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Environmental Effects of Dredging Technical Notes

PROCEDURES FOR EXAMINING THE RELATIONSHIP BETWEEN SEDIMENT GEOCHEMISTRY AND BIOLOGICAL IMPACTS OF CONTAMINANTS

PURPOSE: This note describes the development of procedures for examining the relationship between sediment geochemistry and biological impacts of contaminants. These relationships are illustrated by implementation of procedures in a laboratory experiment to assess the influence of polychlorinated biphenyls (PCB) contaminated sediment on bioaccumulation in estuarine clams.

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, may profoundly affect US Army Corps of Engineers (USACE) dredging and disposal operations. Aquatic disposal of dredged material and selection of aquatic disposal sites may 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 sediment. The USACE is presently investigating the link between contaminant levels in sediment, sediment geochemistry, and 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.

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Introduction

The relationship between sediment-bound contaminants and biological uptake of these contaminants is complex because of the many physical, chemical, and biological factors that can affect the relationship (McElroy and Means 1988). Operational and procedural problems encountered in determining how a sediment-associated contaminant affects aquatic organisms cause additional complications. If sediment quality criteria (SQC) are to be used to regulate dredged material disposal, prediction of biological responses based on changes in sediment

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geochemistry, i.e., sediment physical and chemical properties, and sediment contaminant levels must be possible.

Radioactive tracers can be used to evaluate the effects of changing concentrations of sediment contaminants on aquatic organisms if the assumption can be made that the contaminant does not degrade during the study. Spiking a sediment with contaminants has generally been accomplished by the addition of organic solvent carriers containing the contaminant to the soil or sediment (Adams, Kimerle, and Mosher 1985; Word et al. 1987). Sediments in the aquatic environment are not usually exposed to contaminants dissolved in organic solvents, but to contaminants dissolved in water. However, most organic contaminants of interest exhibit such limited aqueous solubilities that spiking with aqueous solutions is impractical. Therefore, methods that closely simulate aqueous introduction of contaminants are desirable.

The laboratory experiments described in this note were designed to compare sediment amendment procedures; to determine the time necessary for added polychlorinated biphenyls (PCBs) to reach steady-state conditions with sediment interstitial water; to evaluate the utility of a small, simple bioassay apparatus; and to investigate the effect of different sediment PCB concentrations on PCB bioaccumulation by deposit-feeding clams.

Materials and Methods

Sediment amendment and kinetics studies

Sediment from Oakland Inner Harbor, Oakland, CA, was amended with either 0.1 or 1.0 μg PCB-52 ([^{14}C]2,2′,5,5′tetrachlorobiphenyl)/g dry weight. The PCB-52 in a methanol carrier was either added directly to the sediment or indirectly by evenly coating the walls of 25-ml centrifuge tubes and allowing the methanol to evaporate to dryness prior to addition of water-sediment mixtures. Tubes were sampled at 1, 3, 7, 14, 30, and 45 days by centrifuging to remove particulates larger than 0.01 μm from solution, then counting one ml of solution using liquid scintillation (LS). Ten millilitres of the solution was passed through a C-18 Sep-Pak cartridge (Waters Associates, Milford, MA) to separate the dissolved PCB-52 from both PCB-52 associated with suspended microparticulates (smaller than 0.01 μm) and PCB-52 associated with dissolved organic macromolecules, such as humic acids (Landrum et al. 1984). One millilitre of the solution or suspension that had passed through the Sep-Pak was counted by LS.

The experiment was repeated with higher sediment loading (20 µg PCB-52/g dry weight sediment). A water-sediment ratio of 2:1 and sampling times of 2 hr, 6 hr, 24 hr, 3 days, and 7 days were used. The PCB-52 remaining on the glass container walls was also determined.

