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NEW BEDFORD HARBOR SUPERFUND PROJECT, ACUSHNET RIVER ESTUARY ENGINEERING FEASIBILITY STUDY OF DREDGING AND DREDGED MATERIAL DISPOSAL ALTERNATIVES

Report 5

EVALUATION OF LEACHATE QUALITY

by

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NEW BEDFORD HARBOR SUPERFUND PROJECT, ACUSHNET RIVER ESTUARY ENGINEERING FEASIBILITY STUDY OF DREDGING AND DREDGED MATERIAL DISPOSAL ALTERNATIVES

No. in Series	Report Title
1	Study Overview
2	Sediment and Contaminant Hydraulic Transport Investigations
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11	Evaluation of Conceptual Dredging and Disposal Alternatives
12	Executive Summary

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State-of-the-art batch and column leach tests were conducted on anaerobic and aerobic New Bedford Harbor sediment. Batch testing included kinetic tests to determine the time required for dissolved contaminant concentrations to stabilize in batch tests, liquid-to-solids ratio tests to determine the appropriate liquid-to-solids ratio to use in batch tests, and sequential batch leach tests to obtain desorption isotherms and determine distribution coefficients. Column leach tests were conducted in divided-flow permeameters designed to minimize wall effects. Desorption isotherms from sequential batch leach tests and elution curves from permeameter leach tests were used in an integrated approach to obtain information on contaminant release characteristics of New Bedford Harbor sediment.

Desorption of polychlorinated biphenyls (PCBs) and metals from New Bedford Harbor sediment did not follow classical partitioning theory. Therefore, the assumption of

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equilibrium-controlled, linear desorption with constant partitioning is not generally applicable to modeling the leaching of contaminants from New Bedford Harbor sediment.

Anaerobic distilled water PCB desorption isotherms showed nonconstant partitioning (negative slopes) to a critical value referred to in this report as the turning point. After the turning point, PCB desorption tended to follow classical, linear partitioning. Sequential leaching with saline water showed that the nonconstant partitioning portion of the PCB desorption isotherms was associated with changing conductivity, and hence salinity. Conductivity-distribution coefficient correlations provided reliable estimates of PCB concentrations as saline pore water was displaced by infiltration of distilled water.

The shape of the observed PCB elution curves from anaerobic permeameter leach tests agreed with the shape of elution curves predicted from batch desorption isotherms. PCB concentrations in the permeameter tests were significantly lower than PCB concentrations in batch leach tests. Possible reasons for these differences were contaminant adsorption to container walls and particle disaggregation effects related to differences in hydraulic regimes in batch and column testing.

Anaerobic metal desorption isotherms also showed nonconstant partitioning, and some metals showed a turning point followed by classical, linear partitioning. Sequential leaching with saline water showed that nonconstant partitioning of metals was apparently independent of conductivity.

The shape of observed metal elution curves from anaerobic permeameter leach tests agreed with the shape of elution curves expected on the basis of batch desorption isotherms for some metals, but for other metals there was no agreement. For some metals, concentrations in permeameter leachate were in good agreement with concentrations in batch leachate, and for other metals, concentrations in permeameter leachate were lower than concentrations in batch leachate.

Sequential batch leach tests with aerobic sediment indicated that large quantities of nickel and zinc will be present in leachate from aerobic sediment. Because aerobic permeameter leach tests did not entirely satisfy aerobic leach testing objectives, aerobic batch and permeameter data were not compared.

PREFACE

This study was conducted as a part of the Acushnet River Estuary Engineering Feasibility Study (EFS) of Dredging and Dredged Material Disposal Alternatives. The US Army Corps of Engineers (USACE) performed the EFS for the US Environmental Protection Agency (USEPA), Region 1, as a component of the comprehensive USEPA Feasibility Study for the New Bedford Harbor Superfund Site, New Bedford, MA. This report, Report 5 of a series, was prepared by the US Army Engineer Waterways Experiment Station (WES) in cooperation with the New England Division (NED), USACE. Coordination and management support was provided by the Omaha District, USACE, and dredging program coordination was provided by the Dredging Division, USACE. This report covers work conducted during the period August 1987 through June 1988.

Project manager for the USEPA was Mr. Frank Ciavattieri. The NED project managers were Messrs. Mark J. Otis and Alan Randall. Omaha District project managers were Messrs. Kevin Mayberry and William Bonneau. Project managers for the WES were Messrs. Norman R. Francingues, Jr., and Daniel E. Averett.

This study was conducted and the report prepared by Mr. Tommy E. Myers of the Water Supply and Waste Treatment Group (WSWTG), Environmental Engineering Division (EED), and Dr. James M. Brannon of the Aquatic Processes and Effects Group (APEG), Ecosystem Research and Simulation Division (ERSD), of the Environmental Laboratory (EL), WES. The Analytical Laboratory Group of the EED, under the supervision of Ms. Ann B. Strong, assisted with chemical analysis of samples. Ms. Cindy Price, APEG, and Mr. Mark Zappi, WSWTG, assisted with laboratory experimentation and sample analysis. Dr. Douglas Gunnison, APEG, conducted the microbial and polychlorinated biphenyl microdroplet investigations. The report was edited by Ms. Jessica S. Ruff of the WES Information Technology Laboratory.

The study was conducted under the general supervision of Mr. Norman R. Francingues, Jr., Chief, WSWTG; Dr. Thomas L. Hart, Chief, APEG; Dr. Raymond L. Montgomery, Chief, EED; Mr. Donald L. Robey, Chief, ERSD; and Dr. John Harrison, Chief, EL.

COL Dwayne G. Lee, EN, was Commander and Director of WES; Dr. Robert W. Whalin was Technical Director.

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NEW BEDFORD HARBOR SUPERFUND PROJECT, ACUSHNET RIVER ESTUARY
ENGINEERING FEASIBILITY STUDY OF DREDGING AND DREDGED MATERIAL DISPOSAL ALTERNATIVES

EVALUATION OF LEACHATE QUALITY

PART I: INTRODUCTION

New Bedford Harbor Superfund Site

1. In August 1984, the US Environmental Protection Agency (USEPA) reported on the Feasibility Study of Remedial Action Alternatives for the Upper Acushnet River Estuary above the Coggeshall Street Bridge, New Bedford, MA (NUS Corporation 1984). The USEPA received extensive comments on the proposed remedial action alternatives from other Federal, state, and local officials, potentially responsible parties, and individuals. Responding to these comments, the USEPA chose to conduct additional studies to better define available cleanup methods. Because dredging was associated with all of the removal alternatives, the USEPA requested the US Army Corps of Engineers to conduct an Engineering Feasibility Study (EFS) of dredging and disposal alternatives. A major emphasis of the EFS was placed on evaluating the potential for contaminant releases from both dredging and disposal operations.

2. The technical phase of the EFS was completed in March 1988. However, as part of Task 8 of the EFS, the results of the study were compiled in a series of 12 reports, listed below.

a. Report 1, "Study Overview."

b. Report 2, "Sediment and Contaminant Hydraulic Transport Investigations."

c. Report 3, "Characterization and Elutriate Testing of Acushnet River Estuary Sediment."

d. Report 4, "Surface Runoff Quality Evaluation for Confined Disposal."

e. Report 5, "Evaluation of Leachate Quality."

f. Report 6, "Laboratory Testing for Subaqueous Capping."

g. Report 7, "Settling and Chemical Clarification Tests."

h. Report 8, "Compatibility of Liner Systems with New Bedford Harbor Dredged Material Contaminants."

i. Report 9, "Laboratory-Scale Application of Solidification/ Stabilization Technology."

j. Report 10, "Evaluation of Dredging and Dredging Control Technologies."

k. Report 11, "Evaluation of Conceptual Dredging and Disposal Alternatives."

l. Report 12, "Executive Summary."

3. This report is Report 5 of the series. The results of this study were obtained from conducting EFS Task 6, element 4.

Background

4. When contaminated dredged material is placed in an upland or nearshore confined disposal facility (CDF), the potential exists to generate leachates that may adversely impact surface and ground waters.

5. Relatively few studies have addressed the impacts of dredged material disposal in a CDF on ground water and underlying soils. In general, little is known about the formation of leachate in CDFs. The interphase transfer of contaminants from the dredged material solids to pore water depends on the geochemical characteristics of the dredged material and the leaching environment. Many chemical processes potentially control leachate quality in a CDF, including sorption, ion-exchange, hydrolysis, dissolution/ precipitation, oxidation-reduction, and complexation. Generation of leachate is also potentially affected by the fluid mechanics of flow in porous media in the CDF and the hydrogeology of the site. Currently, there is no routinely applied laboratory testing and field-verified protocol for predicting leachate quality in CDFs. Experimental testing procedures were used to provide information on leachate quality needed for evaluation of the confined disposal alternative for New Bedford Harbor dredged material. If leachate quality and quantity can be accurately assessed, the potential impacts of using a CDF for disposal of contaminated dredged material can be determined, thus allowing the most cost-effective site design to be used.

Study Objective and Scope of Report

6. The objective of the leachate testing portion of the New Bedford EFS was to evaluate and apply appropriate testing procedures for estimating leachate contaminant levels from New Bedford sediment proposed for the CDF alternative. These leachate testing protocols are still developmental; thus, descriptions, applications, and limitations of the procedures used are required. This report provides detailed descriptions of the leaching tests, the theory behind the tests, results from the EFS leaching tests, and interpretations of the results. An investigation of factors affecting the desorption properties of the New Bedford sediment is described in Appendix A. The methods used to calculate void volume and to measure dispersion are discussed in Appendixes B and C, respectively.

PART II: METHODS AND MATERIALS

Sediment Preparation

7. The estuary composite sediment sample, representing the midrange polychlorinated biphenyl (PCB) concentration in the Upper Estuary portion of the Acushnet River, was tested in this study. Collection and preparation of this sample is described in Report 3 of the EFS report series. The estuary composite sediment sample was refrigerated at 4° C in sealed containers until it was needed for the anaerobic leaching tests. Sediment used for aerobic testing was placed into 38-ℓ glass aquariums to a depth of approximately 8 cm. The sediment was allowed to oxidize at ambient temperatures, and each week the sediment was thoroughly mixed to expose fresh sediment surfaces to the air. When necessary, distilled-deionized (DDI) water was added to the sediment to maintain proper sediment moisture conditions. At the end of 3 months of mixing/aeration, the sediment was removed from the aquaria, placed into a 208-ℓ barrel, and thoroughly mixed for 2 hr. The sediment was then refrigerated at 4° C until it was needed for the aerobic leachate testing. Chain of custody was maintained on the anaerobic and aerobic sediment throughout leachate testing.

Batch Testing

Kinetic tests

8. Batch testing was performed to determine shaking time necessary to achieve equilibrium or steady-state conditions for metal and organic contaminant leachate concentrations. The general experimental sequence is presented in Table 1.

9. For testing anaerobic metal releases, triplicate 250-ml polycarbonate centrifuge tubes fitted with a leakproof, airtight top were each loaded with 200 g of sediment and deoxygenated DDI water at a 4:1 water-to-sediment dry weight ratio. All operations were conducted in a glove box under a nitrogen atmosphere. Twelve centrifuge tubes were loaded to allow triplicate sampling at 24, 48, 96, and 168 hr. Samples were placed horizontally on a mechanical shaker and shaken at 160 cpm for the allotted time. Three tubes were then removed from the shaker and centrifuged at 9,000 rpm (13,000 × g)

for 30 minutes. The supernatant was filtered under a nitrogen atmosphere through 0.45-μm pore size membrane filters. The filtrate was then acidified to pH 1 with concentrated Ultrex nitric acid and stored in plastic bottles until analyzed.

10. Kinetic testing for organic contaminants was conducted in specially fabricated 450-ml stainless steel centrifuge tubes. Twenty-four centrifuge tubes (sufficient for three replicates), double-rinsed with acetone, were loaded with sufficient sediment and deoxygenated DDI water to obtain a 4:1 water-to-sediment dry weight ratio. The total mass (approximately 350 g) of sediment and water added was regulated to allow the tube to be safely centrifuged at 6,200 rpm (6,500 × g). All operations were conducted under a nitrogen atmosphere. The tubes were then placed in a rotary tumbler and turned end over end at 40 rpm for periods of 24, 48, and 168 hr. At the appointed time, the samples were removed from the tumbler and centrifuged for 30 min. Resulting supernatants were then filtered through a Whatman GF/D prefilter and a Gelman AE filter with a nominal pore size of 1.0 μm. Whatman GF/D prefilters and Gelman AE filters are binderless, glass-fiber filters that generally do not contain detectable quantities of organic contaminants. As a precaution against contamination, the filters used in this study were combusted at 400° C prior to use. Filtration was conducted under a nitrogen atmosphere followed by acidification with 1 ml of concentrated hydrochloric acid to prevent iron precipitation and scavenging of organic contaminants from solution by iron precipitates. Samples were then stored in the dark in acetone-rinsed 2-ℓ glass bottles until analyzed.

