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EFFECTS OF SEDIMENT ORGANIC MATTER
COMPOSITION ON BIOACCUMULATION
OF SEDIMENT ORGANIC CONTAMINANTS

INTERIM RESULTS

by

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Actual concentrations of contaminants in interstitial water were either overestimated or underestimated by the relationship between TOC and humic + fulvic acid organic matter fractions and sediment contaminant concentrations. Prediction of interstitial water concentrations was not as successful as use of APFs. The lack of agreement between predicted and actual interstitial water results was due to factors such as the presence of interstitial water contaminants bound to microparticulates and dissolved organic matter and the kind of organic matter in the sediment.

PREFACE

The research described herein was conducted by the US Army Engineer Waterways Experiment Station (WES), Environmental Laboratory (EL). Funding was provided by the Long-Term Effects of Dredging Operations (LEDO) Program, Work Unit 32571, which is sponsored by the Headquarters, US Army Corps of Engineers (HQUSACE). The LEDO Program is managed within the Environmental Effects of Dredging Programs, Dr. Robert M. Engler, Manager.

The report was prepared by Dr. James M. Brannon and Ms. Cynthia B. Price of the Aquatic Processes and Effects Group (APEG), and Mr. Francis J. Reilly, Dr. Judith C. Pennington, and Mr. Victor A. McFarland of the Contaminant Mobility and Regulatory Criteria Group (CMRCG), Ecosystem Research and Simulation Division (ERSD), EL. Technical reviews were provided by Drs. Douglas Gunnison and Thomas D. Wright, ERSD. The report was edited by Ms. Jessica S. Ruff of the WES Information Technology Laboratory.

Principal Investigators were Dr. Brannon and Mr. McFarland, leaders of the Sediment Geochemistry and Microbiology Team, APEG, and Aquatic Contaminants Team, CMRCG, respectively. The study was conducted under the general supervision of Dr. Thomas L. Hart, Chief, APEG; Dr. Lloyd H. Saunders, Chief, CMRCG; and Mr. Donald L. Robey, Chief, ERSD. Chief of EL was Dr. John Harrison.

COL Larry B. Fulton, EN, was Commander and Director of WES. Dr. Robert W. Whalin was Technical Director.

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EFFECTS OF SEDIMENT ORGANIC MATTER COMPOSITION
ON BIOACCUMULATION OF SEDIMENT ORGANIC CONTAMINANTS

INTERIM RESULTS

PART I: INTRODUCTION

Background

1. The relationship between sediment-bound nonpolar organic contaminants and biological uptake of these contaminants is complex. The complexity is a result of the many physical, chemical, and biological factors that can affect the relationship between sediment and organisms (McElroy and Means 1988). 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). 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 can be used to predict interstitial water concentrations (Brannon et al. 1989, 1990).

2. Procedures for investigating the relationship between sediment-bound contaminants and biota have been developed and tested (Brannon et al. 1989). The test apparatus uses a radiotracer addition to sediment in a manner that closely simulates introduction of contaminants in the aquatic environment. Initial results showed that radiotracers provided a means of examining sediment geochemistry/bioavailability relationships that are consistent with results obtained in traditional laboratory and field studies (Clarke, McFarland, and Dorkin 1988).

3. Results of radiotracer studies can be used to develop models for real-world conditions. Results have indicated that equilibration of contaminants with both sediment and the lipid pool of organisms occurs rapidly. Therefore, long exposures for bioaccumulation testing may be unnecessary.

Objectives

4. This report describes testing conducted to (a) determine the relationships between sediment organic carbon and sediment interstitial water, (b) examine the effects of sediment organic carbon upon bioaccumulation of a selected polychlorinated biphenyl (PCB) and polycyclic aromatic hydrocarbon (PAH) compound by two organisms, and (c) investigate the accuracy of the apparent preference factor as a predictive tool by comparing predicted with actual uptake.

PART II: MATERIALS AND METHODS

5. Three sediments were used in this study: (a) Oakland Inner Harbor sediment from Oakland, CA; (b) Red Hook sediment from the New York Bight, New York; and (c) 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).

6. Clams (*Macoma nasuta*) and worms (*Nereis virens*) were exposed to each of the three sediments amended with either uniformly ring labeled [¹⁴C] 2,2',4,4',5,5' hexachlorobiphenyl (PCB 153) or carbon three labeled fluoranthene. [¹⁴C]PCB 153 had a specific activity of 20 milliCuries per millimole and a radiological purity of >98 percent as determined by high performance liquid chromatography. [¹⁴C]fluoranthene had a specific activity of 55 milliCuries per millimole and a radiochemical purity of >98 percent as determined by thin layer chromatography. The experimental design provided exposure of the two classes of compounds, both of which are of environmental concern, to a broad variety of sediments and to two organisms (clams and worms) having different relationships to the sediment. Clams burrow into and deposit feed on surficial sediments via an incurrent siphon, while worms burrow into and ingest the sediment.

Bioaccumulation Test Procedures

7. Initial studies (Brannon et al. 1989) showed that a sediment bioassay apparatus similar to that used by McElroy and Means (1988) provided an effective means of studying the relationship between sediment geochemistry and bioaccumulation of contaminants. Details of the experimental apparatus are shown in Figure 1. During the experiment, the exposure vessels were randomly distributed and maintained in a water bath at 15° C, the optimum temperature for the worms and clams. Foam plugs (McElroy and Means 1988) were used to trap PCB or fluoranthene volatilized or stripped from the water by aeration.

8. To amend sediments, PCB 153 in toluene or fluoranthene in benzene was added to glass jars and allowed to evenly coat the walls as the solvent evaporated to dryness. The sides of the glass jars were coated with sufficient test compound to yield sediment concentrations of 4 µg/g dry weight. Sediment and sufficient saline water (30 ppt) were added to the jars to give a

water-to-sediment ratio of 3:1. Test jars were shaken for 3 days and allowed to settle for 4 days before the excess water was siphoned off and replaced with fresh portions of saline water. Air bubbling was initiated, and the test apparatus was allowed to aerate for 1 day prior to introduction of test organisms. Three clams or two worms were added to each test unit.

9. Four replicates of each exposure condition for each sampling time and two controls for each exposure were prepared. Organisms were harvested at 2, 10, and 15 days after initiation of the study. Tests were not conducted beyond 15 days because equilibration of PCB with organism lipids occurs rapidly (within 10 days) (Brannon et al. 1989).

10. At each sampling time, the overlying water, interstitial water, foam plugs, and clams or worms were sampled. Foam plugs were extracted by drawing successive 5-ml aliquots of hexane into the syringe holding the plug, allowing the hexane to stand for 15 sec, and then slowly eluting the hexane. The procedure was repeated until no additional radioactive counts could be extracted from the plug. Aliquots of hexane were then pooled, and 1 ml was added to 20 ml of Aquasol Universal LSC Cocktail (LS) (Dupont, Boston, MA) and counted for 10 min three times in a Beckman LS-100 Liquid Scintillation System (Beckman Instruments, Inc., Fullerton, CA) using the external standard, channels ratio method.

11. Interstitial water was sampled by adding 30 g of sediment to a 25-ml stainless steel centrifuge tube and centrifuging at 7,400 RCF (12,000 rpm) for 1 hr at 20° C. This centrifugation time and speed result in removal from solution of particulates larger than 0.01 μm . One milliliter of the interstitial water was counted by LS. Five milliliters of the interstitial water was passed through a C-18 Sep-Pak cartridge (Waters Associates, Milford, MA) to separate the dissolved contaminant from contaminant sorbed to suspended microparticulates (smaller than 0.01 μm) and dissolved organic macromolecules, such as humic acids (Landrum et al. 1984). One milliliter of the solution or suspension that had passed through the Sep-Pak was then counted by LS in a Aquasol-distilled water gel (13 ml Aquasol:6 ml water maintained at 25° C).

12. Water overlying the sediment was prepared for analysis by adding 20 ml to a 25-ml glass centrifuge tube and centrifuging for 1 hr at 7,400 RCF. A 1-ml aliquot of the water was counted by LS.