Clam bioaccumulation study

A sediment bioassay apparatus similar to that used by McElroy and Means (1988) was selected for initial bioaccumulation studies because of its small size and simplicity. Details of the apparatus are shown in Figure 1. Each bioassay apparatus was maintained in a water bath at 17.5° C, the temperature at which the clams were collected. Foam plugs (McElroy and Means 1988) were used to trap PCB-52 volatilized or stripped from the water by aeration. Oakland Inner Harbor sediment was amended indirectly with either 1 or 10 µg PCB-52/g dry sediment. Five clams (*Macoma nasuta*) were introduced to each bioassay apparatus. Overlying water, interstitial water, foam plugs, and clams were sampled, processed, and counted by LS at each sampling period. Clam lipids and organism dry weight were also determined.

Data analysis

All statistical analyses were conducted using methods developed by the Statistical Analysis Systems Institute (Barr et al. 1976).

Results and Discussion

Sediment amendment

Results of the sediment amendment and kinetics studies showed that desorption of PCB-52 from the container walls was rapid and virtually complete and that solution steady-state PCB-52 concentrations were reached within 24 hr after shaking was initiated. Therefore, the indirect spiking method was selected in order to avoid addition of solvent or carrier to the sediment and to simulate introduction of PCB to the sediment via water.

Bioassay

PCB-52 concentrations in interstitial water between sampling times did not substantially change in either the 1 µg PCB/g or 10 µg PCB/g treatments during the bioassay (Figure 2). Losses of PCB-52 from the system through volatilization increased as the experiment progressed, accounting for 0.54 and 1.44 percent of

