



# Environmental Effects of Dredging Technical Notes



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## FACTORS AFFECTING LEACHATE QUALITY

**PURPOSE:** This technical note describes factors affecting leachate quality for dredged material in confined disposal facilities (CDFs). Factors evaluated include desorption kinetics, sediment concentration, and association of PCBs with soluble and colloidal organic matter.

**BACKGROUND:** Contaminated dredged material is often placed in confined disposal facilities where movement of contaminants by leachate is an important environmental concern. No routinely applied laboratory testing protocol to predict leachate quality and quantity from confined dredged material disposal facilities is currently available. In 1984, the US Army Corps of Engineers (USACE) initiated confined disposal facility leachate investigations by developing a theoretical framework for prediction of leachate quality based on mass transport theory. The theoretical framework included both batch and column testing. Batch testing provides a quick, relatively easy method for determining the distribution of contaminants between dredged material and leachate, while column testing more closely approximates contaminant losses under field conditions in a CDF. Operationally defined equilibrium distribution (partitioning) coefficients were derived from batch tests to relate aqueous phase concentration to solid phase concentration. Distribution coefficients derived from batch testing could then be used in conjunction with column operating parameters and mass transport theory to compare predicted results with those observed from column leaching experiments.

The approach recommended for application to dredged material was used in studies at Indiana Harbor, IN; Everett Harbor, WA; and New Bedford Harbor, MA. Results of these studies were evaluated in 1988 at a workshop hosted by Louisiana State University in Baton Rouge. Among the recommendations of the workshop was investigation of desorption kinetics and the impact of colloidal organic matter on interactions between solid and liquid phases. Results of those investigations for PCBs are reported in this Technical Note.

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## Introduction

At present, no laboratory testing protocol capable of routinely predicting leachate quality from confined dredged material disposal sites is available. Testing procedures to predict leachate quality are, therefore, needed in order to fully evaluate contaminant mobility for the confined disposal alternative for dredged material. If leachate quality and quantity can be predicted, the potential impacts of contaminated dredged material disposal in a confined disposal facility (CDF) can be determined, thus allowing use of the most cost-effective and environmentally sound site design.

Experimental procedures for determining leachate quality have been used to evaluate the potential impacts of confined disposal of dredged material from Indiana Harbor, IN; Everett Harbor, WA; and New Bedford Harbor, MA (Environmental Laboratory 1987, Palermo et al. 1988, Myers and Brannon 1989). Results of these laboratory studies, summarized previously in Technical Note EEDP-02-7, were reviewed at a workshop hosted by Louisiana State University in Baton Rouge, LA. Participants concluded that work conducted to date is good and generally validates the basic approaches taken, but that much research remains to be conducted before a leachate test protocol will be ready for routine use.

This Technical Note reports on results of investigations conducted on desorption kinetics of polychlorinated biphenyls (PCBs), the impact of colloidal microparticulates and soluble organic matter on interactions between solid and liquid phases, and the comparability of methodologies using sequential and single-point desorption batch tests.

## Methods

### Desorption kinetics

Desorption kinetics were determined for a saline sediment from Oakland Harbor and a freshwater sediment from the Chicago River. Sediments were treated to a level of  $1 \mu\text{g } 2,2',5,5' [^{14}\text{C}] \text{tetrachlorobiphenyl (PCB-52) / g dry weight sediment}$ . A 4:1 water-sediment ratio was used in the testing. As appropriate desorption times were reached, tubes were centrifuged and 1 ml of the solution was counted by liquid scintillation (LS). A subsample passed through a C-18 Sep-Pak cartridge (Waters Associates, Milford, MA) that traps free PCB and passes organically complexed PCB (Landrum et al. 1984) was also counted.

The procedure in the preceding paragraph was repeated with Oakland Harbor, CA, sediment at 20 ppm PCB-52 and desorption times of 1 hr, 2 hr, 6 hr, 24 hr, 7 days, and 30 days.

Water-sediment ratio

Sediments from Oakland Harbor, CA, Baltimore Harbor, MD, and the Chicago River, IL, were loaded with 20 ppm of PCB-52 at water-sediment ratios of 2:1, 4:1, 25:1, 50:1, and 100:1 and leached for 24 hr. Sediments from Oakland and Baltimore Harbors were leached with saline water (25 ppt); sediment from the Chicago River was leached with distilled-deionized water.