Sediment-water ratio testing

11. Following determination of the shaking time necessary to obtain steady-state concentrations in the leachate, testing in triplicate to determine the proper sediment-to-water ratio was conducted. The general test sequence is presented in Table 2.

12. For metals, anaerobic New Bedford sediment was placed in acid-washed 250-ml polycarbonate centrifuge tubes in water-to-sediment ratios of 4:1, 10:1, 20:1, 30:1, 40:1, 50:1, and 100:1 using double-DDI water. The tubes were then sealed, mechanically shaken horizontally for 24 hr, and then centrifuged. The leachate was filtered through 0.45-μm membrane filters; the resulting supernatant was acidified and stored in plastic bottles prior to analysis as previously described. The anaerobic integrity of the samples was

maintained throughout the preparation, shaking, and filtration of the samples. The testing sequence for aerobic sediment was the same as for anaerobic sediment, except that anaerobic integrity was not maintained and water-to-sediment ratios of 4:1, 10:1, 30:1, 50:1, and 100:1 were tested.

13. Similar procedures were followed for organic contaminants in anaerobic sediment, except that 24-hr shaking was conducted in 450-ml stainless steel centrifuge tubes. Filtration and other sample preparation procedures are as described for organic contaminants in the kinetic testing section. For aerobic sediment, modifications to the test procedure were as described for aerobic metals testing.

Sequential batch testing

14. A 4:1 water-to-sediment ratio and a shaking time of 24 hr were used in the sequential batch leach tests for New Bedford sediment. General test procedures for assessing steady-state leachate and sediment metal and organic contaminant concentrations are detailed in Table 3. New Bedford anaerobic sediment sequential batch tests for metals were conducted in quadruplicate 250-ml polycarbonate centrifuge bottles with leakproof caps. Each centrifuge tube was loaded under a nitrogen atmosphere with anaerobic New Bedford sediment and deoxygenated DDI water to a 4:1 water-to-sediment ratio; the tubes were mechanically shaken for 24 hr. The bottles were then centrifuged at 13,000 × g for 30 min. The majority of the leachate from each 250-ml centrifuge bottle was filtered through a 0.45-μm membrane filter. The unfiltered leachate was analyzed for pH using a combination electrode and a millivolt meter and for conductivity using a Yellow Springs Instrument Company conductivity meter and cell. Fresh deoxygenated DDI water was added to each 250-ml centrifuge tube to replace the leachate removed for analysis. The procedure described above for sequentially contacting anaerobic New Bedford sediment with clean water was repeated seven times. The same general procedure was repeated six times for aerobic sediment sequential batch leach tests for metals.

15. Testing of New Bedford sediment for organic contaminants was conducted in a manner similar to that described for metals except that 450-ml stainless steel centrifuge tubes were used. Filtration procedures used for organic contaminants were as previously described for the kinetic and sediment-to-water ratio testing (Tables 1 and 2). A subsample of filtered leachate was set aside from both the anaerobic and aerobic tests for analysis

of total organic carbon. After each cycle, the sediment was remixed with DDI water, shaken for 24 hr, and then processed as previously described. Three replicates were taken through four leach cycles in anaerobic sediment testing. For aerobic sediment, five replicates were taken through a single leach cycle.

Interstitial water extraction

16. Interstitial water samples for metal and organic contaminant analysis were obtained by centrifugation of the New Bedford sediment. To obtain samples for metals from anaerobic New Bedford sediment, triplicate 250-ml polycarbonate centrifuge tubes fitted with a leakproof, airtight top were loaded with sediment in a glove box under a nitrogen atmosphere. The tubes were then centrifuged at 13,000 × g for 30 min, and the supernatant was filtered under a nitrogen atmosphere through a 0.45-μm pore size membrane filter. The filtrate was then acidified to pH 1 with concentrated Ultrex grade nitric acid and stored in plastic bottles until analyzed. Procedures for obtaining interstitial water for metals analysis from aerobic New Bedford sediment were similar to those described for anaerobic sediment, except that all steps in the aerobic operation were conducted without the use of nitrogen.

17. Interstitial water for analysis of organic contaminants was obtained by centrifugation of anaerobic New Bedford sediment in 450-ml stainless steel centrifuge tubes. Six tubes were loaded with sediment, centrifuged for 30 min at 6,500 × g, then filtered through a Whatman GF/D glass-fiber prefilter and a Gelman AE glass-fiber filter with a nominal pore size of 1.0 μm. All steps in the operation were conducted under a nitrogen atmosphere. Following filtration, the interstitial water was acidified with 1 ml of concentrated hydrochloric acid, then stored in the dark in acetone-rinsed 2-ℓ glass bottles until analyzed. Aerobic interstitial water was obtained in a similar manner, except that anaerobic conditions were not maintained during the operation.

Permeameter Testing

Loading and operation

18. Column leaching tests were conducted in divided-flow permeameters designed to minimize wall effects and provide for pressurized operation (Figure 1). The inner permeameter ring divides flow, separating the leachate flowing through the center of the column from leachate flowing down the walls,

thereby minimizing wall effects on leachate collected from the center outlet. The applied pressure forces water through the sediment at rates sufficient to allow sample collection in a reasonable period of time.

19. Permeameter tests were run to simulate leaching of anaerobic and oxidized sediment, prepared as previously described. Nitrogen was used as the head space gas for anaerobic testing, and breathing air was used as the head space gas for aerobic testing. Separate permeameter tests were run to obtain leachate for metal and organic contaminant analysis, because of the large leachate volume needed to conduct organic contaminant analyses (1 ℓ). Column tests were run in triplicate for analysis of metal and organic leachate concentrations in anaerobic and aerobic New Bedford sediment, for a total of 12 permeameter tests.

20. New Bedford sediment was loaded into the permeameters in lifts averaging 5-cm thickness. The number of lifts depended on the column height desired. Sediment height averaged 17.8 cm in permeameters used to obtain leachate for metal analysis and 35.6 cm in permeameters used to obtain leachate for organic contaminant analysis. A longer column of sediment was needed in the permeameters run for organic analyses because of the greater sample volume required for chemical analyses. As each lift of water-saturated sediment was added, the permeameter was vigorously agitated on a vibrating table to remove trapped air. The weight and height of each lift was measured and recorded following vibration.

21. Sediment void volume in the permeameters was determined by measuring the weight and volume of sediment added to the permeameter, then measuring the weight and volume of sediment samples before and following oven-drying at 105° C. Weight loss upon drying was then equated to the volume of water in the permeable voids. Void volume at the end of testing was determined by measuring the final length of the sediment column and equating the difference in initial and final lengths as reduction in void volume. Void volumes were calculated for the sediment column beginning at the base of the permeameter and extending to the surface of the sediment in the vertical dimension, and beginning at the center of the permeameter and extending to the inner ring of the permeameter in the horizontal dimension.

22. Following sediment sample addition, DDI water was added to the permeameters; the leaching apparatus was then sealed and pressurized with either nitrogen or air, depending on whether the test was conducted on

anaerobic or aerobic sediment, respectively. It was necessary to periodically add DDI water to the permeameters, in approximately 2-ℓ increments, during the course of a test. Effluents from the inner and outer permeameter rings were drained through Teflon tubing into 1,000-ml graduated cylinders. Flow from the center outlet of each permeameter was isolated from the atmosphere by a water trap, and a nitrogen atmosphere was maintained in each collection cylinder receiving leachate from the center outlet (Figure 2). As shown in Figure 2, nitrogen was used to maintain a slight positive pressure, approximately 1 in. (2.54 cm) of water, in the collection vessels. Flow was regulated by adjusting operating pressure. A daily record was maintained of operating pressure and flow from both the inner and outer rings of the permeameter.

Sampling

23. Leachate from permeameters set up for metals was also analyzed for dissolved organic carbon (DOC), conductivity, and pH. Leachate samples for metals and DOC were filtered and preserved using procedures previously described for anaerobic and aerobic metal batch testing.

24. Leachate from permeameters set up for organic analysis was analyzed for DOC and specified organic contaminants. Leachate samples for organic contaminants and DOC were filtered and preserved using procedures previously described for organic contaminant batch testing under anaerobic and aerobic conditions.

Dispersion coefficient measurement

25. The dispersion coefficient, D_p , was determined by operating a separate permeameter specifically for this purpose. This permeameter contained anaerobic sediment and was leached with DDI water containing bromide as a tracer (constant concentration = 1,000 mg/ℓ). Effluent samples were collected periodically, filtered through a 0.45-μm pore size membrane filter, digested using procedures developed by Chain and DeWalle (1975) for chlorides in sanitary landfill leachate, and analyzed for bromide by silver nitrate titration using a recording titrator with a silver-specific ion probe. From these data the dispersion coefficient was computed using the F-curve method described by Levenspiel (1972). Additional details are provided in Appendix C.

Chemical Analysis

26. Leachate and sediment samples were analyzed for PCBs as Aroclors, total PCB (quantitated using a multi-Aroclor standard), selected PCB congeners and polynuclear aromatic hydrocarbons (PAHs), and arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn). Permeameter leachates were also analyzed for iron (Fe) and manganese (Mn) because these metals are indicators of changes in pH and of the potential for contaminant scavenging by iron and manganese precipitation. Concentrations of PCB Aroclors, total PCB, PCB congeners, and PAH compounds in sediment samples were determined following soxhlet extraction (50 percent hexane:50 percent acetone), silica gel cleanup, and quantification in either a Hewlett Packard 5985A gas chromatograph/mass spectrophotometer equipped with a flame ionization detector (for PAHs) or a Hewlett Packard 5880A gas chromatograph equipped with an electron capture detector (for PCBs). Concentrations of PCB and PAH compounds in leachate samples following methylene chloride extraction were determined on the same equipment as for sediment samples. Sediment and leachate samples were analyzed for all metals studied (including Fe and Mn in permeameter testing) using directly coupled plasma emission spectroscopy on a Beckman Spectraspan IIIB plasma emission spectrometer or by atomic absorption spectroscopy using a Perkin-Elmer Model 5000 atomic absorption spectrometer coupled with a Perkin-Elmer Model 500 hot graphite atomizer following appropriate sample digestion procedures (Ballinger 1979). Soluble organic carbon in leachate samples was determined using an Oceanographic International 524B organic carbon analyzer.

Statistical Analysis

27. 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. Regression analyses were used to determine the significance and slope of the line between steady-state sediment and leachate concentrations.

PART III: THEORETICAL BASIS FOR LEACHATE QUALITY EVALUATION

28. The theoretical and experimental approaches used in this report are in an early stage of development, and some changes may be needed before predictive techniques for leachate quality in CDFs can be standardized. The purpose of this section is to describe the theory behind the experimental methods described earlier. For this discussion, it is assumed that water transports contaminants from the dredged material to the boundaries of a CDF. Leaching is defined to be interphase transfer of contaminants from the dredged material solids to the aqueous phase as water moves past the dredged material solids. Upon contact with percolating water, contaminants associated with sediment particles can desorb, increasing contaminant levels in the leachate.

29. The application of mass transport theory to developing predictive techniques for leachate quality from dredged material in confined disposal sites was reviewed by Hill, Myers, and Brannon (1988). This work recommended that equilibrium-controlled, linear desorption be used to model interphase contaminant transfer from the dredged material solids to water. Mathematically equilibrium-controlled, linear desorption is expressed as follows (Voice and Weber 1983; Curtis, Roberts, and Reinhard 1986):

$$q = K_d C \tag{1}$$

where

q = equilibrium contaminant concentration in the sediment phase, mg/kg
K_d = equilibrium distribution coefficient, ℓ/kg
C = equilibrium contaminant concentration in the aqueous phase, mg/ℓ

Batch Leaching Tests

30. Equation 1 is the basis for the design of the batch leaching tests. By sequentially challenging a portion of sediment with successive aliquots of clean water, a table of q and C values can be generated and plotted (successive batches have differing sediment (q) and aqueous phase (C) concentrations). A plot of q versus C yields a desorption isotherm such as that shown in Figure 3. The slope of the isotherm is the equilibrium distribution coefficient for desorption, K_d. The key feature of a classical desorption

isotherm is that the sediment phase contaminant concentration is related to the aqueous phase concentration using a single distribution coefficient.