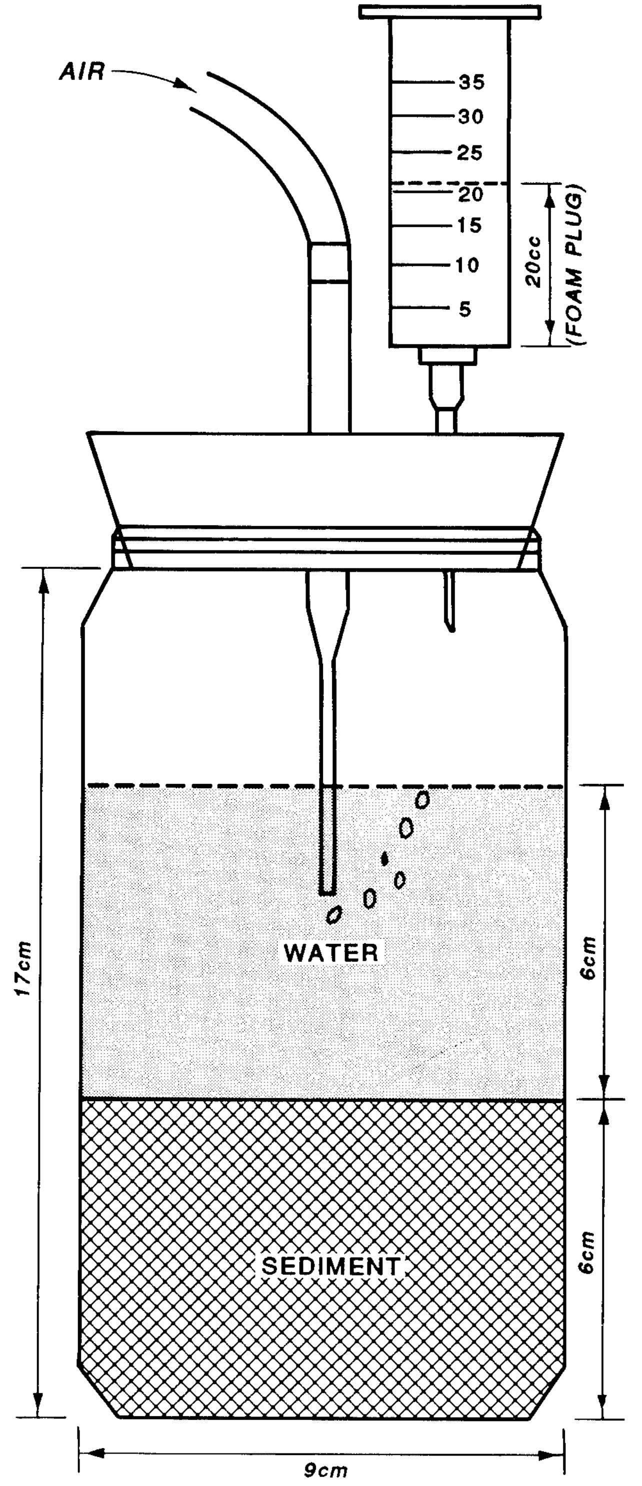
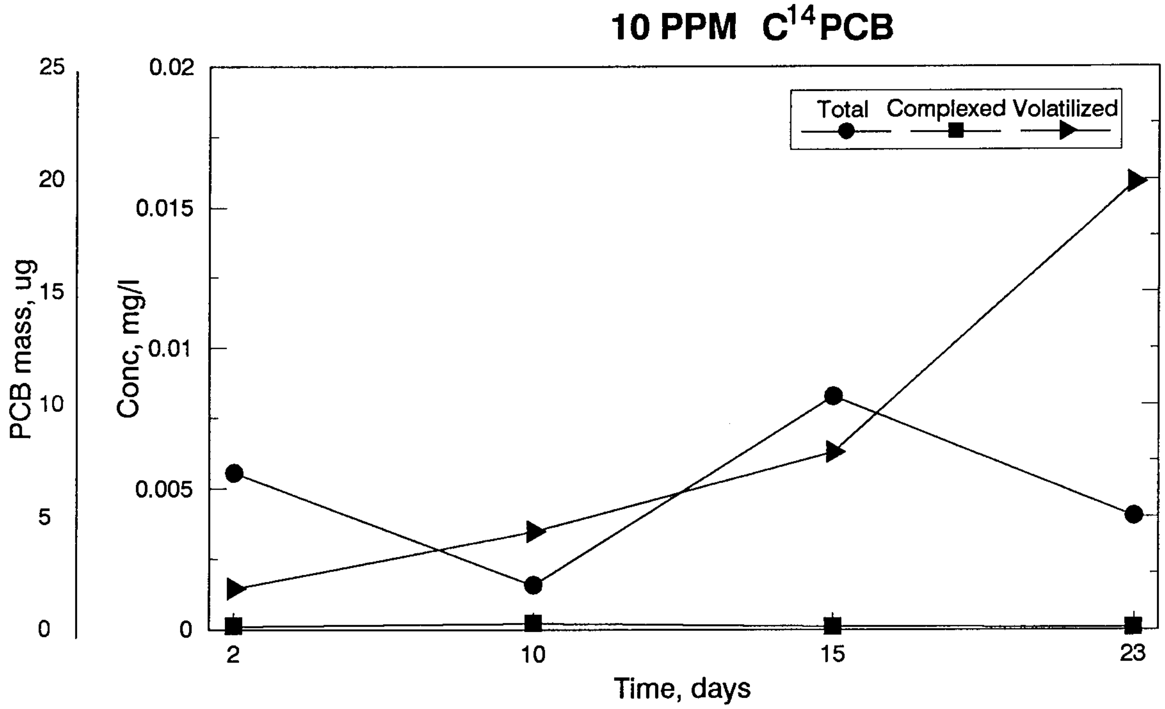


Figure 1. Testing apparatus, showing syringe body containing foam plug for collection of volatile PCB-52



