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# *Environmental Effects of Dredging Technical Notes*

## **Interim Results: The Relationship Between Sediment Organic Carbon and Biological Uptake of Contaminants**

### **Purpose**

This technical note describes testing conducted to determine the partitioning of contaminants between sediment organic carbon and sediment interstitial water, assess the effects of sediment organic carbon upon bioaccumulation of a selected polychlorinated biphenyl (PCB) and polycyclic aromatic hydrocarbon (PAH) by two organisms, and investigate the accuracy of the apparent preference factor as a predictive tool by comparing predicted uptake with actual uptake.

### **Background**

The US Environmental Protection Agency is authorized to develop and implement sediment quality criteria (SQC) under Section 304(a) of the Clean Water Act. SQC, when promulgated, will profoundly affect US Army Corps of Engineers (USACE) dredging and disposal operations. Aquatic disposal of dredged material and selection of aquatic disposal sites will be based on SQC. Most SQC approaches currently under development involve a determination of the relationship between contaminant concentrations in sediment and biological effects on organisms exposed to the contaminated sediment. The USACE is presently investigating the link between contaminant levels in sediment and sediment geochemistry, as well as contaminant levels and effects in aquatic organisms. Knowledge of these interactions will provide the USACE with a means of evaluating the adequacy of proposed SQC approaches for estimating the potential impacts of dredged material disposal.

### **Additional Information**

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## Introduction

Sediment organic carbon has been identified as the most important factor controlling partitioning of nonpolar organic contaminants between sediment and organisms (McFarland and Clarke 1986, McElroy and Means 1988) and between sediment and water (Karickhoff 1981). Many studies have also shown that partitioning of nonpolar organic compounds is strongly related to the octanol-water partitioning coefficient of the compound. Sediment concentrations expressed on a total organic carbon (TOC) basis have been used to predict concentrations of nonpolar organic compounds in organisms (Ferraro, Lee, and Ozretich 1990, Ferraro and others 1991, Lake, Rubinstein, and Pavignano 1987, McElroy and Means 1988, McFarland and Clarke 1986, and Rubinstein and others 1987). This method is currently being pursued by the US Environmental Protection Agency (EPA) to predict interstitial water concentrations for regulatory purposes (Brannon and others 1990).

The EPA approach to predicting interstitial water concentrations is called the Equilibrium Partitioning (EP) approach. The approach allows estimation of the concentration of a contaminant in interstitial water from sediment contaminant concentrations normalized to organic carbon. The calculated interstitial water concentrations are then compared to water quality criteria. If the predicted sediment interstitial water concentration for a given contaminant exceeds its respective chronic water quality criterion, the sediment would be categorized as contaminated by the EP procedure (Brannon and others 1990).

A procedure for investigating the relationship between sediment-bound contaminants and biota has been developed and tested (Brannon and others 1989). The procedure makes use of contaminants labelled with carbon-14 (radiotracer). Contaminants were introduced to sediments in a manner that closely simulated introduction of contaminants in the aquatic environment. Initial results showed that radiotracers provided a means for examining sediment geochemistry/bio-availability relationships that are consistent with results obtained in traditional laboratory and field studies. Results of radiotracer studies can be used to develop models for real-world conditions provided that the radiolabelled compound does not biodegrade during the course of the test, and the radiolabelled compound behaves as would the nonlabelled compound.

Results indicated that equilibration of contaminants with both sediment and the lipid pool of organisms occurred rapidly. Therefore, long exposures for bioaccumulation testing are unnecessary.

The laboratory experiments described in this note were designed to examine the relationships between sediment organic carbon and sediment interstitial water, the effects of sediment organic carbon upon bioaccumulation of a selected

polychlorinated biphenyl (PCB) and polycyclic aromatic hydrocarbon (PAH) by two organisms, and the accuracy of the apparent preference factor as a predictive tool.

## Materials and Methods

Three sediments were used in this study, Oakland Inner Harbor sediment from Oakland, CA; Red Hook sediment from the New York Bight, NJ; and a mixture of sediment from Brown's Lake, a freshwater lake in Vicksburg, MS, with sediment from a salt-marsh channel in Louisiana. The mixed sediment provided a test of organic matter different from that in the two saline sediments (Oakland and Red Hook).