Sequential desorption

Sediments used in the water-sediment ratio batch testing were also subjected to sequential desorption following loading with 20 ppm PCB-52. A 4:1 water-sediment ratio and a shaking time of 24 hr were used in seven sequential cycles of the batch leach tests, details of which are described by Myers and Brannon (1988). The two sediments from saline environments (Oakland and Baltimore Harbor) were leached with distilled-deionized water in one set of tests and with saline (25 ppt) water in another set of tests.

Data analysis

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.

Results and Discussion

Desorption kinetics data for Oakland Harbor and Chicago River sediments with an initial PCB-52 level of 1 µg [<sup>14</sup>C]PCB-52/g dry weight showed that steady-state conditions were attained within 2 hr. This experiment was repeated at higher [<sup>14</sup>C]PCB-52 loading (20 µg/g dry weight) with Oakland Harbor sediment in order to examine the contribution of complexed PCB on PCB desorption kinetics.

Results of this experiment (Figure 1) paralleled those observed in the first experiment and showed that steady-state PCB-52 concentrations were rapidly attained in the leachate, essentially reaching steady-state at the first sampling time (1 hr). Organic and complexed PCB-52 constituted from 4.8 to 9.6 percent of the total PCB-52 in solution and did not change appreciably over time. These results demonstrated that the majority of the PCB-52 was present in uncomplexed form and that complexed PCB-52 did not appreciably change the concentration of

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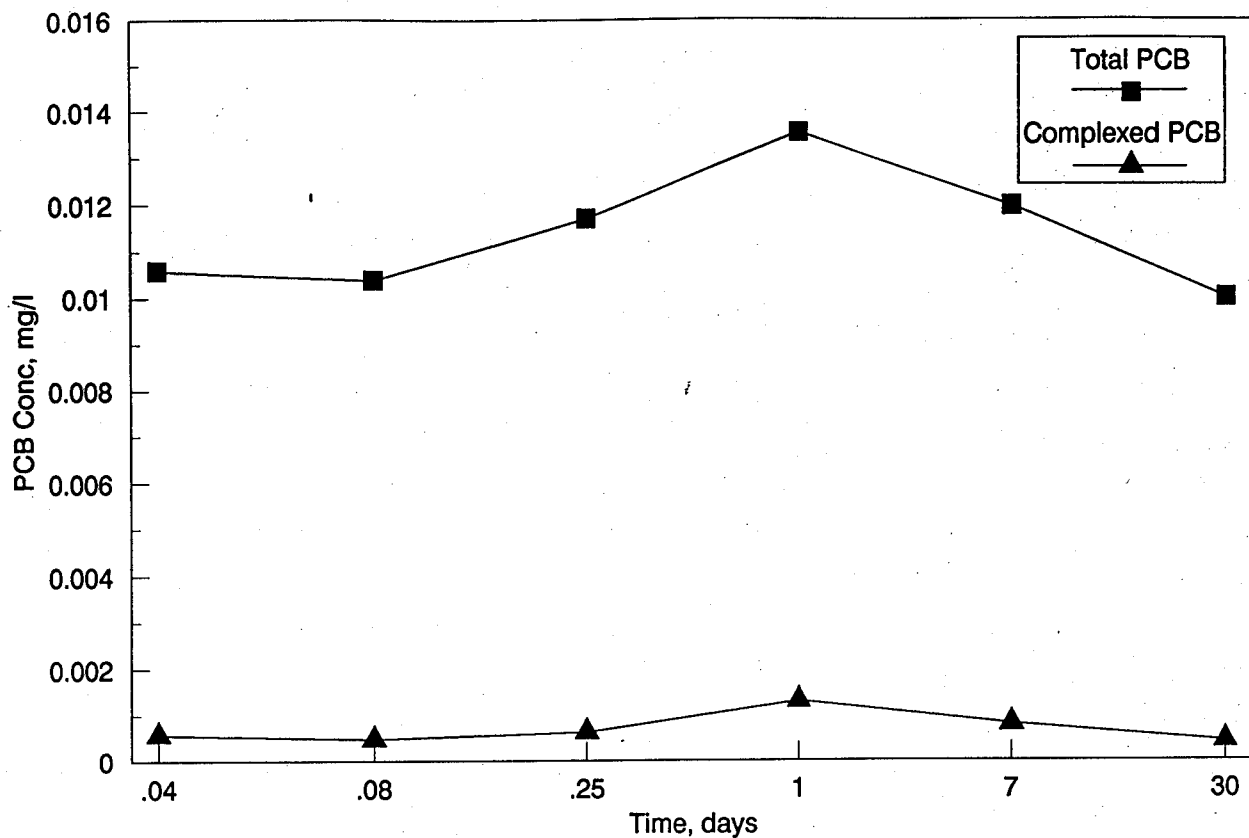