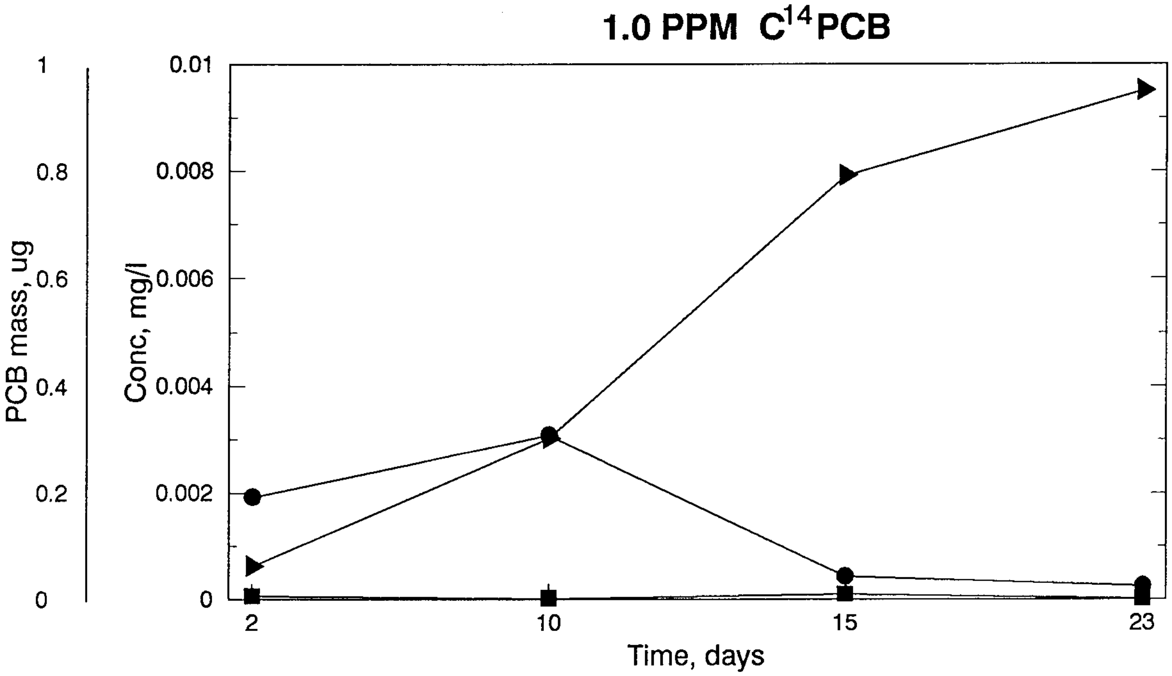


Figure 2. Concentrations (mg/ℓ) of C^{14} PCB-52 in sediment interstitial water (total and complexed) and mass (μg) of PCB-52 lost through volatilization

the total mass of PCB-52 in the 1 and 10 μg PCB/g treatments, respectively. Volatilization losses would affect bioassays with water column organisms if the organic contaminant is stripped from the water faster than it can be replenished from the sediment. This experiment used a deposit-feeding clam that is less affected by water column volatilization losses.

Tissue concentrations (μg/g wet weight) of PCB-52 increased steadily as exposure time increased in both the 1 μg PCB/g and 10 μg PCB/g treatments (Figure 3). Fewer than four replicates are shown at some sampling times because of sample loss through death of organisms, possibly because of disease.

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

$$\mathrm{APF} = (\mathrm{PCB}_s/\%\mathrm{TOC})/(\mathrm{PCB}_o/\%\mathrm{lipid})$$

where

PCB_s = PCB concentration in sediment, μg/g dry weight
%TOC = percent total organic carbon, g/g dry weight
PCB_o = PCB concentration in clams, μg/g wet weight
%lipid = percent lipid in organism extracts, g/g wet weight

This equation, 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). TBP gives the maximum theoretical concentration of a neutral organic compound that can be bioaccumulated from sediment. Percent TOC in the Oakland Harbor sediment was 1.06.

The values of the APFs calculated at 10 days and later in this study (2.3 for 10 μg/g and 3.9 for 1 μg/g PCB-52 treatments) (Figure 4) are similar to those for other empirical determinations reported in the literature (Feraro et al., in preparation; Clarke, McFarland, and Dorkin 1988) and are not greatly different from the theoretical preference factor (pf) of 1.72 calculated by McFarland and Clarke (1986). The observations in this study are consistent with and support previous results and indicate good correspondence between the laboratory results using spiked sediments and field studies involving natural sediments and assemblages of biota (Feraro et al., in preparation; Clarke, McFarland, and Dorkin 1988).

