm²/d and from a capped sediment was 33±6 ng/cm²/d. Towards the end of the experiment the flux from both capped and uncapped sediments were similar. The effective bioturbation mass transfer coefficient for pyrene was 0.7 cm/y. Capping effectively reduced the contaminant release to the water column only in the absence of the worms. In the presence of the worms, a 5 mm layer of cap was found to be less effective in retarding the movement of pyrene from the underlying contaminated sediment to the overlying water.

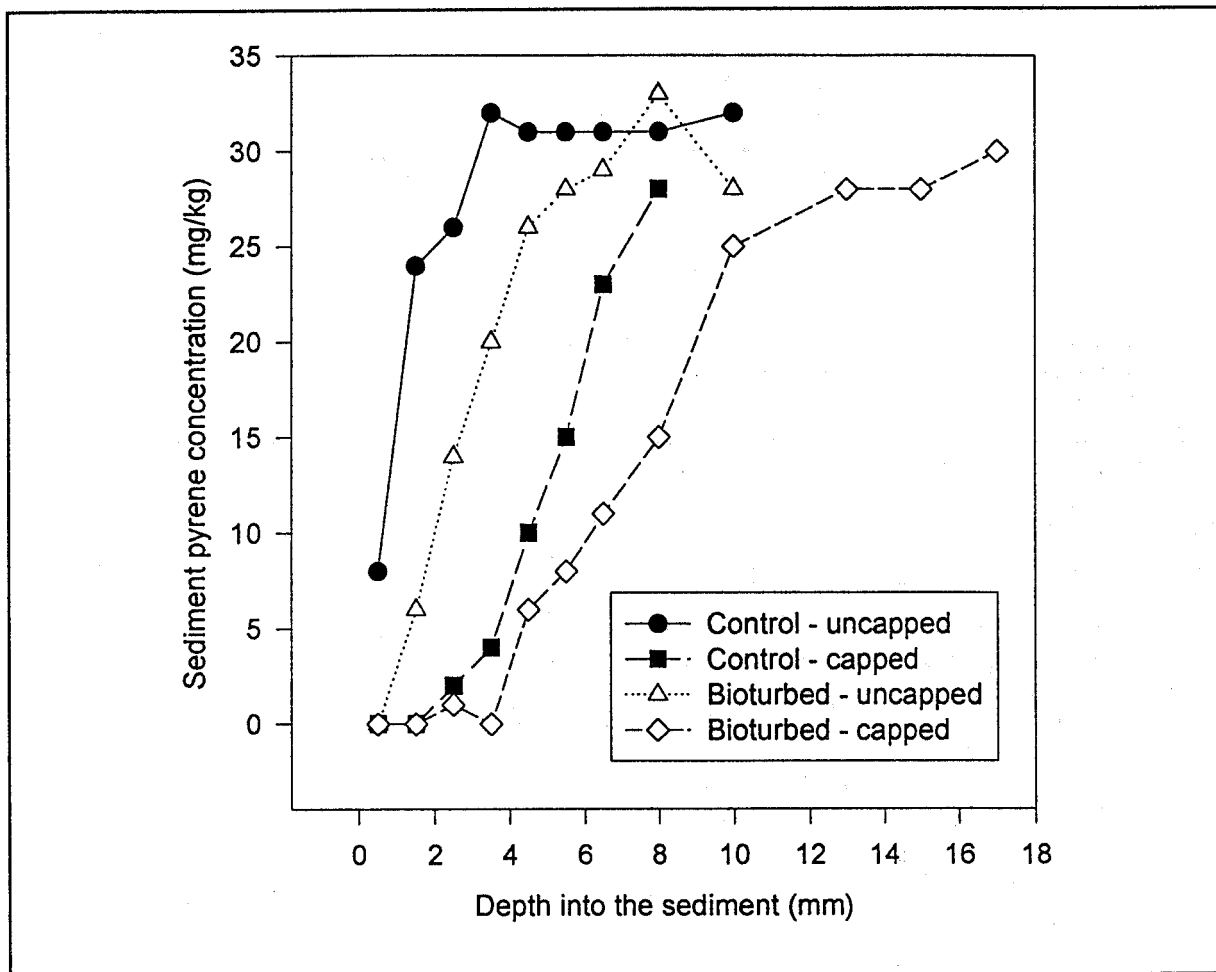


Figure 2. Sediment concentration profile for pyrene in the different microcosms as a function of depth into the sediment.

REFERENCES

- Reible D D, V Popov, K T Valsaraj, L J Thibodeaux, M Dikshit, F Lin, M A Todaro and J F Fleeger (1994), Contaminant fluxes from sediment due to tubificid oligochaete bioturbation, *Water Research* (under review).
- Stimpson K S, D J Klemm and J K Hiltunen (1985), Freshwater tubificidae: Annelida Oligochaeta. *In A Guide to the Freshwater Annelida (Polychaeta, Naidid and Tubificid Oligochaeta and Hirudenia) of North America*, Klemm D J (ed), Kendall/Hunt, Dubuque, IA, p.44.
- Thoma, G J, D D Reible, K T Valsaraj and L J Thibodeaux (1993), Efficiency of capping contaminated sediments in situ 2. Mathematics of diffusion-adsorption in the capping layer, *Environ. Sci. Technol.*, 27, 2412-2419.

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