31. A commonly observed feature of desorption isotherms for metals is that they do not go through the origin (Environmental Laboratory 1987). Instead, they intercept the ordinate at some point (q_r) other than the origin (Figure 3). This value, q_r, is interpreted as material that is resistant to leaching. Failure of desorption isotherms to extend through the origin affects the computation of K_d. Distribution coefficients (K_d) calculated by dividing any q value by the corresponding C may be incorrect, since (0,0) is not necessarily a point on the isotherm. Mathematically, the irreversible fraction is incorporated into an isotherm equation as follows:

$$q_t = K_d C + q_r \tag{2}$$

where

q_t = total contaminant concentration in the sediment phase, mg/kg
q_r = irreversibly adsorbed contaminant concentration, mg/kg

Permeameter Leaching Tests

32. Batch leaching tests, which suffice for determining K_d, cannot duplicate the advective-dispersive transport and other mass transport effects occurring in a CDF. To determine these effects on contaminant release characteristics in New Bedford sediment, continuous-flow columns were set up in divided-flow permeameters (Figure 1).

33. For contaminant leaching by water percolating through dredged material, the governing one-dimensional partial differential equation for steady-state flow conditions is given below (Hill, Myers, and Brannon 1988).

$$D_p \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial z} + S = \frac{\partial C}{\partial t} \tag{3}$$

$$S = -\frac{\rho}{\theta}\left(\frac{\partial q}{\partial t}\right) \tag{4}$$

where

D_p = dispersion coefficient, cm^2/sec

z = space dimension, cm

V = average pore water velocity, cm/sec

S = source term for contaminant leaching, mg/ℓ sec

t = time, sec

ρ = bulk density, kg/ℓ

θ = porosity, dimensionless

34. Equations 1 and 2 describe a materials balance on a representative volume element in a CDF (Figure 4). It should be understood that C and q refer to one contaminant. Equation 1 is the materials balance for the aqueous phase (pore water), and Equation 2 is the materials balance for the solid phase. Equation 2 defines the source term in Equation 1 as the rate of transfer between solid and aqueous phases. Thus, there are two component balances, one for each phase, that must be solved simultaneously.

35. The first term on the left-hand side of Equation 3 represents dispersive transport of contaminant; the second term represents convective transport (bulk flow). The term on the right-hand side, referred to as the accumulation term, represents the change in pore water contaminant concentration with time. The source or reactive term, S , represents interphase transfer of contaminant from the sediment solids to the aqueous phase. Laboratory procedures are available for obtaining coefficients in the bulk flow and dispersion terms of the equation, but standard procedures have not been developed for quantifying the contaminant source term S for dredged material. The primary objective of the laboratory tests performed in this study, therefore, was to describe the source term for selected contaminants in New Bedford Harbor sediment.

36. The importance of a properly formulated interphase transfer term, S , the source term in Equation 3, has been demonstrated in numerous studies of the flow and reaction of solutes through porous media. Several models have been proposed and evaluated that model interphase transfer as equilibrium-controlled, nonequilibrium sorption, or chemical reaction kinetics (Hornsby and Davidson 1973, Gupta and Greenkorn 1974, James and Rubin 1979, Rao et al. 1979, Grove and Stollenwerk 1984, Valocchi 1985). Contaminant transport modeling is relatively complicated (involves seepage velocity, dispersion

coefficient, distribution coefficient, sorption kinetics, and boundary conditions) and typically requires numerical solution of governing equations.

37. A source term formulation that assumes that interphase transfer processes are "fast" with respect to bulk fluid flow is often used because the assumption presents advantages in computational efficiency and eliminates the need for rate coefficients (Jaffe and Ferrara 1983, Grove and Stollenwerk 1984, Valocchi 1985). For this assumption, desorption is equilibrium controlled. Assuming that desorption is equilibrium controlled and is a linear process described by a contaminant-specific distribution coefficient that is constant, the source term can be formulated as follows:

$$S = -\frac{\rho}{\ell}\left(\frac{\partial q}{\partial t}\right) = -\frac{\rho K_d}{\theta}\left(\frac{\partial C}{\partial t}\right) \tag{5}$$

For equilibrium-controlled, linear desorption with constant coefficients, Equation 3 becomes

$$\left(\frac{\partial C}{\partial t}\right) + \frac{\rho K_d}{\theta}\left(\frac{\partial C}{\partial t}\right) = D_p\left(\frac{\partial^2 C}{\partial z^2}\right) - V\left(\frac{\partial C}{\partial z}\right) \tag{6}$$

38. An analytical solution for Equation 6 is presented below (Ogata and Banks 1961):

$$C(z,t) = C_I + (C_o - C_I)0.5 \text{ erfc } \frac{Rz - Vt}{2(DRt)^{0.5}} + 0.5 \exp \frac{Vz}{D} \text{ erfc } \frac{Rz + Vt}{2(DRt)^{0.5}} \tag{7}$$

where

C_I = initial contaminant concentration in the interstitial water, mg/ℓ

C_o = contaminant concentration in the water entering the sediment, mg/ℓ (equal to zero for the test procedures used in this study)

erfc = complementary error function

R = retardation coefficient = $1 + \frac{\rho K_d}{\ell}$, dimensionless

D = longitudinal dispersivity = $\frac{D_p}{V}$, cm

39. The initial and boundary conditions used to obtain Equation 7 are as follows:

$$C(z,0) = C_I$$
$$C(0,t) = C_o$$
$$\partial C/\partial z \ (\infty,t) = 0$$

40. The leach tests described in this report were conducted to test the hypothesis that interphase transfer of contaminants is governed by a unique distribution coefficient for each contaminant and that contaminant leaching in New Bedford Harbor sediment can be modeled using Equations 5, 6, and 7. Interphase transfer of contaminants from sediment solids in New Bedford Harbor sediment did not follow classical desorption theory. Equations 5, 6, and 7 were found to be inappropriate for most contaminants because the basic assumption behind Equation 5--a unique distribution coefficient for each contaminant--was not valid. Details are provided in the discussion of results (Part IV).

Integrated Approach

41. The integrated approach consists of using results from batch tests, column tests, and Equations 3 and 4 to verify the mathematical form of an assumed source term. Application of the integrated approach is illustrated in Figure 5. If predicted and observed permeameter elution curves agree, the conclusion may be reached that transfer of contaminants from sediment solids has been adequately described. If not, other formulations for interphase transfer may be needed. Once a reasonable description of interphase contaminant transfer has been found, contaminant migration by leaching can be evaluated by solving Equations 3 and 4 for the initial and boundary conditions that apply in the field.

PART IV: RESULTS AND DISCUSSION

Sediment Chemical Concentrations

42. Heavy metal concentrations in New Bedford sediment are presented in Table 4. Copper, lead, and zinc, the most abundant metals in New Bedford sediment, were present at concentrations of 1,730, 2,013, and 3,017 mg/kg, respectively. These metal concentrations exceed those normally encountered in dredged material (Brannon, Plumb, and Smith 1980). Concentrations of PAHs in anaerobic New Bedford sediment and New Bedford sediment after 3 months of aeration are presented in Table 5. Concentrations of PAH compounds in anaerobic New Bedford sediment ranged from less than 4.6 mg/kg to 11.8 mg/kg. The PAH concentrations in New Bedford sediment after 3 months aeration are about the same as or slightly higher than PAH concentrations in anaerobic sediment. The differences observed are probably due to lack of homogeneity in the materials sampled, not to real differences in concentrations. Concentrations of PCB Aroclors, total PCB (PCB quantified using a multi-Aroclor standard), and selected PCB congeners are presented in Table 6. (See Table 7 for PCB congener identification key.) Concentrations of PCBs were high in both the anaerobic and aerobic sediment. Although the same concerns about sampling heterogeneous materials apply to the PCB analyses, there appeared to be a loss of PCB from aerobic sediment compared with anaerobic sediment. Concentration decreases of approximately 19 and 32 percent for Aroclors 1242 and 1254, respectively, are indicated in Table 6.

43. A thorough analysis of the processes involved in the losses noted above was beyond the scope of this study. However, a brief discussion of the implications may be useful. Volatilization and biological degradation are two processes that were probably involved. Since the aerobic sediment was not exposed to direct sunlight, photooxidation was probably minimal. Volatilization of organic compounds from moist sediment depends on Henry's Law constant and can be significant if the Henry's Law constant is high, as is the case with PCBs. The fact that PCBs make excellent transformer oil because of their low vapor pressure should not be misconstrued to imply that volatilization of PCBs is negligible in environmental media, where as often as not Henry's Law constant determines volatility (Thibodeaux 1979). Biological degradation of PCBs has been demonstrated in laboratory studies (Kaiser and Wong 1974,

Bopp 1986, Bedard et al. 1987). However, PCB degradation rates for the passive aeration that was provided are not known.

44. The changes shown in Table 6 are not quantitatively indicative of what would occur in a CDF. The New Bedford sediment used for aerobic leachate analysis was kept moist and turned weekly for 3 months. This may represent a gross exaggeration of conditions in the surface layer in a CDF. If the losses are due to volatilization/biodegradation, these processes may be a significant route for PCB loss under certain circumstances. The potential for volatilization/biodegradation is greatest when the dredged material is moist, but not saturated with water, and is exposed to the air. Repeated wetting and drying of exposed sediments would promote volatilization. Volatilization would be far less in the inundated condition with several feet of water above the dredged material. Biodegradation will also be lower in the inundated condition because flooded sediments are generally anaerobic, and anaerobic microbial degradation processes are generally slower than aerobic processes. Dried material has the least potential for volatilization because in this condition volatilization is dependent on vapor pressure, not Henry's Law constant. The importance of biodegradation will also be reduced in dried sediment since biological processes are sensitive to moisture deprivation.

45. It is unlikely that PCB compounds were being fixed during aeration in a form that could not be extracted during the analytical procedure. Otherwise, there should have been a corresponding loss of PAH compounds in the aerobic sediment compared with the anaerobic sediment. Further study is needed to determine the significance of volatilization and biodegradation under the conditions used to aerate New Bedford sediment.

46. The metal and PCB concentrations of interstitial water measured in anaerobic and aerobic New Bedford sediment are presented in Table 8. The data indicate that the interstitial water PCB concentrations in anaerobic and aerobic New Bedford sediment were generally similar.

Kinetic Testing

47. Kinetic batch testing was performed to confirm previous experience that 1 day of shaking time was sufficient to achieve steady-state conditions during batch leaching tests. Waiting on results of kinetic testing prior to

conducting sequential testing on New Bedford sediment would not have allowed the study to proceed in a timely manner.

48. Kinetic testing results for metals are presented in Table 9. Results show that leachate metal concentrations for Cd, Ni, and Zn following 1 day of shaking did not significantly differ ($P < 0.05$) from leachate metal concentrations following 2, 4, or 7 days of shaking, indicating that steady-state concentrations of these metals had been reached in 1 day. Examination of the means for Zn may lead to the conclusion that Zn concentrations were increasing with time. However, the data for Zn became more variable as time of shaking increased so that no statistical differences could be detected in the data. Arsenic concentrations in New Bedford leachate were at peak concentrations following 1 day of shaking. Batch test data for As therefore reflect worst-case concentrations. The Cr and Pb concentrations following 1 and 2 days of shaking were lower than their respective concentrations following 4 and 7 days of shaking. Copper concentrations following 1, 2, and 4 days of shaking were lower than Cu concentrations following 7 days of shaking. Batch leachate concentrations of Cr, Pb, and Cu following 1 day of shaking may therefore slightly underestimate steady-state conditions. In past leaching studies with sediments from Indiana Harbor, Indiana (Environmental Laboratory 1987) and Everett Harbor, Washington (Palermo et al., in preparation), 1 day has been sufficient for steady-state or worst-case metal concentrations to be achieved in the leachate. The reasons for some metals in New Bedford sediment to deviate, although slightly, from this behavior is not evident.

49. Organic contaminant leachate results as a function of shaking time are presented in Table 10. Data showed that there were no significant ($P < 0.05$) differences between leachate concentrations of total PCB, Aroclor 1242, Aroclor 1254, or any of the PCB congeners following 1, 2, or 7 days of shaking. Concentrations of PAH compounds were all below detection limits. A 24-hr shaking time was therefore judged appropriate for batch testing for PCBs and PAHs.

Liquid-to-Solids Ratio Testing

50. Several researchers have reported the distribution coefficients (K_d) determined in batch sorption tests to be dependent on the liquid-to-solids ratio used in the test (O'Conner and Connolly 1980; Di Toro et al.