13. Clams and worms were placed into containers of clean, aerated saline water, each container having a false bottom to prevent reingestion of

depurated sediment. The organisms were allowed to depurate for 24 hr. Clams were shucked, and the soft tissues were frozen. Worm tissue was frozen without further preparation. Five to ten grams (wet weight) of tissue was homogenized and extracted three times with a 1:1 acetone:hexane mixture. At the end of each extraction, the mixture was centrifuged at 4,162 RCF (9,000 rpm) for 10 min to separate the extract from the tissue. Each extract was measured, and 1 ml was counted by LS. Lipids were determined by measuring 0.1 ml of the pooled extract into a tared aluminum pan, air-drying to remove the solvents, and weighing the residue on a microbalance (Rubenstein et al. 1987, Samuelian and O'Connor 1989). Dry weight was also determined on an unextracted tissue subsample by oven-drying for 24 hr at 90° C.

Organic Matter Extraction

14. Humic and fulvic acids were extracted from the sediments using the method of Schnitzer (1982). Following pretreatment with 0.05 N HCl to remove carbonates, the sediment was rinsed with distilled water and allowed to air dry. Ten grams of the air-dried sediment was extracted for 24 hr with 100 ml of deoxygenated 0.5 N NaOH under a nitrogen atmosphere. The supernatant fluid was separated from the remaining sediment by centrifugation and analyzed for total organic carbon (TOC). A subsample of the air-dried sediment was further dried for 12 hr at 105° C to determine percent solids. The TOC in this extract represents contributions from both humic and fulvic acids.

Data Analysis

15. All statistical analyses were conducted using methods developed by the Statistical Analysis Systems Institute (Barr et al. 1976). To test for differences between means, analysis of variance procedures were used.

PART III: RESULTS

Sediment Organic Carbon

16. Sediment TOC content ranged from 1.08 percent in Oakland sediment to 4.63 percent in Red Hook sediment (see tabulation below). Red Hook sediment contained the lowest percentage of humic and fulvic acid, 0.22. The coefficient of variation between replicate determinations of humic and fulvic acids was less than 22 percent.

<u>Sediment</u>	<u>Percent TOC</u>	<u>Percent Humic + Fulvic Acid</u>
Oakland	1.08	0.36
Red Hook	4.63	0.22
Mixed freshwater	2.84	0.40

Interstitial Water

PCB 153

17. The presence of organisms influenced the concentration of PCB 153 in the interstitial water to a limited extent. PCB concentrations ranged from 0.3 to 3.5 $\mu\text{g}/\ell$ and averaged 0.94 $\mu\text{g}/\ell$ for all treatments of clams and worms combined over all sampling periods (Figure 2). The 3.5 $\mu\text{g}/\ell$ of PCB found in interstitial waters of the mixed sediment with worms at day 10 was the only concentration that was significantly higher than other treatments during the day 2 and day 10 sampling. At the end of 15 days of exposure, interstitial water concentrations of PCB 153 in the mixed sediment clam treatment ($0.61 \pm 0.13 \mu\text{g}/\ell$) were significantly higher than concentrations in the worm treatment ($1.28 \pm 0.47 \mu\text{g}/\ell$). The opposite relationship, $0.73 \pm 0.08 \mu\text{g}/\ell$ in the clam treatment compared to $0.30 \pm 0.04 \mu\text{g}/\ell$ in the worm treatment, was observed in Oakland sediment.

Fluoranthene

18. Concentrations of fluoranthene in interstitial water were significantly higher in Red Hook sediment with worms than in the other two sediments (Figure 3). Interstitial water concentrations with clams increased in the order Oakland > Red Hook > mixed sediment, but differences were insignificant at 10 days. Concentrations of fluoranthene in interstitial water (average of 4.4 $\mu\text{g}/\ell$ over all sampling times for both worms and clams) were generally

higher than concentrations of PCB, except in the mixed sediment worm treatment, where concentrations of the two contaminants were comparable.

19. Interstitial water fluoranthene concentrations were significantly higher in the Oakland sediment worm treatment compared to the Oakland sediment clam treatment during the entire exposure period. At the end of 15 days of exposure, interstitial water fluoranthene concentrations in the mixed sediment worm treatment were slightly lower than concentrations in the clam treatment. The same trends were observed in the PCB 153 clam and worm treatments at the day 15 sampling time.

Predicted concentrations

20. Predicted concentrations of PCB 153 and fluoranthene in interstitial water, which were obtained by equilibrium partitioning theory, are compared with actual means for both organisms at day 15 in Figure 4. Predicted interstitial water concentrations were calculated using the equation.

$$C_w = \frac{C_s}{(K_{oc})(f_{oc})} \quad (1)$$

where

C_w = equilibrium concentration of chemical in interstitial water, mg/l

C_s = concentration of chemical in sediment, mg/kg

K_{oc} = organic carbon partitioning coefficient

f_{oc} = decimal fraction of organic matter in sediment

21. The K_{oc} was estimated using an octanol-water partitioning coefficient (K_{ow}). A $\log K_{ow}$ of 5.5 was used for fluoranthene (Tetra Tech, Inc. 1985) and 6.9 for PCB 153 (Shiu and Mackay 1986, Doucette and Andren 1988). The octanol-water partition coefficient is a distribution coefficient of solute monomers between an aqueous phase and a hydrophobic organic phase. Comparing estimated and measured partition coefficient data, Karickhoff (1981) developed a linear relationship between K_{ow} of the solute and the organic carbon content of the sorbent as follows:

$$\log K_{oc} = 0.989 \log K_{ow} - 0.346 \quad (2)$$

22. Interstitial water concentrations of PCB 153 and fluoranthene predicted using Equation 1 and f_{oc} are compared with actual 15-day concentrations in Figure 4. Actual PCB 153 concentrations were consistently higher than predicted values. Actual fluoranthene concentrations were also generally higher than predicted concentrations, although some values at lower TOC concentrations did not significantly differ from predicted values. In general, actual concentrations of PCB 153 and fluoranthene for both worm and clam treatments were either comparable to or higher than predicted using sediment TOC.

23. Interstitial water concentrations of PCB 153 and fluoranthene predicted using Equation 1 and the decimal fraction of humic + fulvic acids in sediment (f_{h+f}) in place of f_{oc} are compared with actual 15-day concentrations in Figure 5. Predictions based on f_{h+f} better approximated the resulting PCB 153 concentrations than those based on f_{oc} . Predicted fluoranthene concentrations in interstitial water were generally higher than actual values.

Bound contaminants

24. PCB and fluoranthene associated with microparticulates and dissolved organic matter (passing a C-18 Sep-Pak) in interstitial water constituted approximately 10 percent of total PCB 153 and from 10 to 30 percent of total fluoranthene (Figure 6). In the worm treatments, the fraction of bound fluoranthene increased in the Oakland and in the mixed sediments as time of contact with the worms increased. In the Red Hook sediment, the data were inconclusive.

25. In clam treatments, values are missing because samples were lost during processing. The fraction of PCB 153 associated with suspended microparticulates or dissolved organic macromolecules remained relatively constant over the course of the experiment (Figure 6). Subtraction of the fraction of bound PCB 153 and fluoranthene from the interstitial water concentrations for day 15 (Figures 2 and 3) would not change the conclusions reached regarding the comparability of predicted and actual interstitial water concentrations. The amount of bound PCB or fluoranthene would be subtracted because the presence of bound contaminants in solution increases the concentration above that predicted by Equation 1.

Overlying Water

PCB 153

26. Concentrations of PCB 153 in the overlying water remained relatively constant during the tests with worms and clams (Figure 7). Only PCB 153 concentrations in water overlying Red Hook sediment with clams at day 15 were significantly higher than other PCB treatments. Concentrations averaged 0.18 and 0.28 $\mu\text{g}/\ell$ in the worm and clam treatments, respectively. These overlying water concentrations were somewhat lower than the average interstitial water concentration of 0.93 $\mu\text{g}/\ell$ in the clam and worm treatments combined.

Fluoranthene

27. Fluoranthene concentrations in the overlying water increased slightly from day 2 to day 15 for both clam and worm treatments (Figure 7). In the worm treatments, mean fluoranthene concentrations increased from 1.94 $\mu\text{g}/\ell$ at day 2 to 3.88 $\mu\text{g}/\ell$ at day 15. A similar rise from 1.16 $\mu\text{g}/\ell$ at day 2 to 4.48 $\mu\text{g}/\ell$ at day 15 was observed in the fluoranthene clam treatment, albeit with higher variability. Average fluoranthene concentrations in the overlying water were comparable to interstitial water concentrations, which averaged 4.4 $\mu\text{g}/\ell$ for all treatments and times.