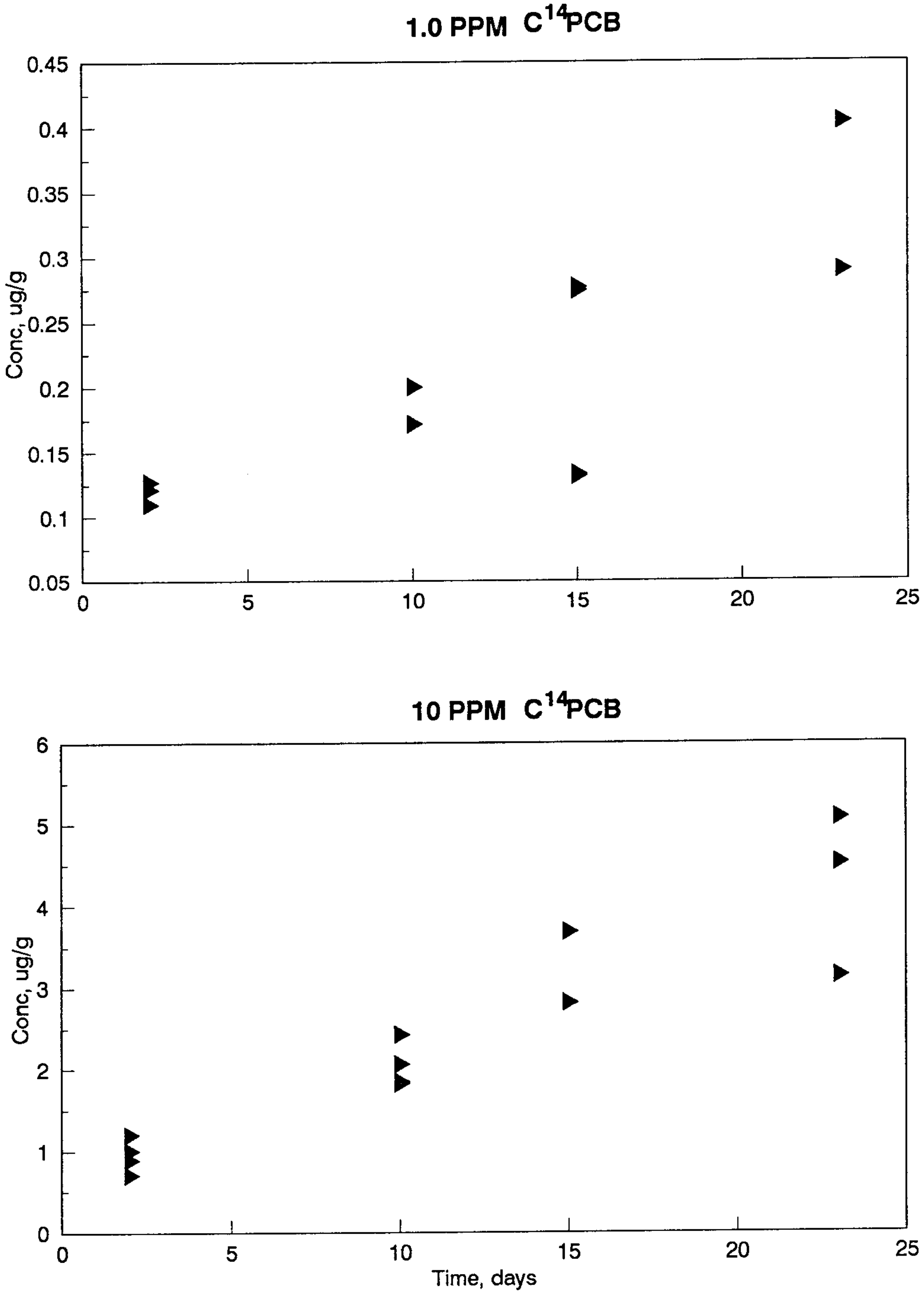


Figure 3. Replicate C^{14} PCB-52 concentrations in clam tissue on a wet weight basis