1982; Voice, Rice, and Weber 1983; Di Toro 1985). The liquid-to-solids ratio in dredged material following sedimentation is approximately 1:1. Batch leaching tests for dredged material should therefore approach a 1:1 ratio as closely as possible but also generate enough leachate for organic contaminant analyses (approximately 1 ℓ). Past testing has shown that a 4:1 liquid-to-solids ratio is the lowest practical ratio for conducting batch leaching tests with sediment (Environmental Laboratory 1987).

51. Although the dependency of K_d on liquid-to-solids ratio is poorly understood, evaluation of the constancy of distribution coefficients is rather straightforward. If desorption isotherms from batch tests conducted using various liquid-to-solids ratios produce straight lines with positive slopes as shown in Figure 3, the distribution coefficient is not dependent on liquid-to-solids ratio. This means that the processes governing release of contaminants are not affected by the liquid-to-solids ratio, and any convenient ratio can be used in batch leach tests to investigate release characteristics.

52. Data from batch testing with varying liquid-to-solids ratios of New Bedford sediment were evaluated using regression analysis and isotherm plots. Results of regression analyses conducted using sediment (q) and leachate metal concentrations (C) after 1 day for varying liquid-to-solids ratios for anaerobic New Bedford sediment are summarized in Table 11. An example of the relationships obtained is presented for Cd and Cr in Figure 6. The data indicate that, except for As, for which too few data points existed, statistically significant relationships existed for the remainder of the metals. The slopes of the isotherms for all metals were negative, implying that as the water-to-sediment ratio was increased, the amount of metal that was mobilized increased. These findings (negative slope) are the opposite of what is expected for a constant distribution coefficient (a positive slope and decreasing metals concentration as liquid-to-solids ratio increases).

53. Results of regression analyses conducted using sediment (q) and leachate metal concentrations (C) after 1 day of varying liquid-to-solids ratios for aerobic New Bedford sediment are summarized in Table 12. The data indicate that statistically significant relationships existed for As, Cr, Cu, and Ni. The slopes of the isotherms were mixed, with positive isotherms noted for As and Ni and negative isotherms observed for Cr and Cu. Arsenic also showed a statistically significant relationship ($r^2 = 0.899$) when log q and log C, the linearized form of the Freundlich isotherm, were subjected to

regression analysis. Contrary to the results noted for anaerobic sediments, some metals behaved in the expected manner, showing positive slopes.

54. Regression analyses were also conducted for steady-state sediment and leachate PCB concentrations. This was not done for PAHs because these compounds were all below detection limits in the leachate. Results of regression analyses of steady-state sediment concentration versus steady-state leachate concentration for anaerobic New Bedford sediment are presented in Table 13. These data indicate that statistically significant relationships existed between steady-state sediment and leachate concentrations for a number of compounds, especially PCB congeners with a high degree of chlorination. An example of the relationships obtained for congener 138 (2,2',3,4,4',5'-hexachlorobiphenyl) is presented in Figure 7. As illustrated in Figure 7, all relationships presented in Table 13 exhibited a negative slope. This indicates that the distribution coefficient decreased as the liquid-to-solids ratio increased.

55. Results of regression analyses of steady-state sediment concentrations versus steady-state leachate concentrations for aerobic New Bedford sediment are presented in Table 14. These data indicate that statistically significant relationships existed between steady-state sediment and leachate concentrations for a number of compounds, especially PCB congeners with five or less chlorine atoms. In contrast to the results observed with anaerobic sediments, many of the relationships presented in Table 14 exhibited a positive slope, indicating constant distribution coefficients for some but not all congeners. The change in environmental conditions from anaerobic to aerobic and changes in sediment properties during the oxidation process may have been responsible for changes in PCB release characteristics.

56. The findings involving isotherms with negative slopes indicate more than just nonconstant distribution of contaminant between solid and dissolved phases. From the literature on nonconstant partitioning of PCBs, the distribution coefficient would be expected to increase with an increase in liquid-to-solids ratio. This effect would yield an isotherm whose slope at any point was always greater than or equal to zero. The negative slopes found in this study are the opposite expected if constant partitioning or the type of nonconstant partitioning previously reported had been followed. As discussed in the next section, the same trends were observed during sequential batch leaching at a fixed liquid-to-solids ratio of 4:1.

Sequential Batch Leaching

General leachate quality

57. Leachate pH values for anaerobic and aerobic sequential batch leaching tests are presented in Table 15. Leachate pH from anaerobic sediment was higher than 7.0 during the first four leaching sequences, then decreased to pH 6.5 in the seventh leach cycle. The changes in leachate pH during the anaerobic leaching procedures should not cause pronounced changes in leachate metal releases. Comparisons between log [leachate metal concentration] and pH for anaerobic sequential batch testing did not result in any significant ($P < 0.05$) linear relationships. However, for aerobic New Bedford sediment, leachate pH was much lower than the values observed for anaerobic sediment. As shown in Table 15, pH values for aerobic New Bedford leachate reached mean values as low as 2.1 on the third leach cycle, then began to rise, reaching pH 5.7 by the fifth leach cycle. This may have been caused by a washout of the acidic materials present in the aerobic sediment.

Metal releases

58. Steady-state metal concentrations in sediment (q) and leachate (C) obtained from the sequential batch leaching tests for anaerobic New Bedford sediment are presented in Tables 16 and 17, respectively. Metal release trends in anaerobic New Bedford sediment can be seen in Figures 8 and 9, which present plots of steady-state sediment concentration versus steady-state leachate concentration for Ni and Zn, respectively. In interpreting figures derived from sequential leaching, the highest values of q are from the initial leach cycle and decrease as sequential leaching proceeds. These data show that leachate concentrations were low initially, then increased as sequential leaching proceeded. These results were similar to results obtained for other metals. As shown in Table 18, statistically significant relationships existed between steady-state sediment and leachate concentrations for all metals determined except As. Slopes of the isotherm lines of best fit derived in this manner (Table 18), with the exception of As, were all negative, but were less negative than those developed by varying the water-to-sediment ratio. However, both data sets show the same negative slopes for all metals but As. Negative slopes in these isotherms indicate that leachate concentrations increase as the water contacting the sediment solids is replenished. It would be expected that the isotherms would reverse, for the trends

noted cannot continue indefinitely, but a definite turn was not evident for most metals following the seven sequential leach cycles. Relatively low amounts of metals were lost from the sediment during the leaching procedure, ranging from a low of 0.15 mg/kg for As to a high of 29.2 mg/kg for Zn, but concentrations of some metals such as Zn reached relatively high levels (1.8 mg/ℓ) in the leachate.

59. Steady-state metal concentrations in sediment and leachate obtained from the sequential batch leaching tests for aerobic New Bedford sediment are presented in Tables 19 and 20, respectively. Metal release trends in aerobic New Bedford sediment can be seen in Figures 10 and 11, which present plots of steady-state sediment concentration versus steady-state leachate concentration for Cd and Zn, respectively. These data show that leachate concentrations of Cd were low initially, then increased as leaching proceeded. Leachate concentrations of Zn were high initially (13.8 mg/ℓ), then increased as leaching proceeded. As shown in Table 21, statistically significant relationships existed between steady-state sediment and leachate concentrations in the aerobic sequential batch testing for all metals tested except Cr, Pb, and Ni. Slopes of the isotherm lines of best fit derived in this manner (Table 21), with the exception of As, were all negative. Similar trends, except for Ni, were observed in isotherms obtained by varying the sediment-to-water ratio for aerobic New Bedford sediment (Table 12). Relatively low amounts of As, Cd, Cr, Cu, and Pb (0.3 to 2.4 mg/kg) were lost from the aerobic sediment during the leaching procedure, but large amounts of Ni (17.0 mg/kg) and Zn (533.6 mg/kg) were lost during the procedure. Metal concentrations in the leachate reached levels of 37.3, 1.3, 0.13, and 0.28 mg/ℓ for Zn, Ni, Cu, and Cd, respectively. Concentrations of Zn in the aerobic leachate greatly exceeded concentrations in anaerobic leachate.

Organic contaminant releases

60. Organic contaminant concentrations present in steady-state sediment and leachate of anaerobic New Bedford sediment are given in Tables 22 and 23, respectively. No PAH compounds were present in detectable quantities in the leachate. Isotherms obtained by plotting steady-state sediment concentration versus steady-state leachate concentrations for congener 118 and Aroclor 1254 are presented in Figure 12 and 13, respectively. These data show PCB isotherms with negative slopes that begin to turn back toward the y axis following the third leach cycle. However, even with the turn during the last leach

cycle, statistically significant linear relationships between steady-state sediment and leachate concentrations were found for anaerobic New Bedford sediment. These relationships are summarized in Table 24. The data show that the slope of the lines of best fit was negative, indicating that leachate PCB concentrations were increasing as leaching progressed. The PCBs in the leachate were present in varying concentrations. Aroclor 1242 concentrations peaked at 2.3 mg/ℓ; PCB congener number 77 showed a peak value of 0.25 mg/ℓ. Many of the concentrations of PCB reported here apparently exceed solubility limits for PCBs in water. However, solubility in such a complex sediment-water system can be affected by a variety of factors, many of which are not well understood. For example, dissolved organic carbon in water is thought to act as a carrier for PCBs, increasing the apparent solubility and mobility of hydrophobic compounds. Examination of the dissolved organic carbon data for the sequential batch testing (Table 25) shows that DOC concentrations for the first, second, and fourth leach cycles were statistically the same. Concentrations of DOC during the third leach cycles were statistically higher than those measured during the other leach cycles. There was, therefore, no clear-cut trend in leachate DOC concentrations paralleling the trends observed for PCB concentrations.

61. This observation also held true for DOC concentrations in leachate obtained from anaerobic New Bedford sediment during testing with differing water-to-sediment ratios (Table 26). Instead of showing an increase in DOC with increasing water-to-sediment ratio, as did PCBs, the DOC concentration decreased. Dissolved organic carbon in the leachate did not, therefore, correlate with PCB concentration. It is possible, however, that certain components of the DOC, not gross DOC, affect the partitioning of PCBs (Voice, Rice and Weber 1983; Gschwend and Wu 1985). If this is true, DOC measurements probably lack the resolution necessary to measure the effect. Investigation of the processes governing the behavior of PCB in the leachate was beyond the scope of this study.

62. Leachate concentrations and single-point distribution coefficients for organic contaminants in aerobic New Bedford sediment are presented in Table 27. These data show that K_d values were generally between 1,000 and 10,000 ℓ/kg. Sequential batch testing was not conducted on the aerobic New Bedford sediment because previous work with Indiana Harbor and Everett Harbor sediments had shown that PCB distribution coefficients could be

estimated using nonsequential batch leach procedures (Environmental Laboratory 1987; Palermo et al., in preparation). The anaerobic tests were therefore conducted sequentially to check the results of previous findings, and aerobic tests were run using nonsequential batch leaching procedures.

Implications of New Bedford Isotherms

63. Examination of Part III, "Theoretical Basis for Leachate Quality Evaluation," shows that the isotherms for New Bedford leachate for both PCBs and metals do not conform to current adsorption/desorption theory. Desorption isotherms should follow the sediment concentration and leachate concentration isotherm illustrated for desorption in Figure 3. For example, during leaching, leachate contaminant concentrations should decrease as sequential leaching proceeds. Alternatively, desorption of the contaminant may be so low that no well-defined isotherm is established, resulting in very low, almost constant concentrations of the contaminant throughout the course of sequential leaching. In this case, desorption behavior can be described by a single-point distribution coefficient that assumes that all of the contaminant associated with the sediment is leachable and that the desorption isotherm passes through the origin. Such distribution coefficients can be obtained by dividing the equilibrium sediment concentration by the equilibrium leachate concentration following a single batch test cycle.

64. New Bedford desorption isotherms behaved in a manner consistent with nonconstant partitioning with decreasing affinity for the solid phase. This concept is illustrated in Figure 14. As can be seen, the distribution coefficient (K1, K2, etc.) changes until the isotherm turns toward the y axis, and the distribution coefficient becomes constant. In the initial part of the isotherm in Figure 14, K_d decreases as the ratio of steady-state sediment (q) and leachate (C) contaminant concentrations is changing, resulting in a change in K_d with q. A plot of K_d versus steady-state sediment Ni concentrations in anaerobic sediment is presented as Figure 15. These data show that K_d values for Ni decrease during the first three leach cycles as fresh water contacts the sediment, and Ni is removed in the leachate. However, as shown in Figure 8, Ni steady-state sediment and leachate values tended to clump following the first three leach cycles, producing relatively constant K_d values thereafter (Figure 15).