Figure 1. Desorption kinetics for PCB-52 in leachate from Oakland Harbor sediment amended with  $20 \mu\text{g C}^{14}\text{PCB-52/g}$  dry weight sediment

PCB-52 in the leachate as the time of shaking increased. The rapid attainment of steady-state conditions by PCB-52 in this study supports the findings of previous desorption kinetics studies (Environmental Laboratory 1987, Palermo et al. 1988, Myers and Brannon 1989), which showed that 24 hr was sufficient to attain steady-state conditions in leachate from dredged material for hydrophobic organic contaminants such as PCBs. Results from this study indicate that for PCB-52, desorption from sediment to water will not appreciably change over one month.

Desorption results from the sediment-water ratio batch testing showed that sediment concentration exerted a pronounced effect on distribution coefficients ( $K_d$ s) derived from a single desorption step (Figure 2). These findings agree with those of other (Voice, Rice, and Weber 1983; Gschwend and Wu 1985; DiToro et al. 1982; O'Connor and Connolly 1980) who reported a pronounced effect of solids on contaminant partitioning, although they did not examine solids concentrations at the high levels reported in this study.

Concentrations of total and complexed PCB-52 in leachate at each sediment concentration are presented in Figure 3. These results suggest that the PCB-52

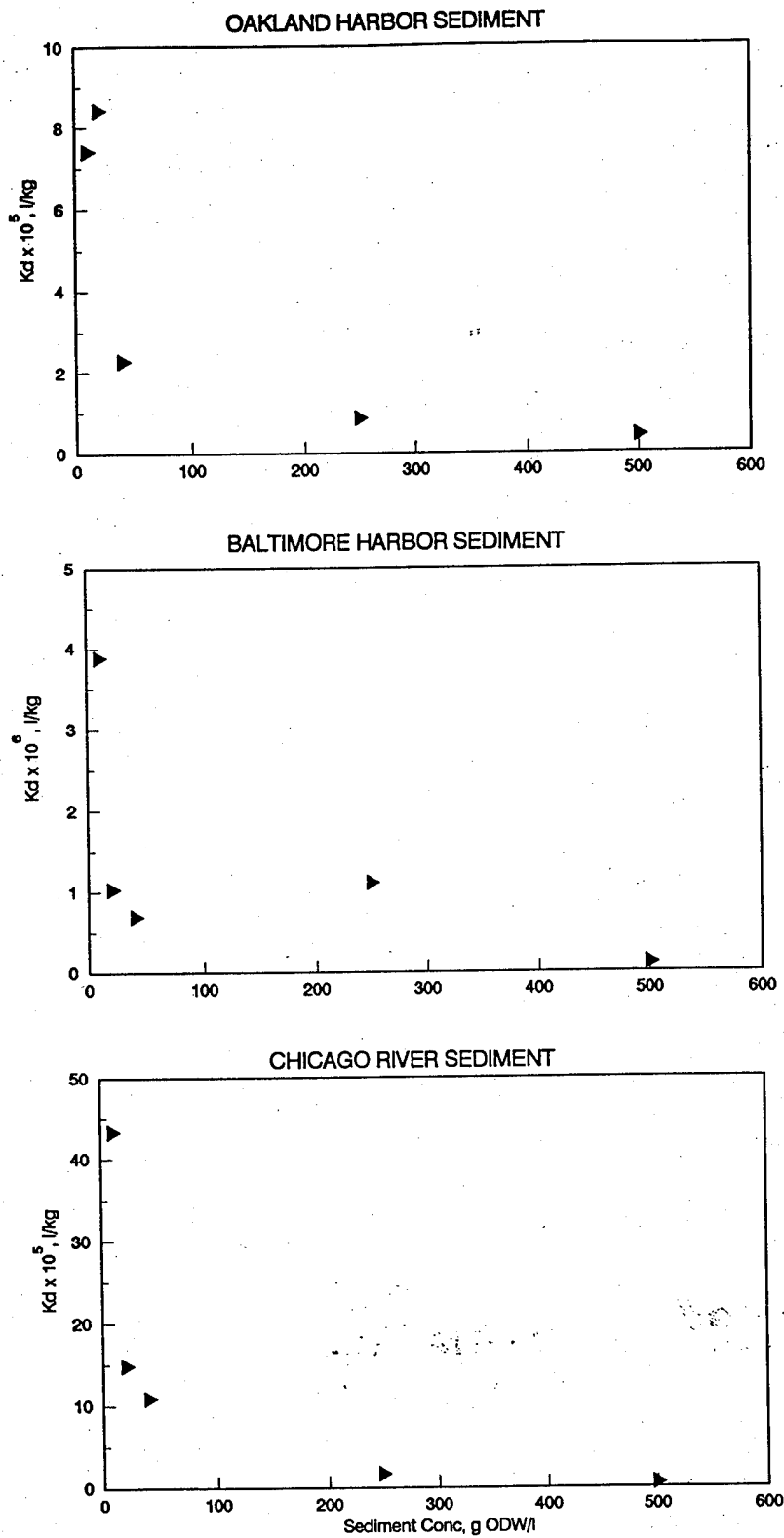


Figure 2. Single-step desorption distribution coefficients at varying sediment concentrations from sediments amended with 20  $\mu\text{g}$   $\text{C}^{14}\text{PCB-52/g}$  dry weight sediment