Volatile Losses

28. Volatile losses from bioassay tests were 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 (Figure 8). Red Hook sediment contained the highest concentration of TOC, which may have acted to bind the contaminants more tightly to the sediment, thereby reducing volatile losses. Volatile losses were 0.21 percent of the total fluoranthene in the system and 0.17 percent of the total PCB 153. These values are considerably lower than the 1.44 percent loss reported previously for sediments treated with 10 $\mu\text{g}/\text{g}$ of PCB 52 in the same test system (Brannon et al. 1989). The difference may be a function of the molecular weight and octanol-water partition coefficient differences between PCB 52 and PCB 153 and fluoranthene.

Bioaccumulation

29. Tissue concentrations (micrograms per gram, wet weight) of PCB 153 and fluoranthene generally increased as exposure time increased in both worm and clam treatments (Figure 9). At 15 days of exposure, worms exposed to PCB-amended sediments had accumulated similar amounts of PCB, an average of $0.77 \pm 0.22 \mu\text{g}$ PCB per gram wet tissue. Fluoranthene concentrations in worms at the end of 15 days of exposure were more variable than PCB concentrations, with worms in Oakland sediment having significantly higher concentrations than in the other sediments. Concentrations of fluoranthene in worms of Oakland sediment ($2.69 \mu\text{g/g}$) were higher than either Red Hook ($0.89 \mu\text{g/g}$) or the mixed sediment ($0.69 \mu\text{g/g}$).

30. Concentrations of fluoranthene in clams following 15 days of exposure increased in the order: Oakland > Red Hook > mixed sediment. Fluoranthene concentration was highest in Oakland clams, $12.9 \mu\text{g/g}$ wet weight. Clams in Oakland sediment ($3.16 \mu\text{g/g}$) were also higher in PCB 153 concentration following 15 days of exposure than clams in Red Hook sediment ($1.33 \mu\text{g/g}$). Data for the mixed sediment are not reported because the clams died during exposure.

Apparent Preference Factor

Theory

31. An apparent preference factor (APF), a measure of the preference of neutral organic contaminants for organism lipids as opposed to sediment organic carbon, was calculated for each time point using the equation

$$APF = \frac{\left(\frac{PCB_s}{\%TOC} \right)}{\left(\frac{PCB_o}{\%lipid} \right)} \quad (3)$$

where

PCB_s = PCB concentration in sediment, $\mu\text{g/g}$ dry weight

$\%TOC$ = percent total organic carbon, g/g dry weight

PCB_o = PCB concentration in clams, $\mu\text{g/g}$ wet weight

$\%lipid$ = percent lipid in organism extracts, g/g wet weight

32. Equation 3, taken from McElroy and Means (1988), is based on the thermodynamic bioaccumulation potential (TBP) equation of McFarland (1984) and the preference factor equation of Lake, Rubinstein, and Pavignano (1987). The TBP gives the maximum theoretical concentration of a neutral organic compound that can be bioaccumulated from sediment.

PCB 153

33. The APF for PCB 153 in worms was highly variable at the 2-day sampling time (Figure 10). Steady-state APF values for PCB 153 had been reached at the end of 10 days of exposure for Red Hook and the mixed sediment. Oakland sediment required 15 days of exposure to reach APF values similar to those of the Red Hook and mixed sediment. The average APF for worms at the end of 15 days of exposure was 3.07. The APF in clams reached steady state at 10 days for the Red Hook sediment; however, 15 days was required for Oakland sediment to attain comparable APF values. The average APF for PCB 153 in clams was 2.79. Steady-state PCB 52 APF values for clams have previously been shown to require 10 to 15 days to attain steady state (Brannon et al. 1989).

Fluoranthene

34. The APF for fluoranthene in worms was near steady state following 2 days of exposure and had reached near theoretical values following 10 days. Average APF for fluoranthene in worms was 2.77, a value that did not significantly differ from the average APF of 3.07 for PCB 153 in worms. However, the APF for fluoranthene in clams averaged 0.73, within the range of values (0.217 to 0.843) reported for total PCBs, 2,3,7,8-TCDD, and 2,3,7,8-TCDF in *Macoma* and *Nereis* (Pruell et al. 1990).

PART IV: DISCUSSION

Interstitial Water

Effect of organisms

35. The presence of organisms can affect the interstitial water concentrations measured in sediment. Significant differences in interstitial water concentrations in sediment containing either worms or clams were observed in Oakland and the mixed sediment, each of which contained lower TOC than Red Hook sediment, where no significant differences existed. The reasons for this behavior are not well understood, but may be a function of the manner in which the organisms process carbon or the increased bioaccumulation of organic contaminants from sediments low in organic carbon. These results indicate that interstitial water concentrations can be influenced by the presence of different species of organisms as well as by the sorption processes between sediment-bound contaminants and interstitial water.

Prediction of interstitial water concentrations

36. Sediment criteria are being based upon prediction of interstitial water concentrations using sediment TOC and concentration of nonpolar organic contaminants in sediment. Data from this study indicate that prediction of interstitial water concentrations using TOC generally underestimated the actual concentrations of PCB 153 and fluoranthene in the interstitial water. However, at lower sediment TOC concentrations, prediction of both PCB 153 and fluoranthene interstitial water concentrations was more consistent with actual concentrations.

37. The lack of agreement between predicted and actual concentrations was partially due to PCB 153 and fluoranthene association with microparticulates and dissolved organic matter. This association results in apparent interstitial water concentrations greater than predicted by Equation 1. Equation 1 concerns nonbound, or truly dissolved, solution concentrations only. The fraction of bound PCB 153 and fluoranthene in the interstitial water was approximately 10 and 30 percent, respectively.

38. Humic + fulvic acid concentrations in Oakland sediment and the mixed sediment were twice as high as in Red Hook sediment, even though Red Hook sediment was highest in TOC. Visual examination of Red Hook sediment showed the presence of small coal or fly ash particles. Coal, the most

probable constituent, is a form of TOC that does not participate to the same extent in partitioning of nonpolar organic contaminants as do the more usual forms of sediment TOC. The occurrence of coal in sediments of industrial areas may result in high TOC concentrations and underprediction of interstitial water concentrations.

39. Comparisons of actual interstitial water concentrations with those predicted using organic matter fractions other than TOC demonstrate the possible utility of such organic matter fractions. Sediment humic + fulvic acid fraction was a better predictor of PCB 153 interstitial water concentrations than was the fraction of sediment TOC. However, the humic + fulvic acid fraction consistently overestimated fluoranthene interstitial water concentrations. Such conflicting results suggest that use of various fractions of sediment organic matter is of potential value, although more research is needed in this area.

Relationship between interstitial water and overlying water

40. Results indicated that volatilization from the overlying water can be a significant loss pathway for both PCB 153 and fluoranthene during bioassay experiments, although to a lesser extent than for PCB 52 (Brannon et al. 1989). Air bubbling required to keep oxygen in the water for respiration can strip organic contaminants such as PCB from the water column. Volatilization losses from the water column did not affect the results of the experiment reported here because a deposit-feeding clam and burrowing worms were used, and the volatilization loss was low relative to the sediment concentrations. However, bioassays with water column organisms such as fish could be affected if the organic contaminant is stripped from the water faster than it can be replenished from the sediment. Possibly as a result of such stripping, interstitial water and overlying water concentrations were not significantly correlated, except for fluoranthene in the clam treatment ($r = 0.72$, $p < 0.05$). Consequently, interstitial water concentrations cannot be linked to biological effects observed in the water column.

Bioaccumulation

41. Bioaccumulation of PCB 153 and fluoranthene from sediments was rapid in clams and worms. PCB 153 clam concentrations following 15 days of exposure were within the range of values reported previously for PCB 52 in

Oakland sediment (Brannon et al. 1989). Bioaccumulation reached apparent steady state relative to the sediment within 10 days for Red Hook and the mixed sediment, and by 15 days for all three sediments. This is evident from the constancy of the APF calculated at 10- and 15-day sample intervals for both clams and worms (Figure 10) and the agreement of final values with theoretical values.

42. Steady-state APF levels contrast with tissue concentrations for whole organisms over the 15 days of exposure. This is especially evident in the clam treatments. Lipid pools in both the clams and worms were generally declining due to absence of food supplements to the test while PCB 153 and fluoranthene increased, resulting in a constant APF. Tissue concentrations and interstitial water concentrations in worm or clam treatments were unrelated.