65. Reasons for the existence of nonconstant distribution coefficients can be traced to the sediment, the leachate, or both. If nonconstant partitioning is caused by the sediment, it will probably be due to changes in phase association or the agent binding the metal or PCB to the sediment. For example, Brannon and Patrick (1987) have shown that the sediment components binding As change during leaching.

66. Changes in the leachate could also be responsible for nonconstant partitioning. At an upland or nearshore site, rainwater would probably be the source of most freshwater input into a site. Therefore, distilled water was used in the leaching experiments. However, as salts in sediment are washed out through successive contact with DDI water, flocculated colloidal material in the sediment may destabilize, disperse, and mobilize metals and PCBs from sediment into leachate by serving as a carrier. In a similar manner, formation of microdroplets of PCB in the leachate that survive the centrifugation and filtration steps of leachate preparation may result in increased PCB leachate concentrations. It is unclear if microdroplet formation could have a similar effect on metals concentrations.

Factors Affecting Nonconstant Partitioning

67. At the completion of the batch tests described above, the need for additional study was evident. Factors affecting contaminant releases were, therefore, investigated in an add-on study. Results from additional testing are described in detail in Appendix A and summarized below.

68. Three factors were investigated: (a) microbe-mediated transfer, (b) formation of microdroplets of PCB, and (c) destabilization of colloidal material as salinity decreased. The testing showed that deviation from classical partitioning theory of PCBs was attributable to conductivity (salinity) decrease with successive distilled water leaches. When conductivity was held constant using saline water leachate, PCB desorption followed classical desorption theory. Metal data did not show substantial differences in release patterns between distilled and saline water sequential batch leach tests.

Permeameter Testing

69. Permeameter testing is a technique for investigating contaminant leaching in a laboratory microcosm of a CDF. This type of testing involves continuous-flow leaching of a sediment column (Figure 1) and has been used in previous studies of contaminated sediment leaching potential (Environmental Laboratory 1987; Palermo et al., in preparation). The purpose of such testing is to simulate contaminant leaching in a laboratory-scale, physical model of a CDF (Hill, Myers, and Brannon 1988).

70. Permeameter leach tests for metals and organic contaminants were carried out in separate sets of permeameters because of the leachate volume needed for chemical analyses. Anaerobic and aerobic sediments were leached in triplicate, resulting in three permeameters each for continuous-flow leaching of anaerobic metals, anaerobic organic contaminants, aerobic metals, and aerobic organic contaminants. The following discussion of permeameter results is therefore organized according to sediment and contaminant type.

Permeameter hydraulics

71. At the start of the permeameter leaching tests, a well-mixed slurry of sediment was placed in the permeameters at uniform density and moisture content. Initially, the sediment was fully saturated and in a fluid state. Once the permeameters were placed in operation, consolidation during testing reduced porosity and increased resistance to flow. Flow was controlled by adjusting operating pressure to maintain constant flow. Average flows according to sediment and contaminant type are listed in Table 28.

72. As resistance to flow increased, operating pressures were increased to maintain a constant flow (Figures 16-19). Initial operating pressures were 0.0 psig for all permeameters. Final operating pressures for anaerobic metals, anaerobic organics, and aerobic organics were 30 psig (207 kPa gage), and the final operating pressure for aerobic metals was 15 psig (103 kPa gage). Initial and final permeabilities are listed in Table 28.

73. Data collected from column studies are usually presented as a plot of leachate quality versus the volume of water passing through the column. The cumulative volume is represented by the number of pore volumes that have passed through the column. Since the sediment in the permeameters was saturated, the volume of pore water in a permeameter was equal to the void volume of the sediment column. Initial void volume was determined from porosity

measurements conducted on sediment samples collected during permeameter loading. Final void volumes were determined at the end of the tests by measuring the lengths of the sediment columns and equating the change in column length to reduction in void volume. The void volume data in Table 28 are for the sediment column beginning at the base of the permeameter and extending to the top of the sediment column in the vertical dimension and beginning at the center of the permeameter and extending to the inner ring of the permeameter in the horizontal dimension (Figure 1).

74. In the discussion that follows, permeameter leachate results are plotted versus the dimensionless parameter pore volumes displaced, S_v/V_v, where S_v is the sample volume (litres) and V_v is the void volume (litres). Two corrections were applied before developing plots of contaminant concentrations versus pore volumes displaced. Since void volume decreased as testing proceeded, it was necessary to correct void volume for consolidation (see Appendix B for details). In addition, the contaminant concentration in a volume of leachate collected for analysis is a composite of the instantaneous contaminant concentrations in the leachate flow during collection. For a sample collected between pore volumes x and y, contaminant concentrations were plotted versus the midpoint pore volume between x and y. For example, contaminant concentrations in leachate collected between 2 and 3 pore volumes would be plotted at 2.5 pore volumes displaced.

General leachate quality for anaerobic metals permeameters

75. As shown in Figure 20, pH was relatively constant during anaerobic, continuous-flow leaching of New Bedford Harbor sediment. Initial pH was in the range of 8.4 to 8.6, and final pH was in the range of 7.8 to 8.4. Overall pH ranged from 7.5 to 8.6. The pH changes shown in Figure 20 play a minor role in controlling metal concentrations because the changes were not of sufficient magnitude to cause pronounced changes in metal solubility.

76. Conductivity is related to ionic strength and salinity and is a function of the amount of dissolved solids. Conductivity in anaerobic metals permeameters followed a classical elution curve with some desorption occurring, as evidenced by the tailing effect after displacement of three pore volumes (Figure 21). These data show that as continuous-flow leaching proceeded, conductivity decreased.

77. Dissolved organic carbon showed little initial change over the first 2 pore volumes (Figure 22). The DOC concentration peaked between 3 and 4 pore volumes and then steadily decreased. Initial values ranged from 32 to 41 mg/ℓ DOC, peak values ranged from 41 to 97 mg/ℓ, and values at the end of testing ranged from 14 to 16 mg/ℓ. The ascending limb on the DOC concentration peak corresponds to rapidly changing conductivity, and the declining limb on the DOC concentration peak corresponds to the development of gradually varying conductivity at about four to six pore volumes (Figure 21).

78. Anaerobic metals. Cadmium concentrations during anaerobic, continuous-flow leaching of New Bedford Harbor sediment are shown in Figure 23. In two of the permeameters, cadmium concentrations were slightly less than 0.0030 mg/ℓ initially and then dropped to near the detection limit (0.0001 mg/ℓ) for the remainder of the test. The cadmium elution curve for these two permeameters followed the form of a classical elution curve. In the other permeameter, cadmium concentrations were consistently near the detection limit throughout the test. These data indicate that cadmium leaching after displacement of the first pore volume was minimal.

79. Chromium concentrations during anaerobic, continuous-flow leaching of New Bedford Harbor sediment are shown in Figure 24. Initial chromium concentrations were below 0.05 mg/ℓ. Chromium concentrations then increased to peak values between 3 and 4 pore volumes that ranged from 0.126 to 0.385 mg/ℓ. Thereafter, chromium concentrations dropped and, after 5 pore volumes, tended to remain steady at concentrations ranging from 0.053 to 0.103 mg/ℓ. The increase in chromium concentrations from the initial values corresponds to rapidly changing conductivity, and the development of relatively steady chromium concentrations corresponds to the development of gradually varying conductivity (Figure 21).

80. Copper concentrations during anaerobic, continuous-flow leaching of New Bedford Harbor sediment are shown in Figure 25. Copper elution curves were similar to those for chromium, except that copper concentration peaks were delayed relative to those for chromium. Initial copper concentrations were at the detection limit (0.001 mg/ℓ). Peak values ranging from 0.007 to 0.017 mg/ℓ appeared between 4.0 and 7.0 pore volumes. Final values ranged from 0.001 to 0.004 mg/ℓ. During the period in which conductivity was rapidly

varying, copper concentrations were relatively steady. The peaks in copper concentrations appeared after conductivity was significantly reduced.

81. Iron concentrations during anaerobic, continuous-flow leaching of New Bedford Harbor sediment are shown in Figure 26. Iron concentrations showed an elution record similar to that observed for conductivity. Iron concentrations dropped rapidly from the initial values and thereafter showed a slow-steady decline. Initial values ranged from 0.642 to 9.24 mg/ℓ, and final iron concentrations ranged from 0.086 to 0.697 mg/ℓ.

82. Manganese concentrations during anaerobic, continuous-flow leaching of New Bedford Harbor sediment are shown in Figure 27. Manganese elution curves were almost identical to those observed for iron. Initial concentrations ranged from 0.245 to 2.94 mg/ℓ, and final concentrations ranged from 0.002 to 0.093 mg/ℓ.

83. Nickel concentrations during anaerobic, continuous-flow leaching of New Bedford Harbor sediment are shown in Figure 28. Nickel elution curves were similar to those observed for copper. There was a slight increase from initial concentrations (0.001 to 0.027 mg/ℓ) to peak values ranging from 0.031 to 0.058 mg/ℓ between 2 and 5 pore volumes. Thereafter, nickel concentrations showed a downward trend, with final concentrations ranging from below the detection limit (0.001 mg/ℓ) to 0.030 mg/ℓ. As with copper, nickel concentrations were relatively steady during the period in which conductivity was rapidly varying, and peak nickel concentrations appeared after conductivity was significantly reduced.

84. Lead concentrations during anaerobic, continuous-flow leaching of New Bedford Harbor sediment are shown in Figure 29. Lead concentrations generally decreased as leaching progressed. Lead concentrations in the majority of leachate samples were near or below the detection limit (0.001 mg/ℓ). Thus, the data indicate that lead was not readily leached under anaerobic, continuous-flow conditions.

85. Zinc concentrations during anaerobic, continuous-flow leaching of New Bedford Harbor sediment are shown in Figure 30. Anaerobic permeameter leachate samples were very low in zinc, with all but one of the samples near or below the detection limit (0.030 mg/ℓ). Thus, zinc did not leach in significant amounts under anaerobic, continuous-flow conditions.

86. Anaerobic organics. The concentrations of five PCB Aroclors and total PCB in leachates from the anaerobic permeameters are listed in Table 29; concentrations of 23 PCB congeners in anaerobic permeameter leachates are listed in Table 30. The PAHs were analyzed in the first set of samples collected from the anaerobic permeameters, but these data are not presented because PAHs were below the detection limit (0.0065 mg/ℓ) in all samples. Because PAH concentrations in the batch leach tests and in the first permeameter samples were below detection limits, PAHs were not included in subsequent analyses.

87. Aroclors 1242 and 1254 were found in the sediment and in anaerobic permeameter leachates. Aroclors 1016, 1221, 1232, 1248, and 1260 were below the detection limit (0.0002 mg/ℓ) in all samples. The occurrence of PCB congeners in detectable concentrations varied depending on PCB congener, pore volumes displaced, and permeameter. Several PCB congeners were below the detection limit (0.00001 mg/ℓ) in many of the samples. The PCB congener C7 was the only PCB congener below the detection limit in all anaerobic permeameter leachate samples. Congeners C167 and C185 were among the PCB congeners usually below the detection limit. Congeners C8, C28, C44, C50, C52, C70, and C77 were among those most frequently measured above the detection limit.

88. The sum of the concentrations of PCB congeners C8, C28, C44, C50, C52, C70, and C77 accounts for most of the total congener mass leached. Thus, most of the PCB leached under anaerobic, continuous-flow conditions was in the form of di-, tri-, and tetrachlorobiphenyls. (See Table 7 for the PCB congener identification key.)

89. Elution curves for total PCB, Aroclors 1242 and 1254, and DOC are shown in Figures 31-34. These figures show a complicated elution record involving the development of peaks in the elution curves. The PCB concentrations first tended to decrease and then increased to peak values after about 3 pore volumes had been displaced. The DOC concentrations increased slightly during leaching.

90. Elution curves for PCB congeners C28, C118, and C155 were representative of the PCB congener data set for anaerobic, continuous-flow leaching and are presented in Figures 35-37. Elution curves for these three PCB congeners illustrate the important features, similarities, and differences in the PCB congener data set. As with the Aroclors and total PCB elution curves, PCB congener elution curves showed the development of concentration peaks after

approximately 3 pore volumes had been displaced. Replication among permeameters and distinctness of peaks were better for PCB congener C28 than for PCB congeners C118 and C155. In addition, concentrations of PCB congeners C118 and C155 were lower than the PCB congener C28 concentrations. In some samples, PCB congener C118 and C155 concentrations were below the detection limit (0.00001 mg/ℓ).