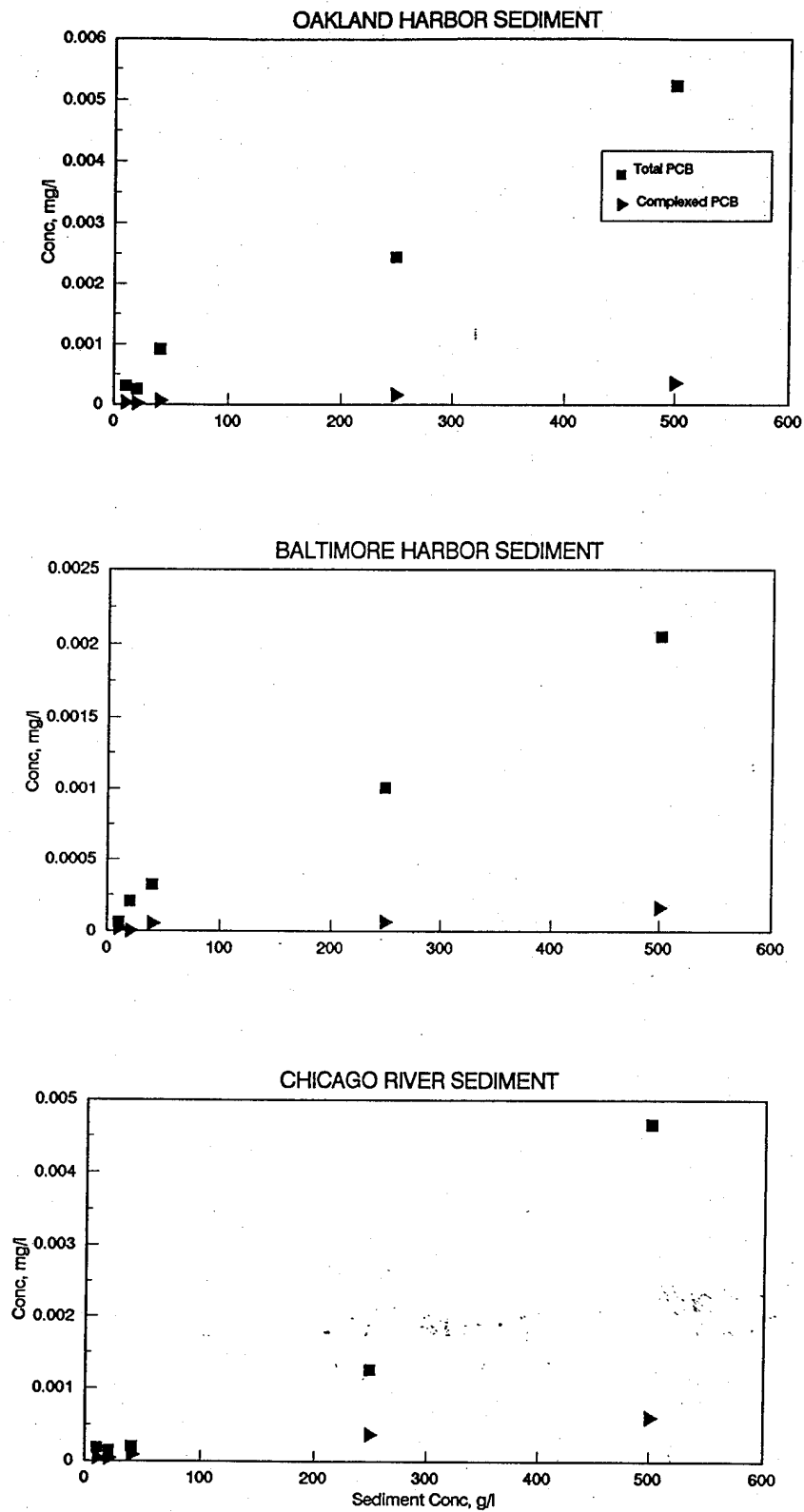


Figure 3. Total and complexed  $C^{14}$ PCB-52 leachate concentrations as a function of sediment concentration (sediments amended with  $20 \mu\text{g } C^{14}\text{PCB-52/g}$  dry weight sediment)

in solution, which includes particulate matter smaller than  $0.01 \mu\text{m}$ , is free and uncomplexed at higher sediment concentrations, e.g., 250 and 500 g/l. Although the amount of complexed PCB-52 does increase slightly with increasing sediment concentration, free PCB-52 constitutes most of the total leachate PCB-52. The implication of these results for leachate testing is that desorption isotherms obtained by conducting batch tests with varying sediment-water ratios will not yield a useable  $K_d$ . The isotherms resulting from such data exhibit a negative slope (the slope of the line is  $K_d$ ). Negative  $K_d$ s cannot be used in mass transport equations.

Sequential desorption testing indicated that pronounced differences existed between the behavior of PCB-52 in leachate from freshwater and saline sediments. In saline sediments leached with fresh water, the fraction of complexed PCB-52 in leachate increased as leaching proceeded, peaked at the third leach cycle, and then decreased (Figure 4). This is possibly due to release of dissolved organic carbon from sediment as salinity decreased in the leachate (Myers and Brannon 1988) during sequential leaching of saline sediment with freshwater. This mechanism is supported by results for freshwater Chicago River sediment leached with freshwater. For Chicago River sediment, the fraction of complexed PCB-52 decreased as leaching proceeded, a phenomenon that was also observed when sediments from saline areas were leached with saline water. The fraction of complexed PCB-52 peaked at less than 0.35 (35 percent of total leachate PCB-52) in saline sediments leached with freshwater.

Sequential batch testing results indicate that complexed and free PCB-52 are both important components of leachate for saline sediments leached with freshwater. Instead of decreasing as leaching proceeds as predicted by theory, leachate PCB-52 concentrations increase and then decrease in saline sediments leached with freshwater. Peak concentrations of leachate PCB-52 in saline sediments leached with freshwater were almost double the peak concentrations reached when saline sediments were leached with saline water. In saline sediments leached with saline water almost all PCB-52 released was free (>95 percent) following the initial leach cycle.

Results of sediment ratio and sequential batch testing from PCB-52 indicate that sediment concentration and release of both complexed and free PCB-52 during leaching are important factors affecting leach test results. The use of saline water or freshwater also exerts a pronounced effect on sequential batch leaching results, producing a peak in the middle of the leach cycle instead of steadily