43. Rapid equilibration of PCB with lipid reserves of sediment-exposed organisms was also observed by McElroy and Means (1988) in a deposit-feeding clam (*Yoldia limatula*) and a soft-bodied infaunal polychaete (*Nephtys incisa*) exposed to a hexachlorobiphenyl. Brannon et al. (1989) observed similar trends for *Macoma nasuta* exposed to PCB 52. Results of the present study, in conjunction with results of McElroy and Means (1988) and Brannon et al. (1989), imply that long exposures for the purposes of bioaccumulation testing may not be necessary in the case of PCBs and fluoranthene.

Apparent Preference Factor

44. The values of the APFs calculated at 15 days in this study were similar to those for other empirical determinations reported in the literature and were similar to the theoretical preference factor (pf) of 0.58 calculated by McFarland and Clarke (1986). Ferraro et al. (in review) exposed *M. nasuta* to six contaminated sediments collected from the field and found that mean APFs for a wide variety of nonpolar organic compounds ranged from 0.48 to 6.25. The lowest APFs were calculated for the most contaminated sediments.

45. In field studies on the Calumet Harbor confined disposal facility (CDF), the average APF of total PCBs was 0.34 (Clarke, McFarland, and Dorkin 1988). In the same study, APFs were higher and more variable for data on sediments and biota taken from areas of very low PCB contamination compared to areas of high contamination (>1.1 ppm). The observations in this study are consistent with, support the previous results of, and indicate good

correspondence between laboratory results using spiked sediments and results with field-contaminated sediments and biota.

PART V: SUMMARY AND CONCLUSIONS

Sediment Organic Carbon and Interstitial Water

46. Use of TOC and humic + fulvic organic matter fractions in sediments to predict interstitial water concentrations was not as successful as use of APFs. Actual concentrations of contaminants in interstitial water were either overestimated or underestimated. Such results are due to factors such as the presence of contaminants bound to microparticulates and dissolved organic matter, which result in interstitial water concentrations higher than predicted by partitioning theory. Associated factors, such as the kind of organic matter, can also affect contaminant partitioning. For example, Red Hook sediment, which possessed the highest concentrations of TOC, contained the lowest concentrations of humic + fulvic acids, indicating that organic matter in this sediment differed fundamentally in character from the other sediments. Use of various fractions of sediment organic matter for prediction of interstitial water concentrations demonstrated the potential usefulness as well as limitations of such approaches.

Bioaccumulation

47. 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.

Apparent Preference Factor

48. The APF values 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 the purposes of bioaccumulation testing may not be necessary for PCBs and fluoranthene. The APF values were close to the theoretical value for sediments with different amounts and kinds of organic matter. Use of sediment TOC in conjunction with octanol-water partition coefficients of nonpolar organic contaminants is a

viable approach for predicting bioaccumulation of such compounds by infaunal organisms.

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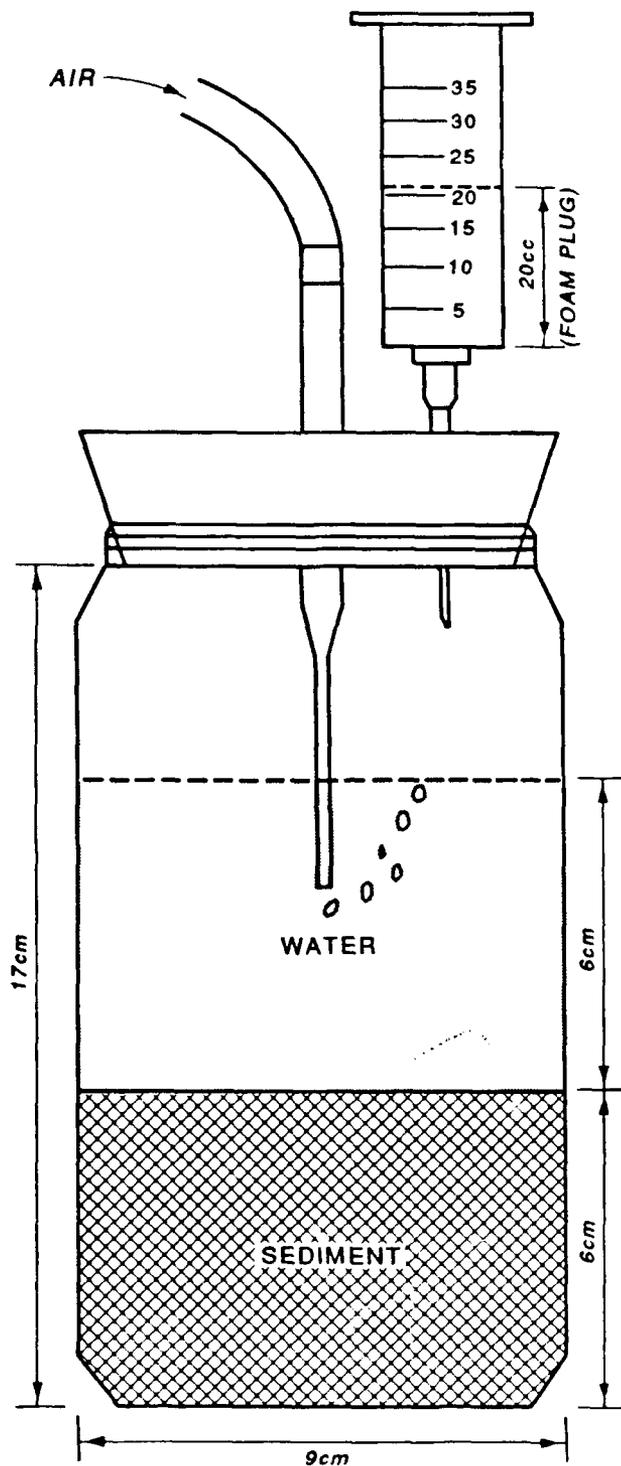


Figure 1. Testing apparatus, showing syringe body with foam plug for collection of volatile PCB 153 and fluoranthene