91. The decrease in PCB concentrations from initial values corresponds to the period in which conductivity would be rapidly decreasing, and the increase to peak concentrations corresponds to the period following development of lower, relatively constant conductivity values. Conductivity was not measured on leachates from permeameters set up for leaching organics because the sample was at a premium, and none could be sacrificed for the conductivity analysis. The conductivity elution curves for the anaerobic metals, however, can be used to approximate the elution of conductivity in the anaerobic permeameters monitored for organics because the flow characteristics in anaerobic metals and organics permeameters were similar.

General leachate quality for aerobic metals permeameters

92. As shown in Figure 38, pH changed significantly during continuous-flow leaching of aerobic New Bedford Harbor sediment. Initially, pH was in the range of 3 to 6. After the initial samples were collected, pH increased and remained relatively constant in the 7.3 to 8.3 range. Thus, after 1 pore volume, pH in the aerobic permeameters was basically the same as pH in the anaerobic permeameters. As previously discussed in the section on batch test results, a low initial permeameter leachate pH is to be expected because the process used to prepare aerobic New Bedford Harbor sediment for testing involved aeration that resulted in a lower sediment pH. The increase in pH to the pH levels in the anaerobic permeameters is thought to indicate a shift from aerobic conditions to anaerobic conditions. Since aerobic permeameter testing involved leaching of partially oxidized sediment in a flooded condition, the oxygen in the water used for leaching was depleted by the residual sediment oxygen demand, resulting in reestablishment of anaerobic conditions in the permeameters. A shift to anaerobic conditions has been noted in previous permeameter testing (Environmental Laboratory 1987; Palermo et al., in preparation).

93. Conductivity in aerobic permeameters for metal leaching of New Bedford Harbor sediment decreased as water passed through the sediment column (Figure 39). Conductivity elution curves showed classical elution in two of the three permeameters (Figure 39), with one curve displaying a slight departure from classical form.

94. Dissolved organic carbon showed a complicated elution record in aerobic permeameters (Figure 40). There were two DOC concentration peaks, one appearing between 1 and 3 pore volumes and the second at about 5 pore volumes. In between these peaks were the lowest DOC concentrations. The ascending limb of the first DOC peak corresponds to rapidly changing conductivity, and the beginning of the declining limb of the first DOC concentration peak corresponds to the development of slowly changing conductivity. Thereafter, there appears to be no correlation of DOC with conductivity.

95. Aerobic metals. Cadmium concentrations during aerobic, continuous-flow leaching of New Bedford Harbor sediment are shown in Figure 41. As shown in Table 31, there was a one-to-one correspondence of initial cadmium concentration to initial pH. Initial cadmium concentrations ranged from 0.0014 to 0.0113 mg/ℓ. Cadmium concentrations decreased dramatically after the initial samples were collected to concentrations that were at or near the detection limit (0.0001 mg/ℓ). These data show that minimal interphase transfer of cadmium from the sediment solids to the pore water occurred after the initial pore volume was displaced. Although the cadmium elution curves are similar to a classical elution curve, the pH data (Figure 38) and the cadmium data (Figure 41) indicate that cadmium concentrations were pH controlled. Except for the initial concentrations, which were up to 10 times the cadmium concentrations in anaerobic permeameter leachate, the cadmium concentrations in aerobic permeameter leachates were similar to the cadmium concentrations in anaerobic permeameter leachates.

96. Chromium concentrations during aerobic, continuous-flow leaching of New Bedford Harbor sediment are shown in Figure 42. Chromium elution curves for aerobic permeameters were very similar to chromium elution curves for anaerobic permeameters, including initial concentrations and the appearance of a peak. Initial chromium concentrations were below 0.055 mg/ℓ, as were the initial chromium concentrations for the anaerobic permeameters. Chromium concentrations then increased to peak values between 4 and 5 pore volumes that ranged from 0.100 to 0.116 mg/ℓ. Thereafter, chromium concentrations

decreased steadily to final values ranging from 0.042 to 0.058 mg/ℓ. Chromium concentrations in leachate from the aerobic permeameters were in the same range as chromium concentrations in the anaerobic permeameters.

97. Copper concentrations during aerobic, continuous-flow leaching of New Bedford Harbor sediment are shown in Figure 43. The copper aerobic permeameter data showed a very complicated elution record. Copper concentrations increased after pH and conductivity stabilized in all three permeameters. However, the pore volumes displaced before appearance of peak values differed among permeameters and, as shown in Figure 43, copper elution records varied for the three permeameters after pH and conductivity stabilized. Copper concentrations in leachate from the aerobic permeameters were in the same range as copper concentrations in the anaerobic permeameters.

98. Iron concentrations during aerobic, continuous-flow leaching of New Bedford Harbor sediment are shown in Figure 44. Initial iron concentrations ranged from 169 to 319 mg/ℓ. As shown in Table 31, there was a one-to-one correspondence of initial iron concentration to initial pH. Iron concentrations decreased dramatically after the initial samples were collected. The pH data (Figure 38) and the iron data (Figure 44) indicate that the decrease in iron concentrations was pH controlled. Iron concentrations in the initial leachate samples from the aerobic permeameters were one to two orders of magnitude higher than the iron concentrations in the initial leachate samples from anaerobic permeameters. In subsequent samples, iron concentrations in leachate from the aerobic permeameters were in the same range as iron concentrations in the anaerobic permeameters.

99. Manganese concentrations during aerobic, continuous-flow leaching of New Bedford Harbor sediment are shown in Figure 45. The elution curves for manganese are very similar to the iron elution curves. Manganese elution curves should follow iron elution curves since the geochemistry of iron and manganese is very similar. Initial manganese concentrations ranged from 2.64 to 7.19 mg/ℓ. There was a one-to-one correspondence between initial manganese concentrations and initial pH (Table 31). After the initial samples were collected, manganese concentrations in the aerobic permeameters decreased. After pH stabilized, manganese concentrations tended to stabilize at concentrations that were in the same range as manganese concentrations in the anaerobic permeameters.

100. Nickel concentrations during aerobic, continuous-flow leaching of New Bedford Harbor sediment are shown in Figure 46. Although the correspondence of initial nickel concentration to initial pH was not one-to-one (Table 31), the pH data (Figure 38) and the nickel data (Figure 46) show that initial nickel concentrations were probably pH controlled. Initial nickel concentrations ranged from 0.159 to 23.7 mg/ℓ. Nickel concentrations decreased as the number of pore volumes of water through the permeameters increased, following the form of a classical elution curve. Final concentrations ranged from below the detection limit to 0.086 mg/ℓ. Initial nickel concentrations in aerobic permeameter leachate were higher than the maximum nickel concentrations in anaerobic permeameter leachate by factors of 2 to 500. Final nickel concentrations in aerobic and anaerobic permeameter leachates were similar.

101. Lead concentrations during aerobic, continuous-flow leaching of New Bedford Harbor sediment are shown in Figure 47. Like copper, the lead aerobic permeameter data showed a very complicated elution record. In the case of lead, however, part of the variability is related to chemical analysis near the detection limit. As with the anaerobic permeameter lead data, lead concentrations in aerobic permeameter leachates were generally at or near the detection limit (0.001 mg/ℓ). Thus, the data show that lead was not readily leached under aerobic, continuous-flow conditions.

102. Zinc concentrations during aerobic, continuous-flow leaching of New Bedford Harbor sediment are shown in Figure 48. As shown in Table 31, initial zinc concentrations were related to initial pH, but the correspondence was not one-to-one. Initial concentrations ranged from 0.13 to 1.61 mg/ℓ. Zinc concentrations decreased as pH increased, resulting in zinc concentrations at or near the detection limit (0.03 mg/ℓ) after the initial sampling. The rapid decrease in zinc concentrations suggests that zinc concentrations were pH controlled and that advection and dispersion were relatively unimportant. Except for the initial values, aerobic permeameter zinc concentrations were similar to anaerobic zinc concentrations.

103. <u>Aerobic organics.</u> The concentrations of five PCB Aroclors and total PCB in leachates from the aerobic permeameters are listed in Table 32, and the concentrations of 23 PCB congeners in aerobic permeameter leachates are listed in Table 33. Aroclors 1242 and 1254 were the predominant Aroclors in aerobic permeameter leachates. Aroclors 1016, 1221, 1232, 1248, and 1260

were below the detection limit (0.0002 mg/ℓ) in all samples. The occurrence of PCB congeners in detectable concentrations varied depending on PCB congener, pore volume sampled, and permeameter. Several of the PCB congeners (C153, C167, C180, and C185) were below the detection limit (0.00001 mg/ℓ) in most of the samples. Congener C7 was the only PCB congener below the detection limit in all the aerobic permeameter leachate samples. The predominant PCB congeners in aerobic permeameter leachate were C8, C28, and C52. Congeners C44, C50, and C77 concentrations were frequently above the detection limit (0.00001 mg/ℓ), but these were less frequently detected in substantial amounts. The penta-, hexa-, and heptachlorobiphenyls were usually at or near the detection limit (0.00001 mg/ℓ) in the aerobic permeameter leachates. Most of the PCB leached under aerobic, continuous-flow conditions was in the form of di-, tri-, and tetrachlorobiphenyls. (See Table 7 for the PCB congener identification key.)

104. Elution curves for total PCB, Aroclors 1242 and 1254, and DOC are shown in Figures 49-52. As was the case with the anaerobic PCB elution curves, the aerobic permeameter PCB data showed a complicated elution record involving the development of peaks in the elution curves. The elution curves for total PCB and Aroclor 1242 show a steady increase from initial values, which were at the detection limit (0.0002 mg/ℓ), to peak values between 2 and 4 pore volumes. The elution curve for Aroclor 1254 similarly showed an increase from the initial values, which were also at the detection limit (0.0002 mg/ℓ). The peak, however, was not as well defined as for total PCB and Aroclor 1242, and Aroclor 1254 concentrations in one permeameter were still increasing at the end of the test. The DOC concentrations tended to vary between 10 and 50 mg/ℓ. No distinct trends in the DOC elution curves were noted.

105. Elution curves for PCB congeners C28, C118, and C155 are presented in Figures 53-55. The trends displayed for these three congeners are representative of the elution curves for the PCB congener data set for aerobic, continuous-flow leaching. Elution curves for PCB congeners C28, C118, and C155 also showed the development of concentration peaks. However, peak development, overall shape, and permeameter replication were different.

106. The elution curves for PCB congener C28 (Figure 53) showed a steady increase in C28 concentration from initial values that were below the detection limit (0.00001 mg/ℓ) to peak values at around 2 pore volumes.

The PCB congener C28 concentrations then sharply decreased, and in one permeameter, the final concentration was below the detection limit. The elution curve for PCB congener C118 (Figure 54) showed initial concentrations below the detection limit. However, with increasing pore volumes, congener C118 exceeded detection limits and persisted, although with high variability, in the leachate longer than congener C28. A well-defined peak associated with a pore volume displacement was not evident in the PCB congener C118 elution curves. The elution curves for PCB congener C155 (Figure 55) showed that when concentrations reached detectable levels following the initial sampling, they tended to persist, as with PCB congener C118. The peaks in the elution curves for PCB congener C155 were better defined than those for PCB congener C118, but replication for PCB congener C155 was not as good as for PCB congener C28.

107. The increase to peak concentrations corresponds to the period following development of steady conductivity values. As previously discussed, conductivity was not measured on leachates from permeameters set up for leaching organics because the sample was at a premium, and none could be sacrificed for the conductivity analysis. The conductivity elution curves for the aerobic metals, however, can be extrapolated to represent the elution that would be expected from the aerobic permeameters for organics because the elution curves are based on the number of pore volumes of water that have contacted the sediment solids.

Summary of permeameter results

108. Lead and zinc were leached at such low levels under anaerobic, continuous-flow conditions that no trends other than insignificant release were evident. Cadmium, iron, and manganese releases under anaerobic, continuous-flow conditions followed classical elution in which concentrations monotonically decreased from initial values. Chromium, copper, and nickel showed complicated elution curves under anaerobic, continuous-flow conditions, with peaks appearing after displacement of one or more pore volumes. Peak metal concentrations under anaerobic, continuous-flow conditions are presented in Table 34.

109. Contaminant leaching in the aerobic permeameters was affected by a shift from acidic to alkaline conditions, probably due to a shift from aerobic to anaerobic conditions. Iron, manganese, and zinc leaching in the aerobic permeameters was pH controlled. Leaching of cadmium and nickel was also influenced by pH, particularly initial concentrations. As a result of low

initial aerobic permeameter leachate pH, peak concentrations of cadmium, iron, nickel, and zinc were significantly higher in leachate from aerobic permeameters than in leachate from anaerobic permeameters (Table 34). Lead was not leached in significant amounts in the aerobic permeameters. Leaching of chromium and copper in the aerobic permeameters was characterized by complicated elution curves involving the development of peaks in the elution curves as leaching proceeded.