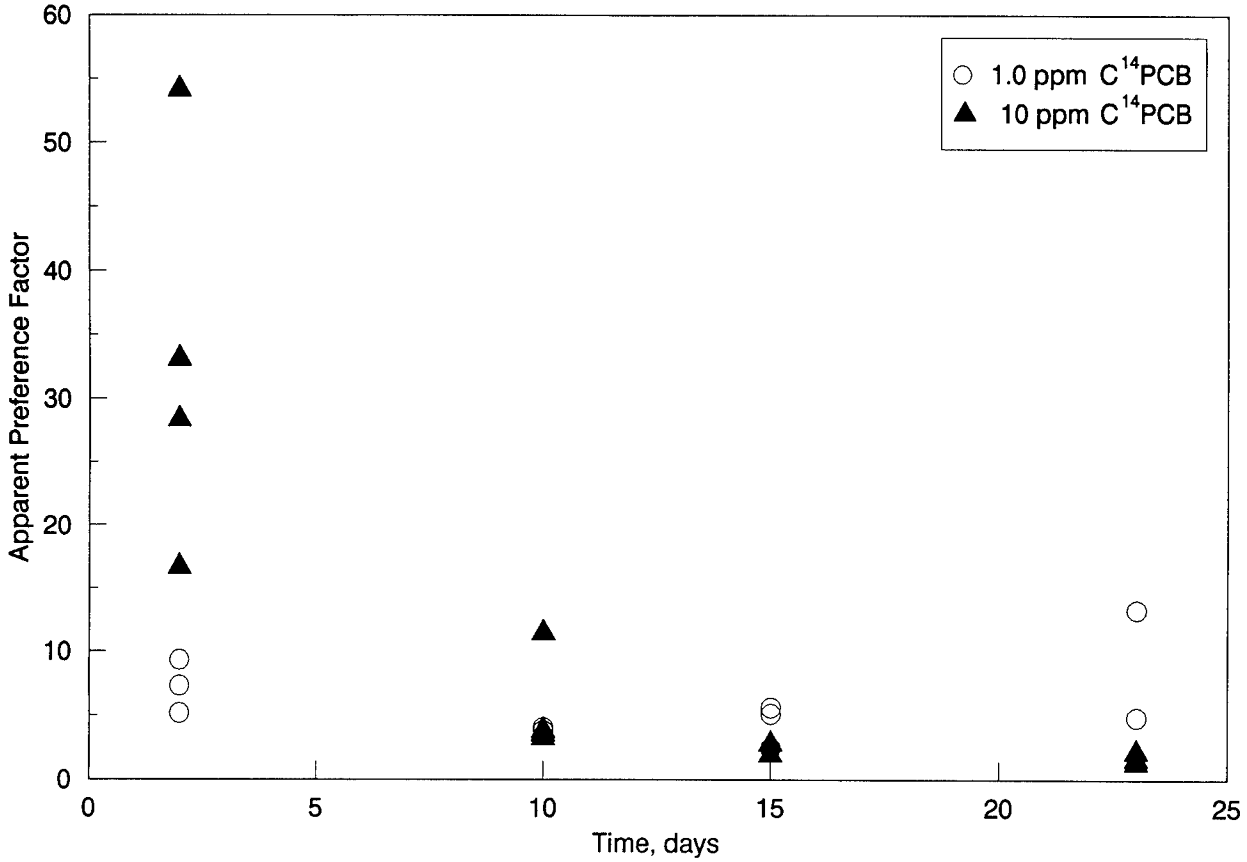


Figure 4. Replicate APFs for C^{14} PCB-52 in clam tissue

Summary of Findings

- The sediment bioassay apparatus has proved to be versatile experimental tool suitable for further studies.
- Sediment spiking with radioisotopes provides a means of examining sediment geochemistry/bioavailability relationships that favorably compares to results obtained with real-world sediment.
- PCB-52 volatilization losses from the bioassay experimental units raise questions about linking interstitial water PCB concentrations to biological effects observed in the water column.
- Equilibration of PCB-52 with lipids occurs rapidly in the deposit-feeding clam, *Macoma nasuta*; lipid normalization of contaminant data, as carried out in the equation for calculating APF, may obviate the need to carry out bioaccumulation tests for similar chemicals for longer than 10 days.