Two organisms having different feeding modes were used in this study: clams (*Macoma nasuta*), which burrow into and deposit-feed on surficial sediments via an incurrent siphon, and worms (*Nereis virens*), which burrow into and ingest the sediment. Clams and worms were exposed to each of the three sediments amended with 4  $\mu\text{g}$  of either [ $^{14}\text{C}$ ] PCB 153 ([ $^{14}\text{C}$ ]2,2',4,4',5,5'-hexachlorobiphenyl) or [ $^{14}\text{C}$ ]fluoranthene per gram dry sediment weight using methods described previously (Brannon and others 1989). At all sampling periods, concentrations of PCB 153 and fluoranthene were determined in the overlying water, interstitial water, foam plugs for trapping volatiles, and clams and worms at all sampling periods. Details of the experimental procedure used in this study are given elsewhere (Brannon and others 1991).

## Results and Discussion

### Interstitial Water

Concentrations of free and bound (complexed with dissolved organic carbon and microparticulates) fluoranthene in interstitial water during 15 days of organism exposure are presented in Figure 1. Significant differences in both free and bound interstitial water fluoranthene concentrations for sediment containing either worms or clams were observed in all sediments tested. These differences may be a function of the manner in which the organisms disturb the sediment and process carbon or the increased bioaccumulation of organic contaminants from sediments low in organic carbon.

The ability of EP to predict interstitial water PCB 153 and fluoranthene concentrations in sediment was tested by comparing estimated  $K_{oc}$  with measured  $K_{oc}$  values.  $K_{oc}$  is the partition coefficient for sediment organic carbon and is one of the key components used in EP for predicting interstitial water concentrations. Estimated  $K_{oc}$  values were computed by substituting values of  $\log K_{ow}$  (octanol/water partition coefficient) for fluoranthene (5.5) (Tetra Tech 1985) and PCB 153 (6.92) (Hawker and Connell 1988) in the equation of Karickhoff (1981) that relates  $K_{ow}$  to  $K_{oc}$ . Measured values of  $K_{oc}$  were determined by dividing the TOC