110. Leaching of PCBs under anaerobic, continuous-flow conditions also showed complicated elution curves involving the development of peaks in the elution curves as leaching proceeded. Peak concentrations of total PCB, Aroclor 1242, and Aroclor 1254 under anaerobic, continuous-flow conditions were 0.018, 0.0121, and 0.0086 mg/ℓ, respectively (Table 34). Results from aerobic permeameters showed similar elution curves, with peaks appearing as leaching proceeded. Peak concentrations of total PCB, Aroclor 1242, and Aroclor 1254 in aerobic permeameter leachates were 0.0175, 0.0066, and 0.0033 mg/ℓ, respectively (Table 34).

111. The appearance of peaks in the elution curves indicates nonconstant sediment geochemistry and nonconstant distribution coefficients. If constant distribution coefficients existed, contaminant concentrations would never have exceeded initial values. Thus, the permeameter data show that, under continuous-flow conditions, the geochemical properties of the sediment solids changed as leaching proceeded. The correspondence of the appearance of peaks in elution curves with washout of conductivity is evidence that nonconstant geochemistry is associated with conductivity changes in the sediment. Thus, the permeameter data are consistent with the batch leach tests, which showed nonconstant distribution of contaminant between solid and dissolved phases during sequential batch leaching.

Integrated Approach

112. The integrated approach, previously described in Part III on the theoretical basis for leachate quality prediction, is a procedure for evaluating source term formulations that has not been fully developed. The basic concept of the procedure is as follows: if elution curves predicted using source term formulations based on data from sequential batch leach tests agree with observed elution curves from permeameter testing, then the theory used to

describe interphase transfer of contaminant from sediment solids to water is adequate for the development of reliable estimates of leachate quality in a CDF. When predicted and observed elution curves do not agree, a conservative approach to evaluation of leachate quality in a CDF may be required, depending on the availability of an adequate explanation for the differences in predicted and observed values.

The role of the distribution coefficient

113. Because of the central role played by distribution coefficients in the application of the integrated approach and the effort directed during this study toward determination of equilibrium distribution coefficients, a discussion of the practical significance of distribution coefficients in comparing batch and permeameter data is needed before the comparison the of predicted and observed elution curves is addressed. The role of the distribution coefficient is discussed below in terms of constant partitioning and then in terms of nonconstant partitioning.

114. Constant partitioning. Constant partitioning means that there is one contaminant- and sediment-specific distribution coefficient that describes the equilibrium distribution of contaminant between sediment solids and water. The water in contact with the solids can be pore water in a CDF or a laboratory permeameter or the water used in a sequential batch leach test. For constant partitioning, the distribution coefficient does not change during sequential leaching in a laboratory test or a CDF.

115. A constant distribution coefficient affects dissolved contaminant concentrations in two ways. First, the initial contaminant concentration in the water depends on K_d ; second, K_d controls the tendency of initial aqueous phase concentrations to persist during leaching.

116. The initial dissolved contaminant concentration before leaching is given by

$$C = \frac{q}{K_d} \tag{8}$$

where C is the equilibrium contaminant concentration in the water (mg/ℓ) and q is the solid phase contaminant concentration (mg/kg) that is in equilibrium with the water. This equation assumes that the contaminant distribution between dissolved and solid phases is controlled by equilibrium partitioning.

Equation 8 shows that the larger K_d, the lower the water contaminant concentration. As K_d approaches infinity, C approaches zero. The physical interpretation of K_d approaching infinity is that the contaminant is so strongly partitioned into the solid phase that there is no desorption. As K_d approaches zero, C becomes larger and approaches infinity. In reality, C cannot exceed the solubility limit. Although Equation 8 is undefined for K_d equal to zero, Equations 6 and 7, previously discussed, are defined for K_d equal to zero. In terms of Equations 6 and 7, the physical interpretation of K_d equal to zero is that there is no partitioning (adsorption or desorption) of contaminant between dissolved and solid phases.

117. Equation 8 also shows that as q decreases, C decreases. Thus, constant partitioning predicts that as contaminant is leached from dredged material solids, the pore water contaminant concentrations will monotonically decrease. Similarly, the contaminant concentrations in leachate from a sequential batch leach test should decrease with each cycle in the sequential leach procedure, producing a desorption isotherm such as shown in Figure 3.

118. The value of K_d also affects the tendency of initial concentrations to persist during sequential leaching, whether it be in a sequential batch leach test, a continuous-flow column leach test, or in a CDF. The larger the value of K_d, the longer the initial dissolved concentration will tend to persist. The effect of K_d on persistence is illustrated in Figure 56. In this figure, elution curves are presented for two values of K_d. As shown, the initial contaminant concentration is lower for the larger K_d. However, this concentration tends to persist while the leachate contaminant concentration for the lower value of K_d decreases.

119. In general, when the distribution coefficient is constant and greater than 100 ℓ/kg, the elution curve from a permeameter should be a flat line for an extended period. The sensitivity of the elution curve to K_d is shown in Figure 57. This figure, which was prepared for a freshwater sediment using Equation 7, indicates that no change in contaminant concentration would be expected over a reasonable study period if K_d exceeds 100 ℓ/kg.

120. Nonconstant partitioning. In Figure 14, nonconstant partitioning is represented as a changing distribution coefficient that decreases during sequential leaching with distilled water to a turning point, after which K_d is constant. For PCBs in New Bedford Harbor sediment, nonconstant partitioning is related to decreasing conductivity (salinity washout) during sequential

leaching with DDI water (Appendix A). As discussed in Appendix A, destabilization of the colloidal system associated with the sediment solids is thought to occur as conductivity decreases.

121. Theoretically, the elution curve for a contaminant with a desorption isotherm such as shown in Figure 14 should show the development of a peak that coincides with the turning point on the desorption isotherm. Thereafter, the elution curve should follow a classical elution curve since K_d is constant after the peak (or turning point). Thus, the tendency of the peak to persist depends on the value of the distribution coefficient after the turning point.

General trends in batch and permeameter leach tests

122. In the following discussion, qualitative comparisons are made between trends expected on the basis of desorption isotherms obtained from sequential batch leach tests and trends observed in permeameter tests for anaerobic New Bedford Harbor sediment. Comparisons between batch and permeameter leach tests for aerobic sediment are not discussed because leaching conditions in the aerobic batch and permeameter leach tests were not equivalent. As previously discussed, aerobic permeameters become anaerobic shortly after the initiation of the tests. Because of this shift to anaerobic conditions, leaching conditions with regard to pH and oxidation-reduction potential were substantially different from those in the aerobic sequential batch leach tests. Therefore, trends in elution curves from the aerobic permeameters were not compared with trends predicted on the basis of the aerobic sequential batch leach tests.

123. Anaerobic metals. The sequential batch leach tests showed that cadmium, chromium, copper, lead, nickel, and zinc concentrations were low in the first cycle, increased to maximum values, and then decreased (Table 17). When plotted as desorption isotherms, these data show nonconstant partitioning and turning points on the isotherms associated with the maximum metal concentrations. Figures 8 and 9 are examples. These results indicate that permeameter testing should show complicated metal elution curves that involve development of peaks.

124. Qualitatively, chromium, copper, and nickel elution curves from anaerobic permeameters (Figures 24, 25, and 28, respectively) were in good agreement with sequential batch leach tests. Concentrations increased from

initial values to peaks that were well defined relative to initial values. Cadmium, lead, and zinc (Figures 23, 29, and 30, respectively) did not elute as expected. The cadmium elution curves followed a classical elution form consistent with constant partitioning. Although lead showed an elution curve with a peak, the difference in initial and peak values was not significant. Zinc elution curves were essentially flat (concentrations were at or near the detection limit of 0.03 mg/ℓ) except for one value.

125. The concentrations of cadmium, chromium, and nickel in permeameter leachate were similar to concentrations in batch leachate. Copper, lead, and zinc concentrations in batch leachates were one to two orders of magnitude higher than in the permeameter leachates. Thus, the permeameter tests showed lower releases of copper, lead, and zinc than predicted by the batch tests. The differences are not easily explained. Differences in contaminant concentrations between batch and permeameter tests are discussed following the section on anaerobic PCBs.

126. Anaerobic PCBs. Sequential batch leach tests showed nonconstant partitioning of PCBs (increasing PCB concentration as sequential leaching proceeded) and turning points on the desorption isotherms that represented changeover to constant partitioning (Figures 12, 13, and A6). These results indicate that permeameter testing should show complicated PCB elution curves that involve development of peaks. The anaerobic permeameter PCB data are qualitatively in good agreement with the sequential batch leach tests. Peaks were observed for total PCB, Aroclor 1242, and Aroclor 1254 (Figures 31, 32, and 33, respectively). Peak development for PCB congeners was also evident (Figures 35-37).

127. The PCB concentrations in leachate from anaerobic permeameters were much lower than in leachate from the anaerobic sequential batch leach tests. For example, peak Aroclor 1242 and 1254 concentrations in batch tests were higher than peak concentrations in permeameter tests by approximately two orders of magnitude. A discussion of these differences follows.

128. Concentration differences. Contaminant concentrations in permeameter leachate were lower than the concentrations in batch leachate for most contaminants. Generally, pore water would be expected to be more contaminated than water equilibrated against suspended solids at liquid-to-solids ratios greater than the pore water-to-sediment solids ratio. A higher liquid-to-solids ratio dilutes the pore water contaminant concentrations for those

contaminants that are not partitioned or exchanged (ion-exchange). The effect of increasing the liquid-to-solids ratio on contaminants governed by partitioning and ion-exchange is given by

$$C_2 = \frac{K_d + (L/S)_1}{K_d + (L/S)_2} C_1 \qquad (9)$$

where L/S is the liquid-to-solids ratio (in litres per kilogram) and the other terms are as previously defined. The subscripts refer to different liquid-to-solids ratios, not sequential leaching. If K_d is constant and $(L/S)_2$ is greater than $(L/S)_1$, then C_2 is less than C_1; that is, the batch leachate contaminant concentrations (L/S = 4) should have been slightly less than the permeameter leachate contaminant concentration (L/S = 1).

129. The conductivity values for the second step in the sequential batch leach test (Table A1) and in the first permeameter leachate samples collected (Figure 21) were approximately the same. This implies that the distribution coefficients governing desorption in the second step of the sequential batch leach test and during the initial leaching in the permeameter should not differ widely due to differences in conductivity. If batch and permeameter distribution coefficients are similar, contaminant concentrations in the second step of the batch leach tests and the first permeameter samples should be similar. Comparison of batch and permeameter data shows that the batch concentrations are significantly higher (one or more orders of magnitude) for most contaminants, especially PCBs.

130. Several possible explanations for the differences in contaminant concentrations in batch and permeameter leachates are discussed below. No single explanation satisfactorily explains all the information available. Four explanations for the lower contaminant level in the permeameters than in the batch tests are as follows:

a. Short-circuiting in the permeameters allowed clean water to reach the bottom and dilute samples.

b. Desorption in the permeameters was not equilibrium controlled.

c. Contaminants were adsorbed by collection vessels and/or tubing leading from the permeameters to the collection vessels.

d. Batch distribution coefficients underestimate distribution coefficients applicable to permeameters.

131. It is difficult to reconcile the first explanation with all the information available. If short-circuiting were significant, then all the contaminants would have been similarly diluted. Some contaminant concentrations, however, were not reduced relative to the batch tests, and others were reduced by orders of magnitude. In addition, results from the dispersion test show that short-circuiting was not a problem (Appendix C).

132. The second explanation is not as easily discounted. For desorption in the permeameters to be equilibrium controlled, desorption must be fast with respect to pore water velocity and dispersion (Valocchi 1985). Without specific information on desorption kinetics, it is not possible to determine the maximum velocity and dispersion consistent with the local equilibrium assumption. James and Rubin (1979) concluded that the local equilibrium assumption is valid when the ratio of the hydrodynamic dispersion coefficient to the molecular diffusion coefficient is near unity. Typical molecular diffusion coefficients are on the order of 10^{-6} cm^2/sec. Several investigators, however, have shown that the local equilibrium assumption was valid where hydrodynamic dispersion was significantly greater than molecular diffusion (Valocchi 1985). Pore water velocities and dispersion coefficients in the studies reviewed by Valocchi (1985) ranged from 10^{-2} to 10^{-5} cm/sec and from 10^{-2} to 10^{-5} cm^2/sec, respectively. Average pore water velocities in the New Bedford Harbor permeameters study were on the order of 10^{-6} cm/sec, and dispersion coefficients were on the order of 10^{-6} cm^2/sec. These values are in the range that the local equilibrium assumption has been found valid, suggesting that contaminant concentrations in permeameter leachate should not differ from equilibrium values by orders of magnitude.