- The average (10, 15, and 23 days) APF for PCB-52 in the 10 µg PCB/g exposures to spiked sediments (1.94) compares well to the reported (Feraro et al., in preparation; Clarke, McFarland, and Dorkin 1988) APFs of PCB-52 in natural sediments (0.52 to 2.1), and to the theoretical preference factor (1.72).

References

Adams, W. J., Kimerle, R. A., and Mosher, R. G. 1985. "Aquatic Safety Assessment of Chemicals Sorbed to Sediments," *Aquatic Toxicology and Hazard Assessment: Seventh Symposium*, R. D. Cardwell, R. Purdy, and R. C. Bahner, eds., ASTM STP 845, American Society for Testing and Materials, Philadelphia, PA, pp 429-453.

Barr, A. J., Goodnight, J. H., Sall, J. P., and Helwig, J. T. 1976. "A Users Guide to SAS 76," SAS Institute, Inc., Raleigh, NC.

Clarke, J. U., McFarland, V. A., and Dorkin, J. 1988. "Evaluating Bioavailability of Neutral Organic Chemicals in Sediments—a Confined Disposal Facility Case Study," *Proceedings*, Seminar, Water Quality '88, R. G. Willey, ed., Hydrologic Engineering Center, Davis, CA, pp 251-268.

Ferraro, S. P., Lee, H. II, Smith, L. M., Ozretich, R. J., and Specht, D. T. "Accumulation Factors for Eleven Polychlorinated Biphenyl Congeners," *Bulletin of Environmental Contamination and Toxicology* (in preparation).

Lake, J. L., Rubinstein, N. I., and Pavignano, S. 1987. "Predicting Bioaccumulation: Development of a Simple Partitioning Model for Use as a Screening Tool in Regulating Ocean Disposal of Wastes," K. L. Dickson, A. W. Maki, and W. A. Brungs, eds., *Fate and Effects of Sediment-Bound Chemicals in Aquatic Systems*, Proceedings of the Sixth Pellston Workshop, Flourrisant, CO, 12-17 August 1984, SETAC Special Publications Series, Pergamon Press, New York, pp 151-166.

Landrum, P. F., Nihart, S. R., Eadie, B. J., and Gardner, W. S. 1984. "Reverse Phase Separation Method for Determining Pollutant Binding to Aldrich Humic Acid and Dissolved Organic Carbon of Natural Waters," *Environmental Science and Technology*, Vol 18, pp 187-192.

McElroy, A. E., and Means, J. C. 1988. "Factors Affecting the Bioavailability of Hexachlorobiphenyls to Benthic Organisms," *Aquatic Toxicology and Hazard Assessment: 10th Volume*, ASTM STP 971, W. J. Adams, G. A. Chapman, and W. G. Landis, eds., American Society for Testing and Materials, Philadelphia, PA, pp 149-158.

McFarland, V. A. 1984. "Activity-based Evaluation of Potential Bioaccumulation from Sediments," *Dredging '84 Proceedings*, American Society of Civil Engineers, New York, Vol 1, pp 461-467.

McFarland, V. A., and Clarke, J. U. 1986. "Testing Bioavailability of Polychlorinated Biphenyls from Sediments Using a Two-Level Approach," US Army Engineer Committee on Water Quality, 6th Seminar, *Proceedings*, R. G. Willey, Ed., Hydrologic Engineering Center, Davis, CA, pp 220-229.

Word, J. Q., Ward, J. A., Franklin, L. M., Cullinan, V. I., and Kiesser, S. L. 1987. "Evaluation of the Equilibrium Partitioning Theory for Estimating the Toxicity of the Nonpolar Organic Compound DDT to the Sediment Dwelling Amphipod *Rhepoxynius abronius*, SCD# 11," US Environmental Protection Agency, Office of Water Regulations and Standards, Criteria and Standards Division, Washington, DC.