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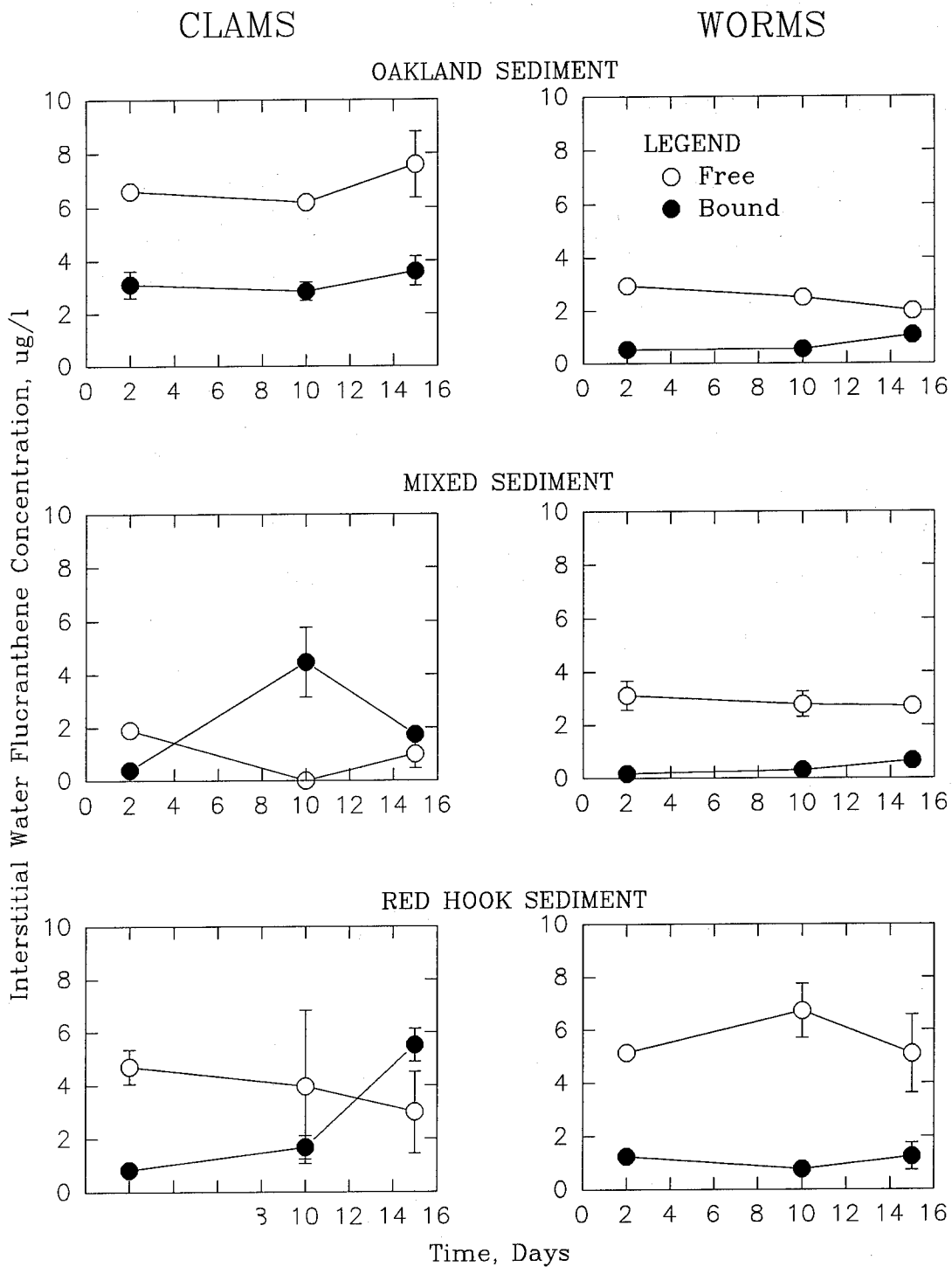


Figure 1. Free and bound (associated with dissolved TOC and microparticulates) interstitial water concentrations of <sup>14</sup>C-labelled PCB 153 and fluoranthene during bioaccumulation testing

normalized sediment concentration of either PCB 153 or fluoranthene by the free interstitial water concentration of the respective compounds.

Comparison of measured and estimated  $K_{oc}$  values for the 15-day sampling (Figure 2) showed that agreement was poor for both fluoranthene and PCB 153. Because of the log scale of the figure and the log nature of  $K_{oc}$  values, a difference of one unit is an order of magnitude difference in partitioning between water and sediment TOC. Measured  $K_{oc}$  was consistently lower than estimated  $K_{oc}$  for PCB 153, but showed no consistent pattern for fluoranthene. Therefore, EP did not provide accurate estimates of free interstitial water concentrations of PCB 153 and fluoranthene in the sediments tested. Such inaccuracy could result in sediment categorizations that are inconsistent with the actual environmental impacts of the dredged material.

An additional problem was identified that may frequently occur in sediment from industrial areas. TOC concentrations measured using whole sediments were:

Sediment	Percent TOC
Oakland	1.08
Mixed	2.84
Red Hook	4.63

Investigation of the Red Hook sediment revealed numerous small lumps of shiny black coal. Sorption of PCB and fluoranthene on such surfaces should be minimal in comparison to sorption on sediment organic matter because of the tremendous difference in surface area. Passage of the sediment through a No. 40 mesh sieve to remove coal prior to TOC determination resulted in a 37 percent reduction in sediment TOC to 2.92 percent. This TOC concentration was then used to compute measured  $K_{oc}$  and apparent preference factors because of the insignificant role of the coal fraction as a sorptive phase for fluoranthene or PCB 153 compared to other forms of sediment TOC. The TOC without coal was used to generate the Red Hook data (Figure 2).