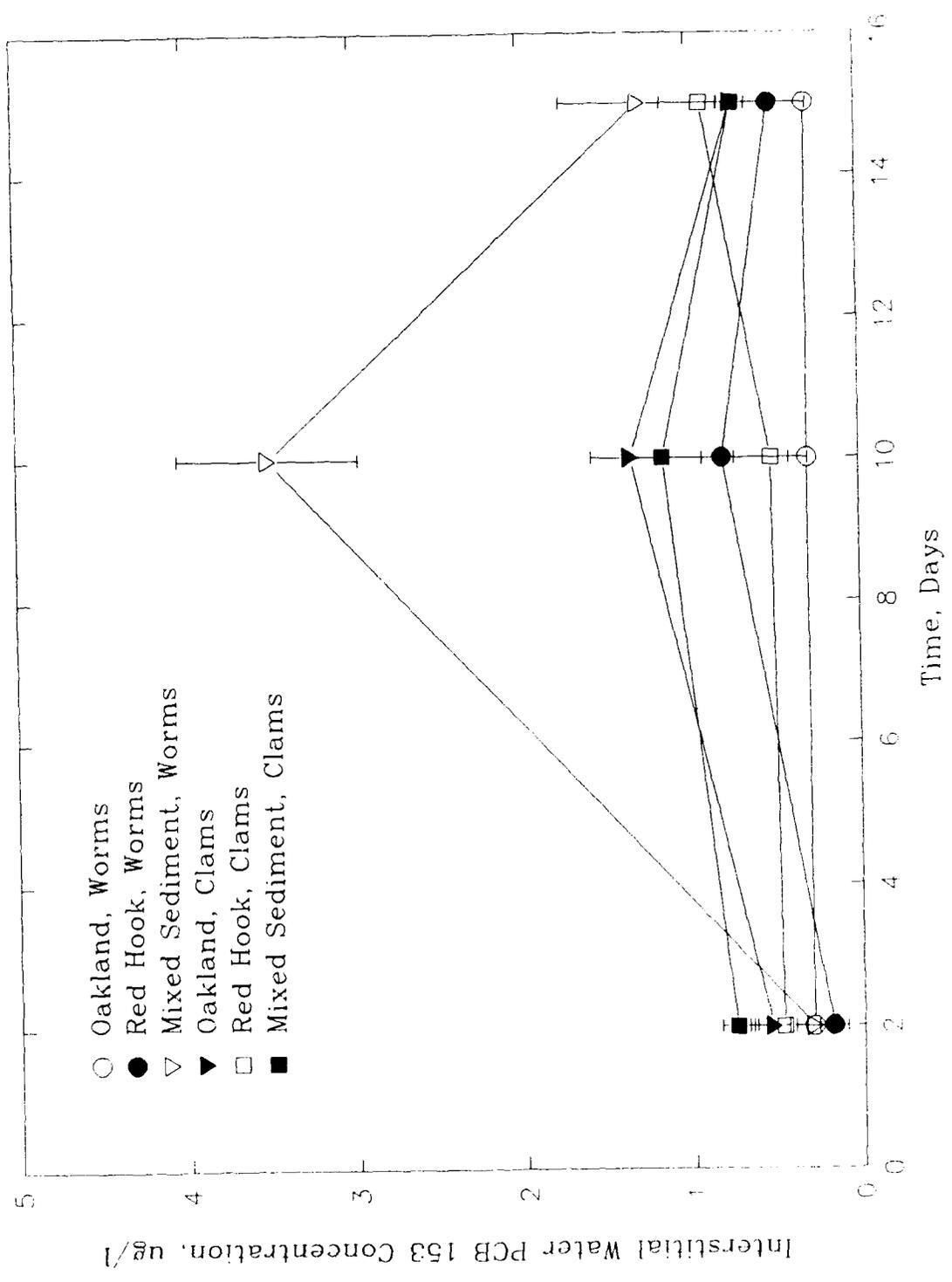


Figure 2. Concentration of [¹⁴C] PCB 153 in interstitial water

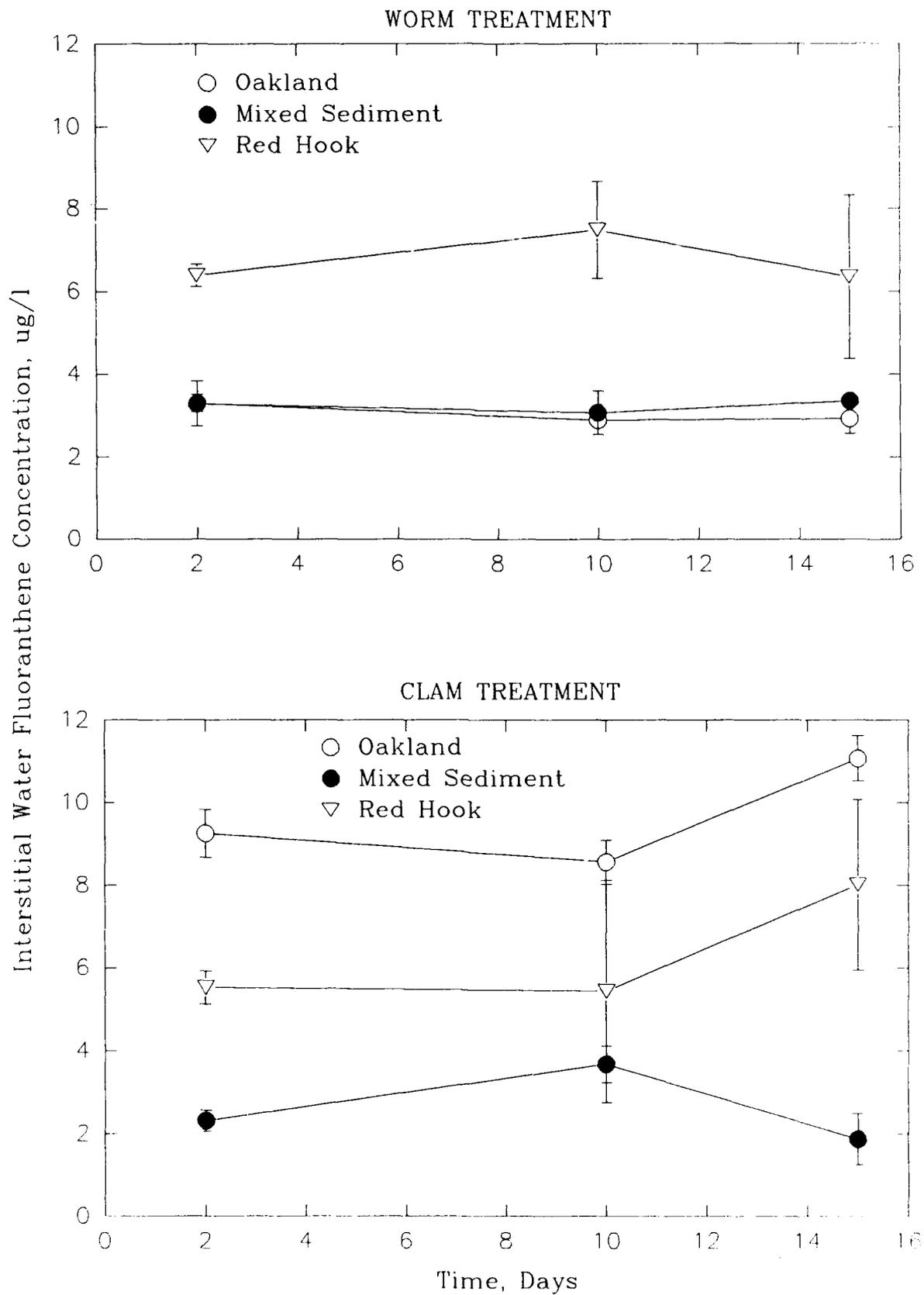


Figure 3. Concentrations of [^{14}C] fluoranthene in interstitial water

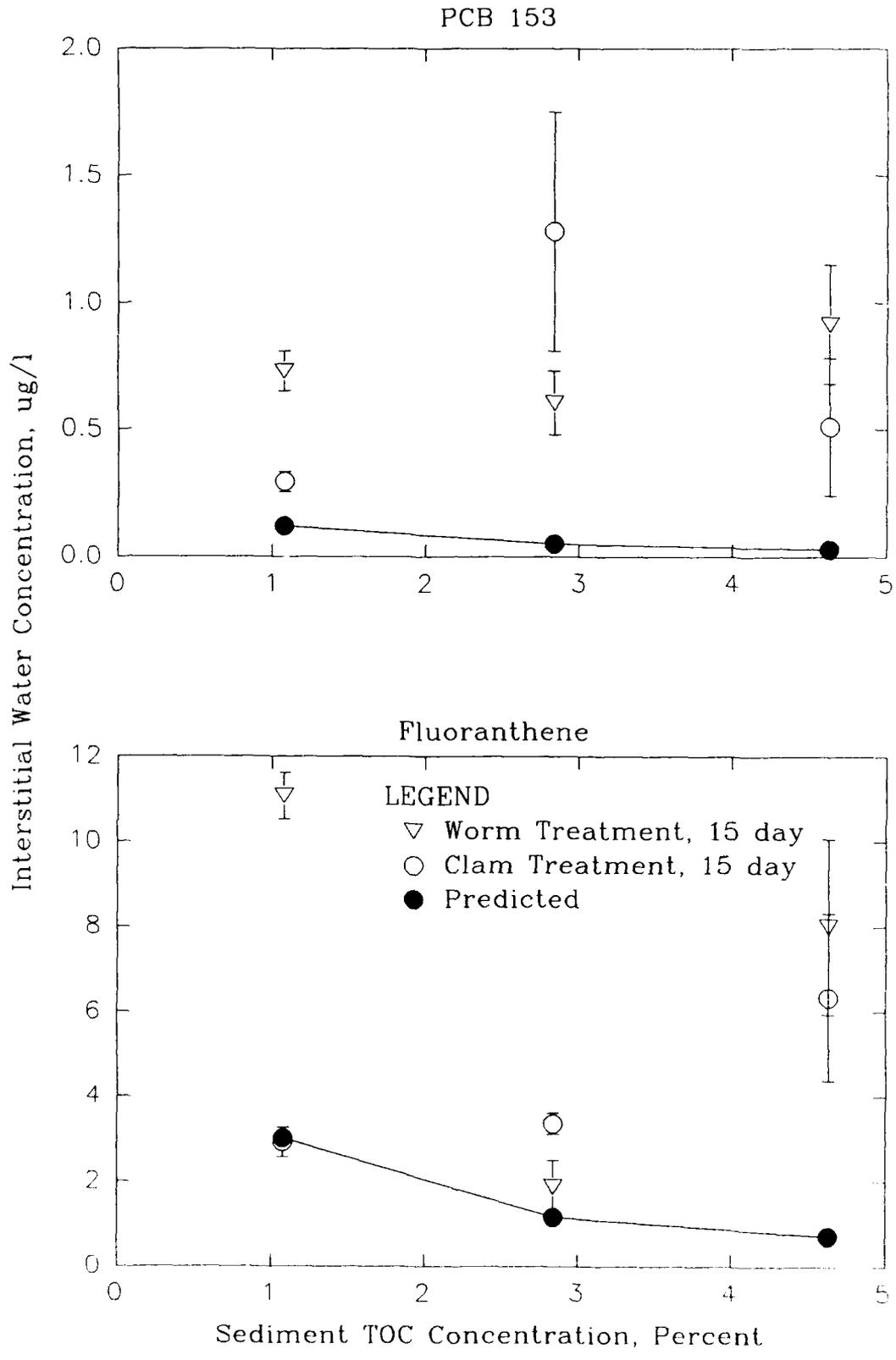


Figure 4. Interstitial water concentrations predicted using f_{oc} TOC versus actual (15-day) concentrations of C^{14} PCB 153 and fluoranthene