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# SALINE

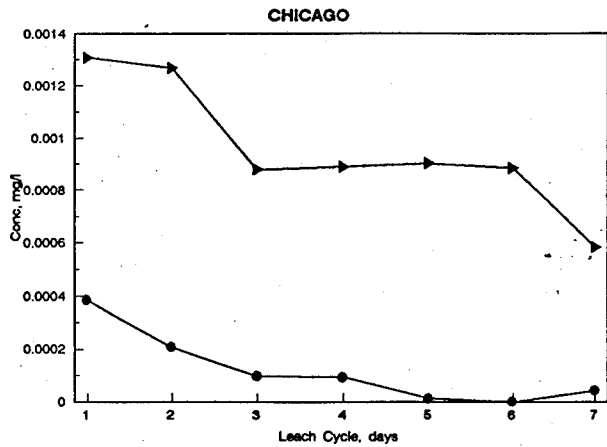
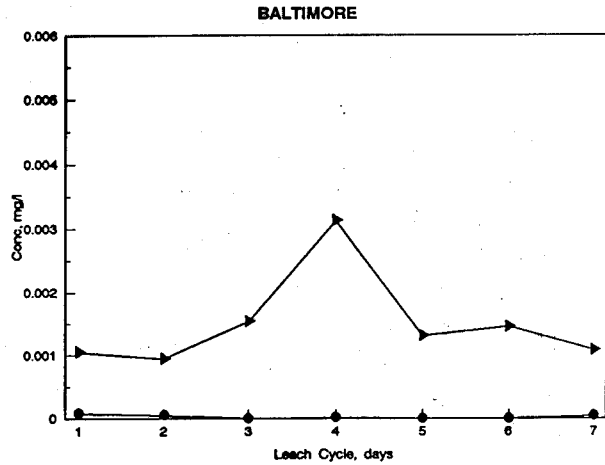
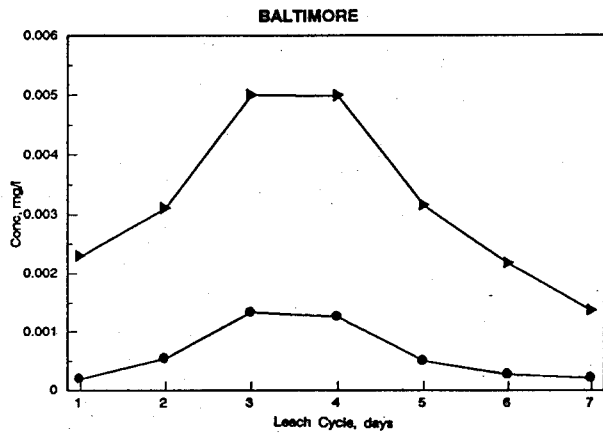
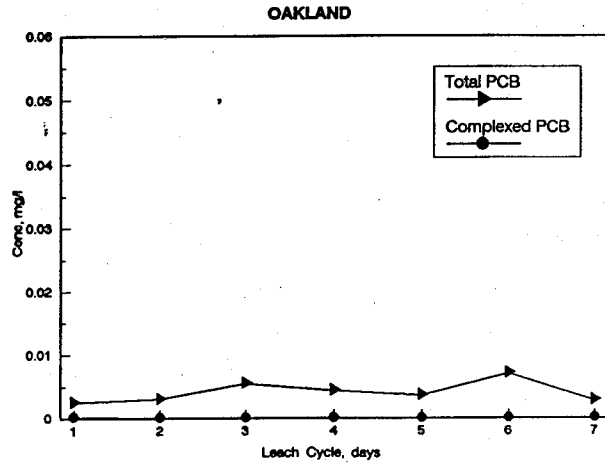
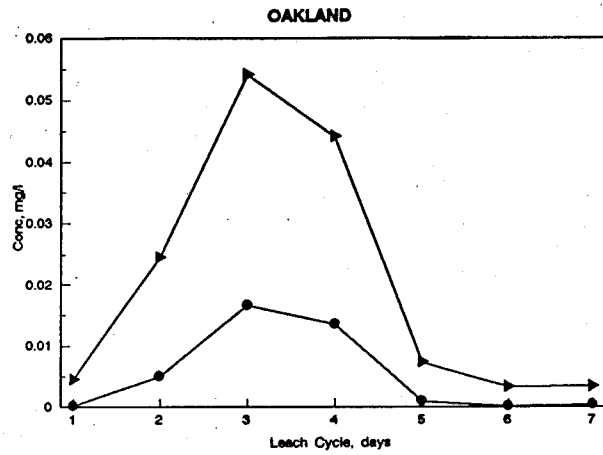


Figure 4. Concentration of total and complexed  $C^{14}$ PCB-52 in sequential batch leachate from sediments amended with  $20 \mu\text{g } C^{14}\text{PCB-52/g}$  dry weight sediment and leached with fresh and saline water

decreasing leachate concentrations. This behavior by free and complexed PCB in sequential leachate from saline sediments is complex. Therefore, development of distribution coefficients for describing leaching of hydrophobic organic compounds from saline sediment with freshwater is difficult, but possible.

Desorption batch testing results with varying sediment concentrations indicate that for PCB-52, sediment concentration should be kept as high as possible to closely simulate the sediment concentrations found in deposited sediments. Batch tests that involve a series of tests using varying sediment concentrations will not provide distribution coefficients for predicting the desorption of PCB-52 at the high sediment concentrations found in confined disposal facilities.

The studies reported here provide a basis for evaluating the application of batch test procedures for determining PCB losses from dredged material in CDFs. The expanded understanding of mechanisms by which PCBs partition between water and sediment at high solids concentrations contributes significantly to development of appropriate test procedures for hydrophobic organic compounds.

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