Measured  $K_{oc}$  values for PCB 153 (average  $\log K_{oc} = 6.34$ ) were in better agreement with the estimated  $K_{oc}$  value of 6.5 using the sediment humic + fulvic acid fraction rather than sediment TOC. Measured  $K_{oc}$  values for fluoranthene (average  $\log K_{oc} = 5.7$ ) consistently exceeded the estimated  $K_{oc}$  value (5.09). These results demonstrated the possible utility of the humic + fulvic acid fraction and suggest that fractions of sediment organic matter other than TOC are potentially useful for predictive purposes. However, more research is needed before such approaches can be made useful.

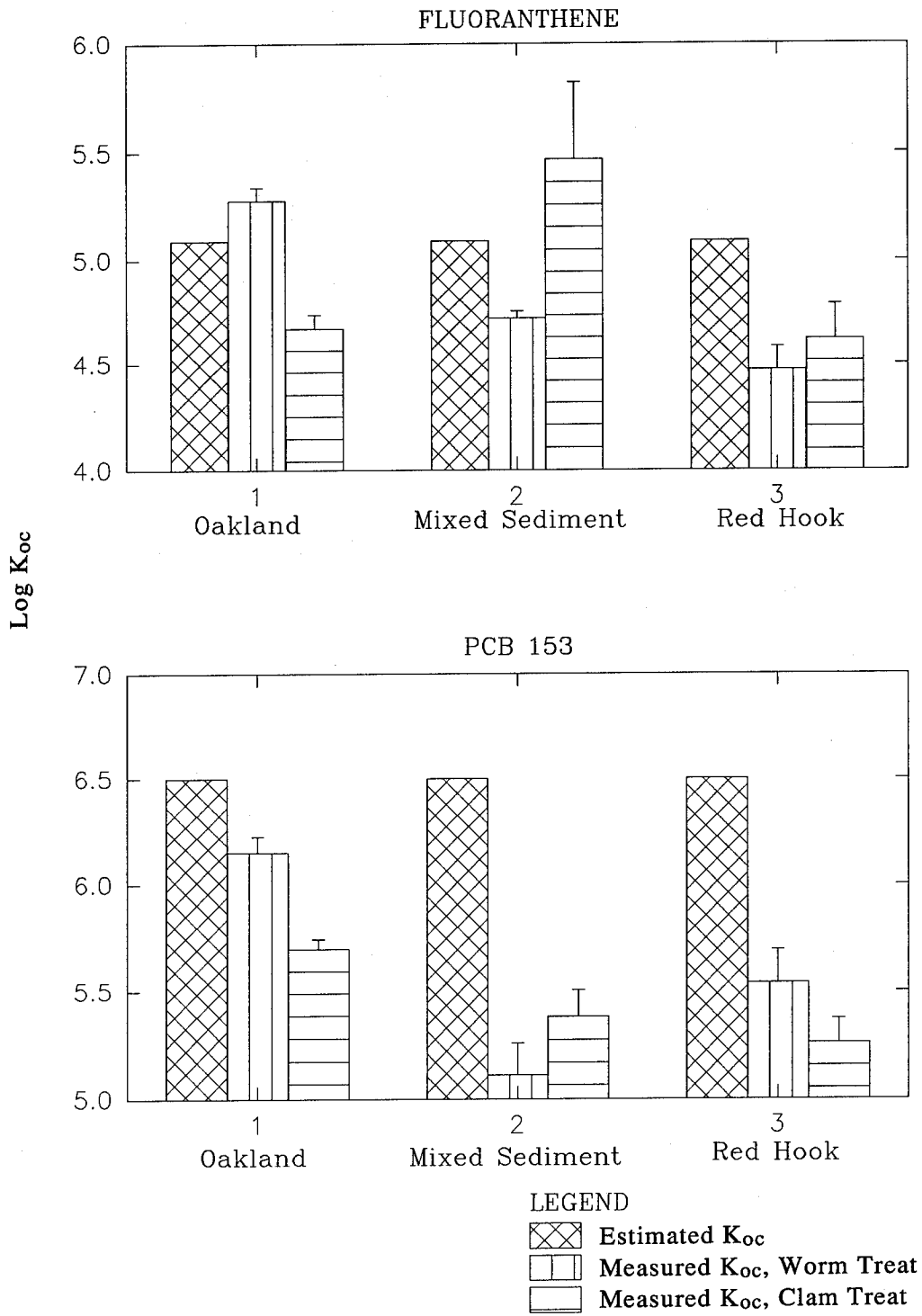


Figure 2. Estimated and measured  $K_{oc}$  values following 15 days of incubation