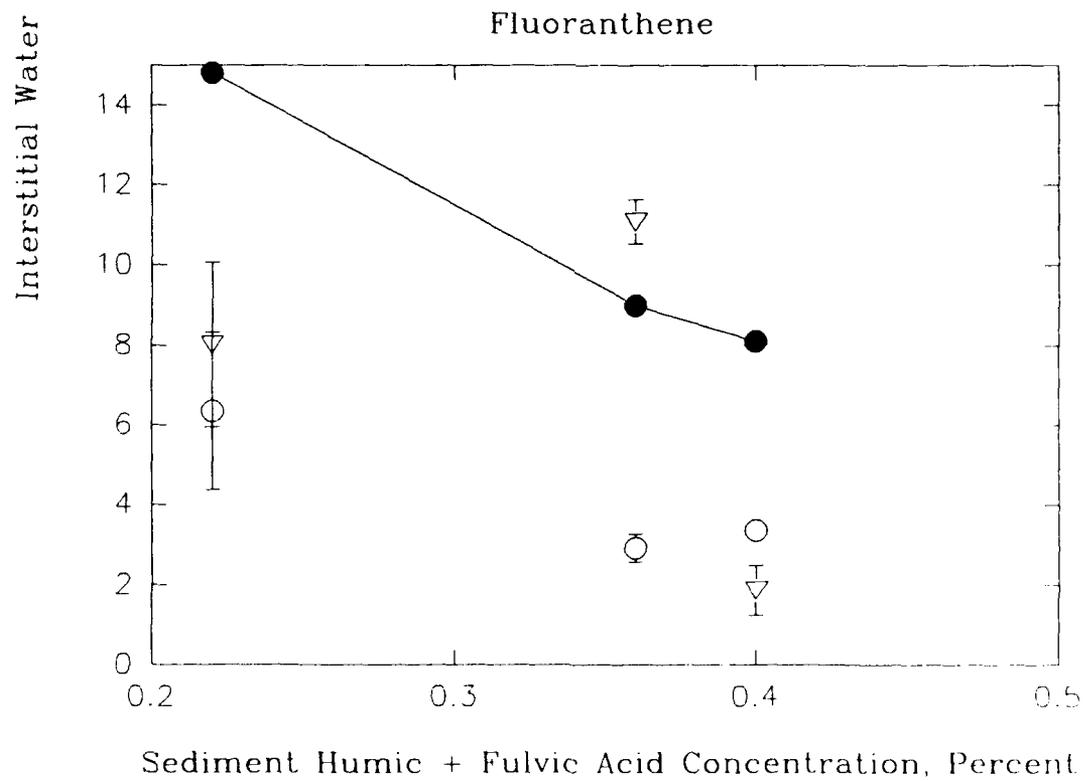
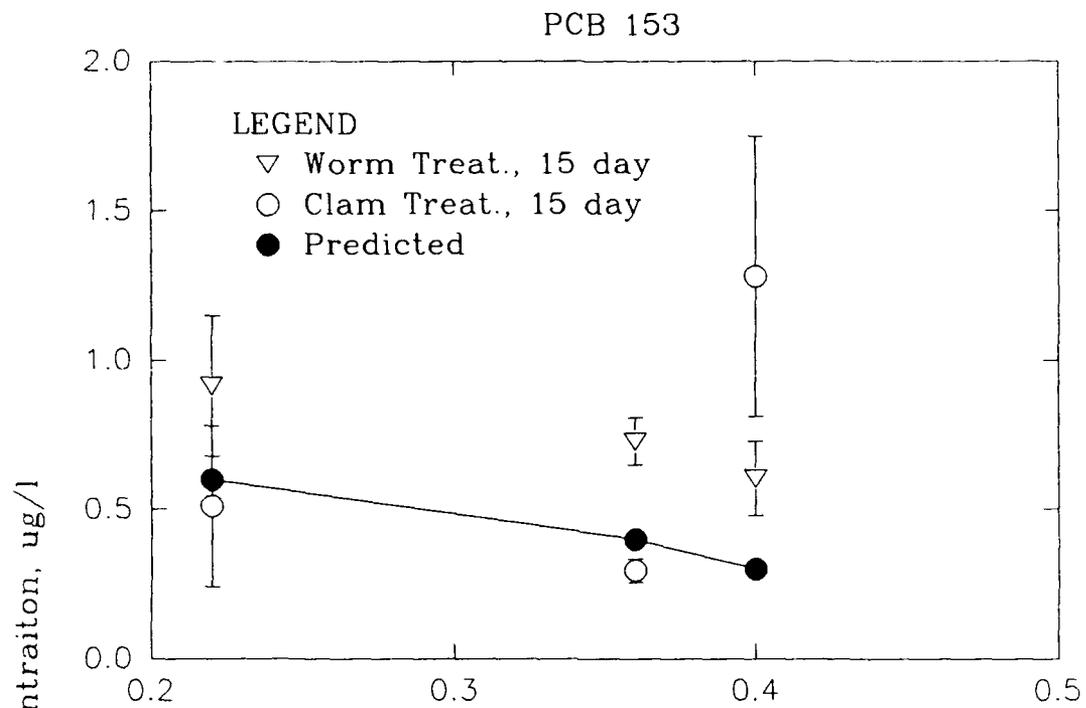
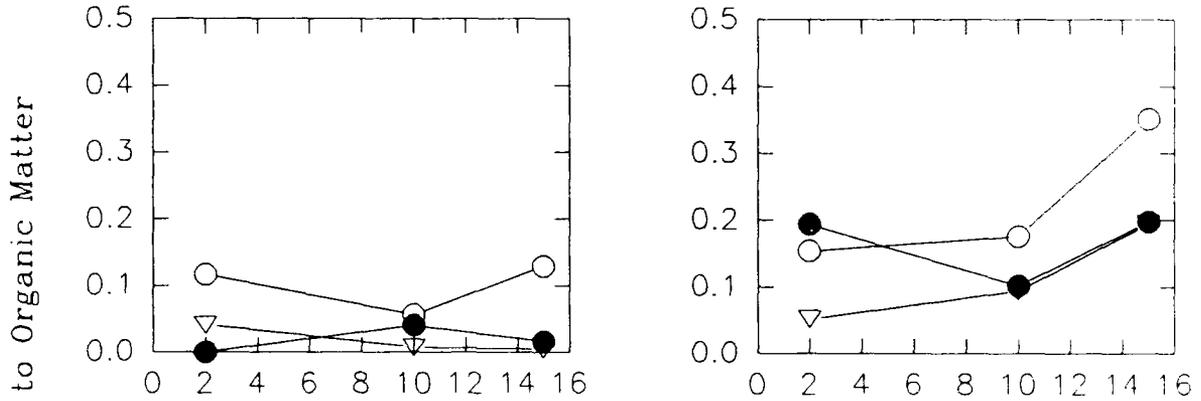


Figure 5. Interstitial water concentrations predicted using f_{oc} humic + fulvic versus actual (15-day) concentrations of C^{14} PCB 153 and fluoranthene