## Relationship between Interstitial Water and Overlying Water

Results indicated that volatilization from the overlying water can be a loss pathway for both PCB 153 and fluoranthene during bioassay experiments. Volatile losses from bioassay tests were significantly higher in the worm treatments than in clam treatments for both PCB 153 and fluoranthene in all but Red Hook sediment, where losses for the two treatments were comparable. Volatile losses for the three sediments averaged 0.21 percent of the total fluoranthene and 0.17 percent of the total PCB 153. Possibly as a result of such losses, interstitial water and overlying water concentrations were not significantly correlated, except for fluoranthene in the clam treatment ( $r = 0.72$ ,  $p < 0.05$ ) (Brannon and others 1991). Consequently, the linking of interstitial water concentrations to biological effects in the overlying water column may be difficult.

## Apparent Preference Factor

Apparent preference factors (APFs) calculated at 10- and 15-day sample intervals for both clams and worms were in close agreement in all sediments except Oakland Harbor (Brannon and others 1991). Slow stabilization of Oakland Harbor PCB 153 and fluoranthene APFs was unexpected, because only 10 days had been required for PCB 52 to attain steady state APFs in Oakland Harbor sediment during a previous study (Brannon and others 1989). Tissue concentrations and interstitial water concentrations in worm and clam treatments were unrelated (Brannon and others 1991).

The values of 15-day APFs (Table 1) were similar to those for other empirical determinations reported in the literature for both field and laboratory studies and studies using both spiked and "naturally" contaminated sediment (Figure 3). The observations in this study are not only consistent with, and supportive of, results of a previous study (Brannon and others 1989), but also indicate good correspondence between laboratory results using spiked sediments and results

Sediment	Clams		Worms	
	Fluoranthene	PCB	Fluoranthene	PCB
Oakland	3.77 (3.4)	4.79 (1.77)	0.8 (0.17)	4.78 (0.65)
Mixed	2.47 (0.79)	Samples lost	1.05 (0.18)	1.41 (0.29)
Red Hook	0.55 (0.84)	0.49 (0.19)	3.31 (1.27)	4.79 (2.50)

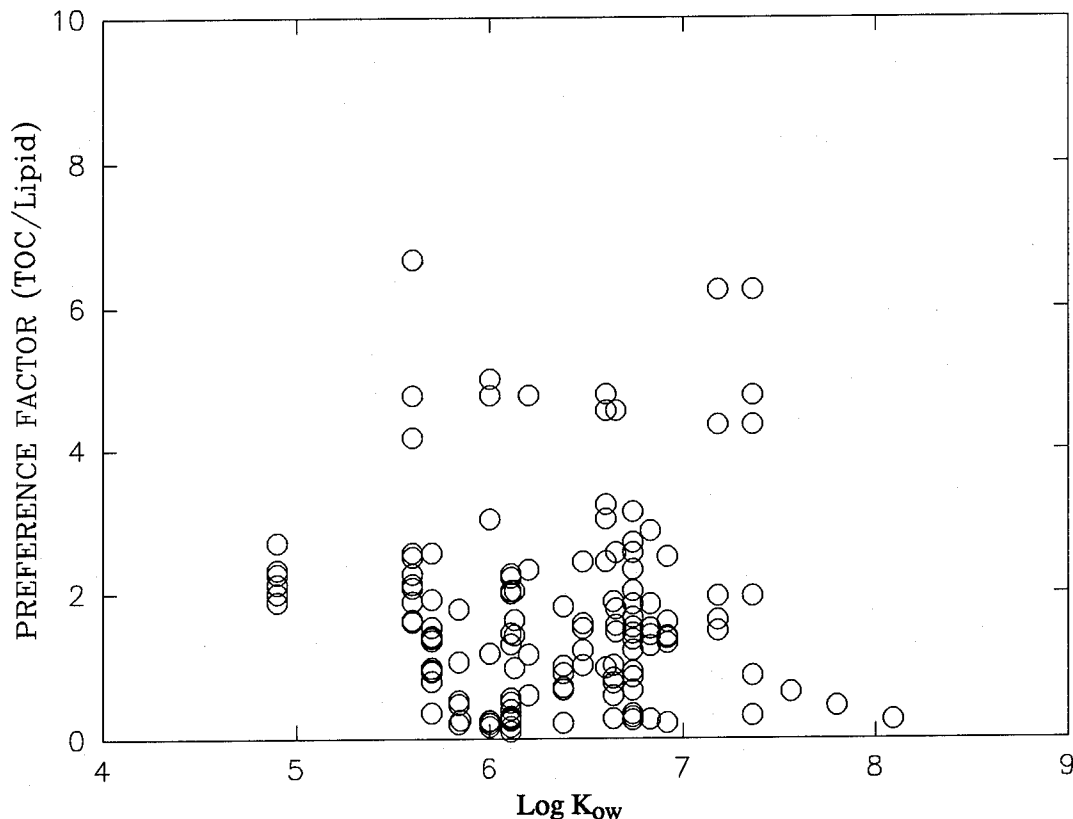


Figure 3. Literature preference factor values (Bierman 1988, Clarke, McFarland, and Dorkin 1988, Ferraro and others 1990, Ferraro and others 1991, Lake, Rubinstein, and Pavignano 1987, McElroy and Means 1988, Pruell and others 1990, and Rubinstein and others 1987)

with field-contaminated sediments and biota. In addition, results of Brannon and others (1991), McElroy and Means (1988), and Brannon and others (1989) showed rapid attainment of constant preference factors, implying that long exposures for the purposes of bioaccumulation testing are not necessary for PCBs and fluoranthene.

### Summary of Findings

Values of  $K_{oc}$  measured using free interstitial water concentrations of fluoranthene and PCB 153 were either substantially higher or lower than estimated  $K_{oc}$  values. The data indicated that concentrations of PCB 153 and fluoranthene in interstitial water will be either overestimated or underestimated when using equilibrium partitioning, estimated  $K_{oc}$  values, and TOC. In a regulatory framework, predictive methods with a high degree of uncertainty are not a good foundation upon which to base pass/fail decisions. The geochemistry affecting interstitial water concentrations must be better understood before rigid regulatory criteria based upon predicted interstitial water concentrations are promulgated.

The sediment humic + fulvic acid fraction was investigated as a method to normalize sediment concentrations and predict interstitial water concentrations.

Measured  $K_{oc}$  based on the sediment humic + fulvic acid fraction were in close agreement with estimated  $K_{oc}$  values for PCB 153, but not for fluoranthene. These results demonstrated the potential usefulness of examining discrete fractions of sediment TOC as a means of normalizing sediment concentrations, but also indicated that much work remains to be done in this area. Interstitial water and overlying water concentrations were not significantly correlated, except for fluoranthene in the clam treatment. These results demonstrate the difficulty in linking interstitial water concentrations to biological effects in the overlying water column.

Bioaccumulation of PCB 153 and fluoranthene by worms and clams was observed in all sediments. Even though tissue concentrations increased as time of exposure increased, APF values showed that steady state was reached between sediment-bound contaminants and organism lipid pools. No relationship was found between tissue concentrations of worms or clams and interstitial water concentrations of contaminants. This result suggests that interstitial water may not be the primary source of contaminant exposure for sediment-associated organisms.

The APFs for PCB 153 and fluoranthene in worms and clams were in close agreement with field and laboratory values reported in the literature. These results imply that long exposures for bioaccumulation testing are not necessary for PCBs and fluoranthene. The presence of coal in the Red Hook sediment demonstrated that care must be exercised when using TOC values for sediment from industrial areas. However, the use of sediment TOC in conjunction with partition coefficients, such as APFs, is a viable approach for predicting bioaccumulation of nonpolar organic contaminants by infaunal organisms.

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