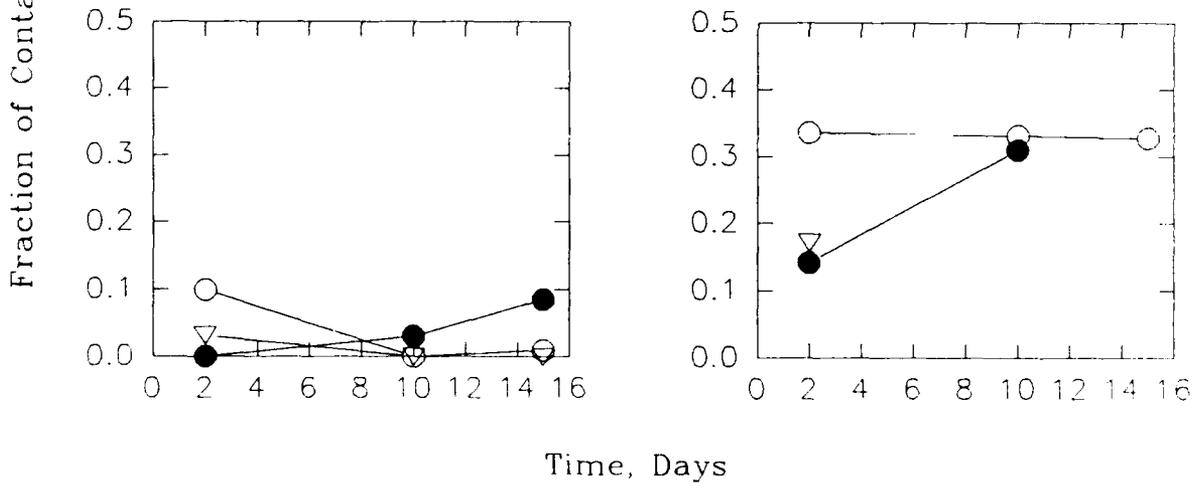
PCB 153

FLUORANTHENE

WORM TREATMENT



CLAM TREATMENT

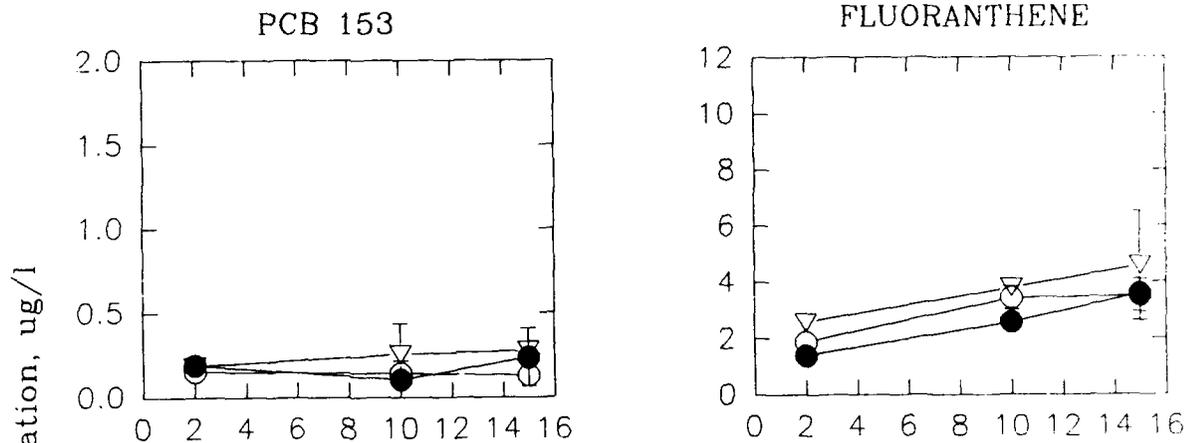


LEGEND

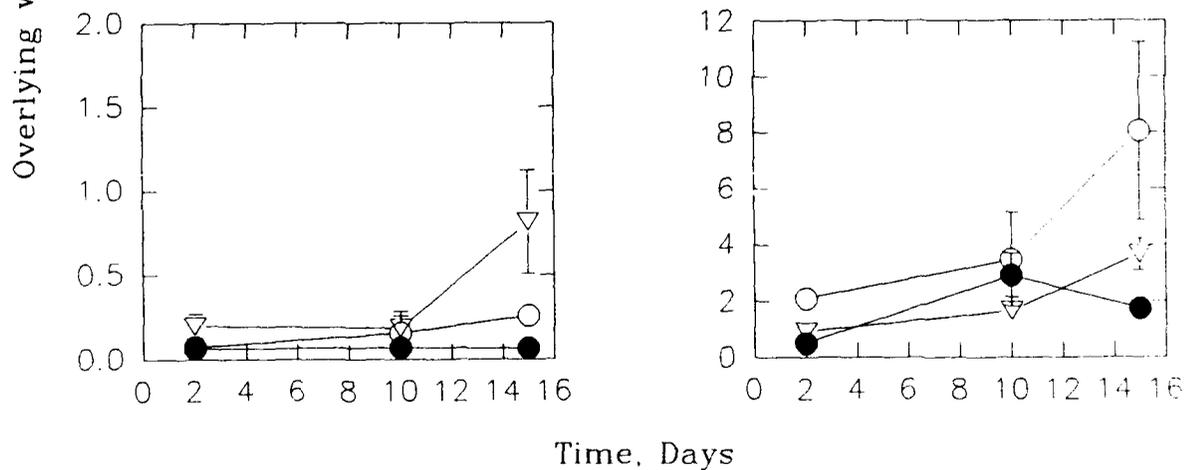
- ▽ Mixed Sediment
- Red Rock
- Oakland

Figure 6. Fraction of contaminants bound to microparticulates and dissolved organic matter (fraction passing C-18 Sep-Pak) in interstitial water

WORM TREATMENT



CLAM TREATMENT



LEGEND

- ▽ Red Hook
- Mixed Sediment
- Oakland

Figure 7. Concentrations of [¹⁴C] PCB 153 and fluoranthene in the overlying water

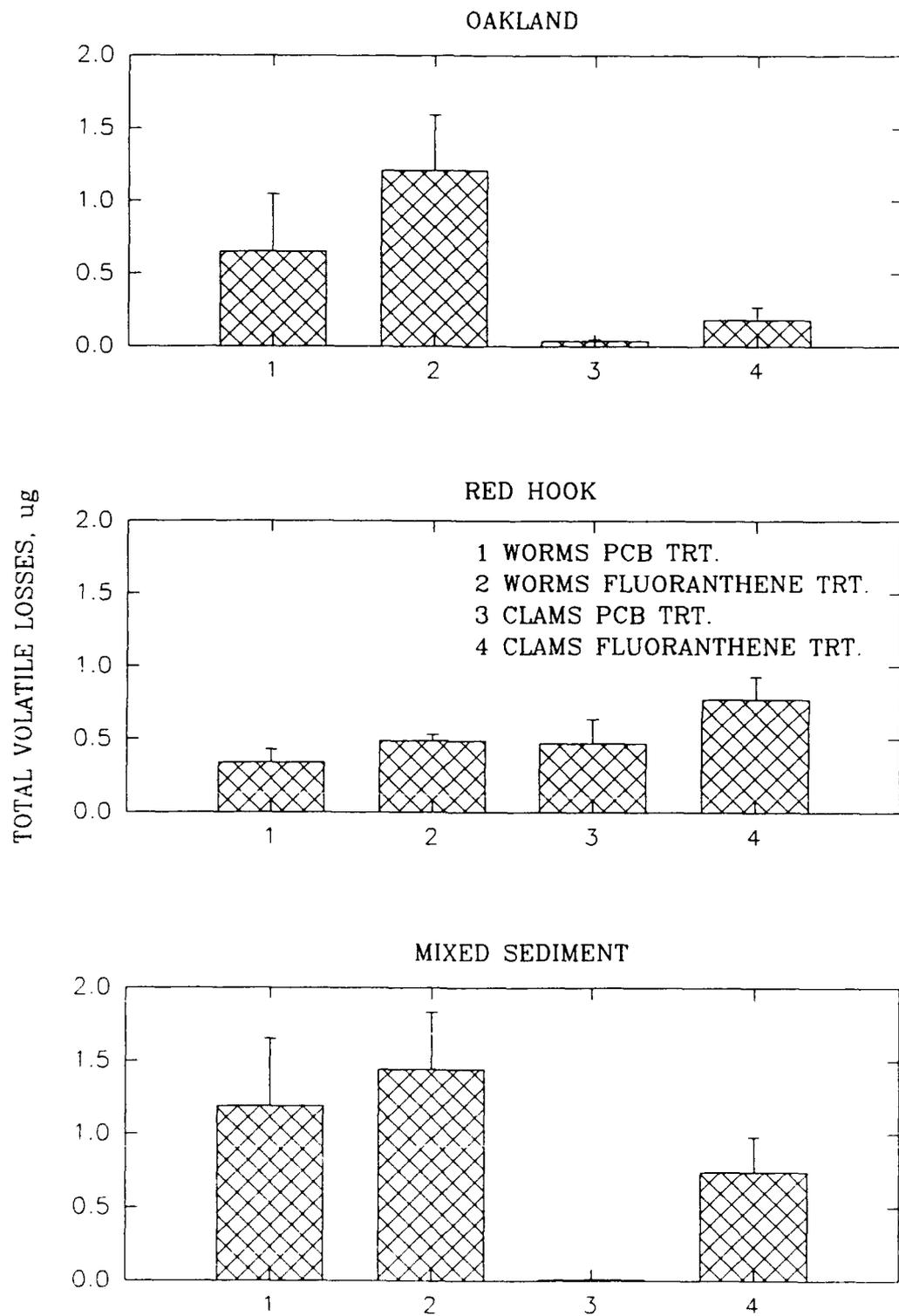
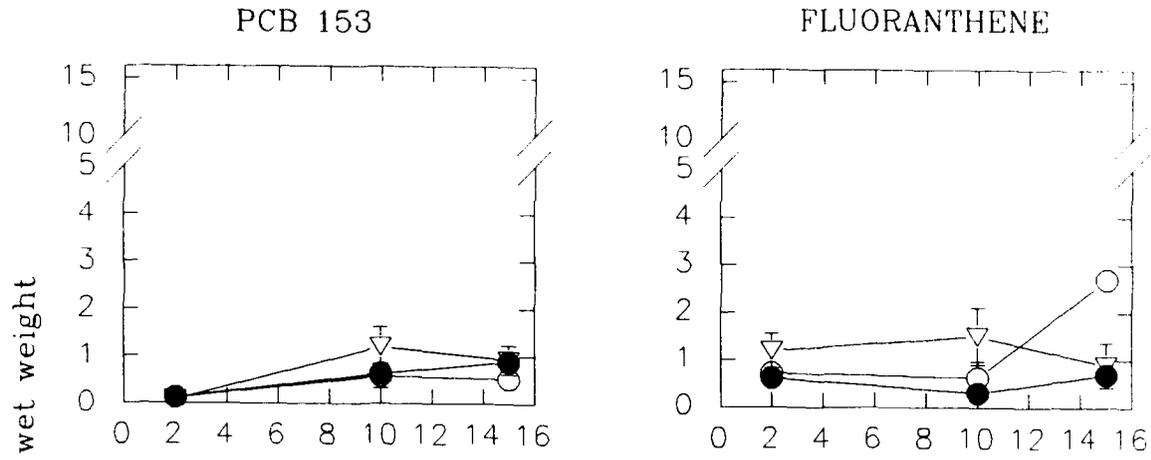
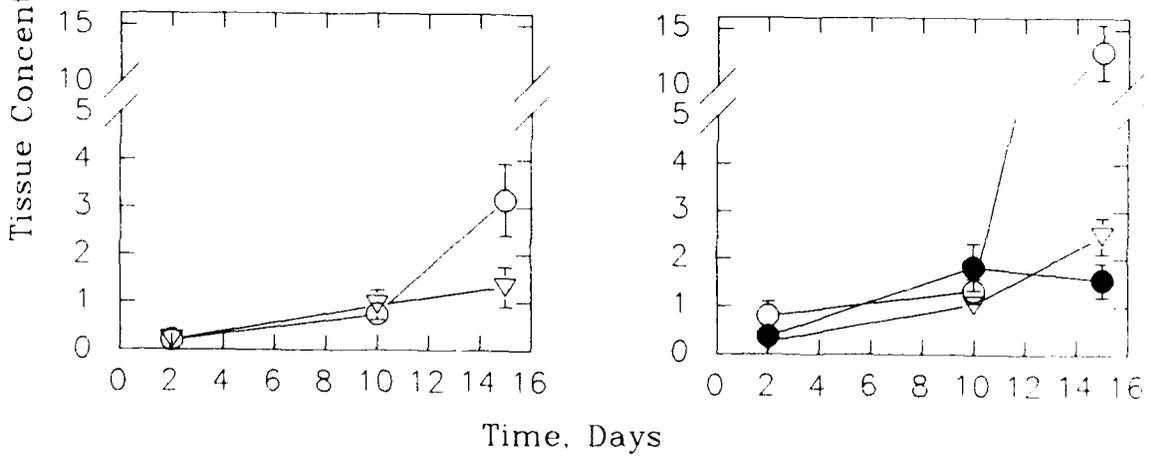


Figure 8. Volatile losses of [^{14}C] PCB 153 and fluoranthene following 15 days of incubation

WORM TREATMENT



CLAM TREATMENT

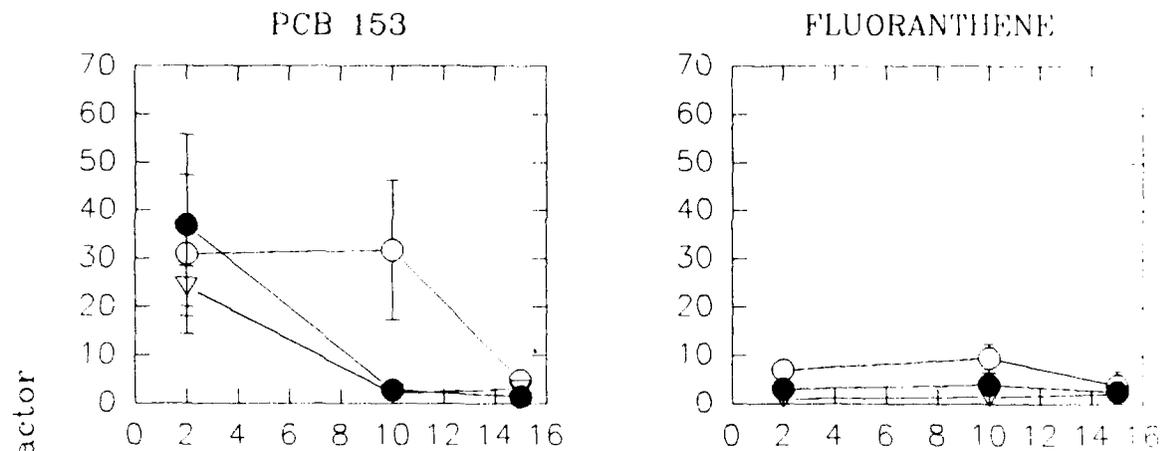


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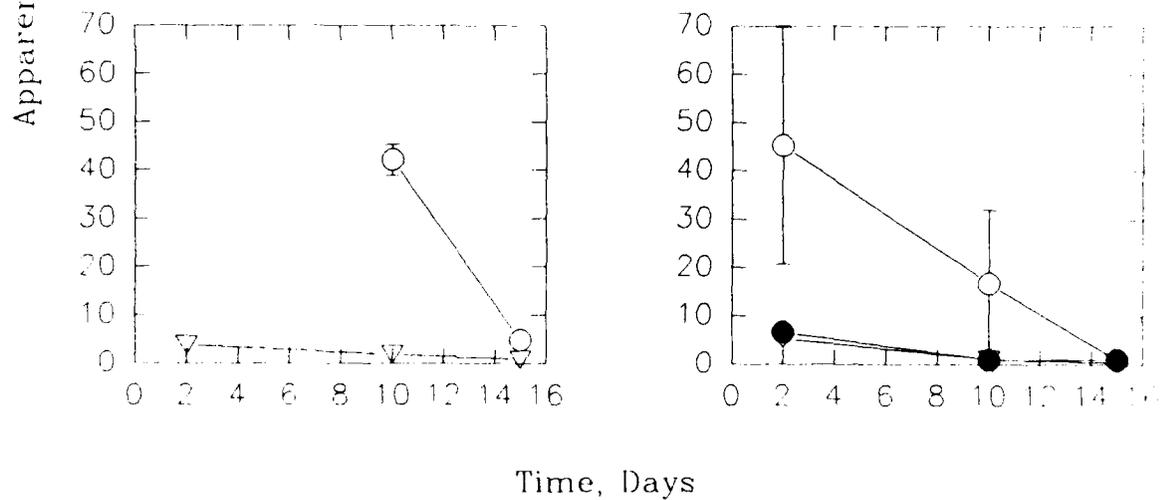
- Oakland
- Mixed Sediment
- ▽ Red Hook

Figure 9. Concentrations ($\mu\text{g/g}$ on a wet weight basis) of [^{14}C] PCB 153 and fluoranthene in clam and worm tissue

WORM TREATMENT



CLAM TREATMENT



LEGEND

- Oakland
- Mixed Sediment
- ▽ Red Hook

Figure 10. Apparent preference factors for [¹⁴C] PCB 153 and fluoranthene in clam and worm tissue