133. Adsorption of contaminants by experimental apparatus always occurs to some extent. Sorption by the Teflon tubing leading to the collection vessels should have been minimal. Sorption by the glass collection vessels could have been a problem. Brownawell (1986) has shown that PCB adsorption by glass laboratory apparatus can be significant. In the present study, samples remained in glass collection vessels for periods sometimes exceeding 30 days, after which they were filtered for analysis. To have extracted the collection vessels and included the extract in the sample analysis would have defeated the purpose of the filtration step. Filtration was part of the operational definition of "dissolved" used in the batch and permeameter leach tests. If the collection vessels had been extracted, solids sorbed to collection vessel

walls could have been an important source of PCB in sample collection vessel extracts. Although suspended solids were not visibly evident in permeameter leachate, deposits on the filters indicated that some solids were removed by filtration. Since suspended solids were not measured and the collection vessels were not extracted, the significance of contaminant losses by sorption to collection vessels in this study is not known and cannot be evaluated.

134. The major difficulty with the sorption explanation is that some metal concentrations in permeameter leachate were in the same concentration range as metal concentrations in batch leachate while others were not. Also, if adsorption to container walls reduced some PCB and metal concentrations by two orders of magnitude, it did not eliminate the elution trends predicted by the batch tests. If container wall sorption had been a controlling factor for permeameter leachate concentrations, the permeameter data would be expected to be more variable, showing more randomness. The sorption by experimental apparatus explanation is especially difficult to reconcile with the development of peaks. It would be more likely that sorption losses would eliminate or obscure contaminant release trends rather than confirm peak development predicted by the batch tests.

135. Differences between contaminant concentrations in batch and permeameter leach tests can also be explained as differences in equilibrium distribution coefficients. If the K_d applicable to a continuous-flow system is substantially higher than the K_d measured in a batch test, then the contaminant concentrations in the continuous-flow system will be lower than those measured in a batch test. Differences in distribution coefficients can be explained by a variety of mechanisms, all of which are related to differences in the hydraulic regime between a shake test and a column test. In a column test, the water velocity across particle surfaces and, hence, the shear are substantially reduced compared with the velocity and shear in a batch test. The vigorous shaking inherent in a batch test eliminates or significantly reduces the boundary layer around particles so that water-solids interactions are not hindered. The slower the water movement in a column test, the thicker the film thickness and the further removed the contaminant concentrations in the flowing water are from the equilibrium concentration measured in a batch test. Although film effects are usually modeled as a nonequilibrium process involving diffusion-limited mass transfer, the effect is that of applying a

distribution coefficient to the continuous-flow system which is higher than the distribution coefficient indicated by a batch test.

136. Vigorous agitation also breaks up the aggregation of particles characteristic of the in situ sediment, exposing surfaces previously within particle aggregates and dispersing colloidal material. The entire character of the solid phase is altered by increasing the number of sorption sites interacting with the aqueous phase. Thus, the difference in distribution coefficients could be due to particle disaggregation. In the absence of vigorous agitation, interstitial water extraction using centrifugation followed by filtration should provide a pore water quality comparable to the quality of the first permeameter leachate samples. Comparison of the anaerobic interstitial water data (Table 8) with the first anaerobic permeameter samples (Figures 23-33) showed fair to good agreement for metals and extremely poor agreement for PCBs. Chromium, nickel, lead, and zinc concentrations were similar. Copper was lower in permeameter samples by a factor of approximately 9, and cadmium was higher in permeameter samples by a factor of approximately 7. Interstitial water PCB concentrations were one to two orders of magnitude higher than permeameter leachate concentrations. The interstitial water and permeameter PCB data are, thus, inconsistent with a disaggregation explanation for differences in batch and permeameter data and consistent with a sorption loss explanation. The interstitial water and permeameter metals data, however, are generally consistent with a disaggregation explanation and inconsistent with a sorption loss explanation.

137. No discussion of batch-determined distribution coefficients would be complete without consideration of the literature on the solids concentration dependency of distribution coefficients. Several investigators have reported that the distribution coefficient decreases as the solids concentration in a batch test increases (O'Conner and Connolly 1980; Di Toro et al. 1982: Voice, Rice, and Weber 1983), and several explanations have been suggested for this effect (Curl and Keoleian 1984; Di Toro 1985; Gschwend and Wu 1985; Wu and Gschwend 1986). The liquid-to-solids ratio testing in this study showed a significant increase in dissolved PCB as the liquid-to-solids ratio was increased--exactly the opposite of the effect reported in the literature. As previously discussed, the effect in the present study is thought to be due to destabilization of colloidal organic matter with conductivity changes as the liquid-to-solids ratio is increased.

138. Several mechanisms are discussed above that could explain the differences in batch and permeameter data. The short-circuiting explanation can be eliminated on the basis of data presented in Appendix C. The nonequilibrium explanation is probably inadequate to account for differences of two orders of magnitude. Explanations based on hydraulic shear, disaggregation of solids, and sorption to container walls, while intuitively sound, do not adequately explain all the data. It is likely that explanations given in paragraphs 130c and d, alone or in combination, account for the differences in batch and permeameter contaminant concentrations. Since the differences in some cases are significant, further study is needed to determine the cause or causes.

Source term modeling for anaerobic PCBs

139. As previously discussed in Part III on the theoretical basis for predicting leachate quality, several approaches to modeling the source term have been proposed and evaluated. These models were formulated to describe the distribution of contaminant concentrations versus time for brief episodes of contaminant input to a clean soil or sediment column. During the desorption phase, the models simulate leaching of contaminated solids with clean water. Because constant partitioning is assumed by these models, the models predict contaminant elution from contaminated soils or sediment to follow the form of a classical elution curve; that is, contaminant concentrations monotonically decrease. These models are not, therefore, applicable to leaching of New Bedford Harbor sediment with DDI water.

140. Development and verification of a model describing the complex interplay of advection, dispersion, and nonconstant partitioning was beyond the scope of this study. However, it was possible to simulate anaerobic PCB elution during nonconstant partitioning by coupling PCB concentrations in permeameter leachate to conductivity. The development of simulated anaerobic PCB elution curves during nonconstant partitioning is outlined in Figure 58. The basic approach was to model conductivity elution for advection, dispersion, and reaction using Equation 7. From simulated conductivity values, PCB elution curves accounting for nonconstant partitioning were simulated. The details of this approach are discussed below.

141. As shown in Figure 58, one of the first steps in calculating PCB concentrations in permeameter leachate as a function of conductivity was to correlate PCB distribution coefficients and conductivity in the sequential

batch leach tests. Plots of $\ln K_d$ versus conductivity for the first five cycles in the anaerobic sequential batch leach test using DDI water (Appendix A) are shown in Figures 59-61 for total PCB, Aroclor 1242, and Aroclor 1254, respectively. Point distribution coefficients for each cycle were calculated as $K_d = q/C$ using the sediment and leachate data in Tables A8 and A9. The line of best fit in Figures 59-61 was determined using least squares analysis. Regression coefficients are provided in Table 35. The least squares model was as follows:

$$\ln K_d = A + B\ [\mathrm{COND}] \tag{10}$$

where A (ℓ/kg) and B (ℓ/kg-mmhos) are coefficients obtained by linear regression and [COND] is conductivity (mmhos). Linear regression was performed over the leach cycles representing the nonconstant partitioning region of the desorption isotherms (Tables A8 and A9 and Figure A6). For total PCB, Aroclors 1242 and 1254, and most PCB congeners, nonconstant partitioning was evident in the first five leach cycles. For highly chlorinated PCB congeners, such as C155, nonconstant partitioning was evident throughout the sequential batch leach tests.

142. The r^2 values in Table 35 indicate good correlation between $\ln K_d$ and conductivity for total PCB and Aroclors 1242 and 1254. The r^2 values in Table 35 for three selected PCB congeners (C28, C118, and C155) indicate a trend for decreasing goodness of fit with increasing chlorination.

143. Maximum leachate PCB concentrations were observed in cycle 5, the turning point on the desorption isotherm. The conductivity at the turning point in the sequential batch leach tests conducted with DDI water was approximately 0.4 mmho. Thus, Equation 10 evaluated for conductivity equal to 0.4 mmho approximates the distribution coefficient at the turning point in the batch leach tests. Since the peak concentrations in the sequential batch leach tests were significantly higher than the peak concentrations in permeameter leachate, Equation 10 with the values provided in Table 35 for A and B will underestimate the apparent distribution coefficient at the turning point in the permeameters. A more accurate model for the permeameters was achieved using the apparent K_d at the peak concentrations in the permeameters to calculate an equivalent permeameter A, denoted as A' and given by

$$A' = \frac{1}{3} \sum_{i=1}^{3} \frac{q_o}{C_{p,i}} - B\,[\mathrm{COND}_{tp}] \tag{11}$$

where

q_o = PCB concentration on the sediment solids (as given in Table 6 for anaerobic sediment)

$C_{p,i}$ = peak PCB concentration in the i^{th} permeameter (as given in Table 29)

B = change in $\ln K_d$ with respect to conductivity, ℓ/kg-mmhos (given in Table 35)

$[\mathrm{COND}_{tp}]$ = conductivity at the desorption isotherm turning point (0.4 mmho)

144. The index, i , refers to permeameter replicate number. The initial PCB concentration on the sediment solids, q_o , was used to calculate A' because the change in PCB concentration on the sediment solids during permeameter leaching was insignificant. The A' values for total PCB and Aroclors 1242 and 1254 are listed in Table 35. Using A' from the permeameter data and B from the sequential batch leach data, the equation for modeling permeameter PCB distribution coefficients as a function of conductivity is as follows:

$$\ln K_d = A' + B\,[\mathrm{COND}] \tag{12}$$

145. Conductivity in anaerobic permeameters was modeled using the computer program ONED1 (International Ground Water Modeling Center 1985) to solve Equation 7 for the system-specific inputs given in Table 36. A retardation coefficient of $R = 1.4$ was needed to model the relatively constant conductivity observed after passage of three pore volumes. (For a conservative parameter, R is equal to 1.) The value for the retardation coefficient was determined by calibrating the model to the conductivity elution curve in the anaerobic metals permeameters. Figure 62 shows predicted and observed conductivity in anaerobic metals permeameters.

146. Elution curves for total PCB and Aroclors 1242 and 1254 were simulated by using simulated conductivity in organic permeameters to calculate distribution coefficients (Equation 12), and then using the distribution

coefficients to calculate PCB concentrations (Equation 8). This simulation method was used up to the turning point conductivity value established in the batch test.

147. After the turning point, PCB elution from anaerobic organic permeameters was modeled using a complete mix equation (Equation 13 below).

$$C = C_I \exp \left[\left(1 + \frac{\rho K_d}{\theta} \right)^{-1} \left(-PV \right) \right] \tag{13}$$

where

C_I = initial concentration

ρ = 0.6676 bulk density, kg/ℓ

θ = porosity = 0.7159, dimensionless

PV = pore volumes displaced after the turning point, dimensionless

The other terms are as previously defined; however, since Equation 13 models PCB elution after the turning point, C_I is assigned the simulated peak value. Two types of simulations were made using Equation 13. One simulation modeled no desorption ($K_d = 0$), and one modeled desorption using slope-derived distribution coefficients from the sequential batch leach tests (Table 37). Slope- and point-derived distribution coefficients, as defined in Figure 3, calculated from cycles 5, 6, and 7 for the sequential batch leach tests conducted with DDI water (Tables A8 and A9), are listed in Table 37 for total PCB and Aroclors 1242 and 1254. Predicted and observed elution curves for total PCB, Aroclor 1242, and Aroclor 1254 are shown in Figures 63-65.

148. The predicted elution curves during nonconstant partitioning are in relatively good agreement with the observed elution curves. There were some differences in location of the peaks on the elution curves and in predicted and observed peak values for Aroclor 1254. The peak concentrations on the simulated elution curves were slightly delayed compared with the observed peak concentrations. The predicted peak value for Aroclor 1254 was lower than two of the observed values because one of the replicate permeameter values used to calculate A' for Aroclor 1254 was low relative to the other two replicates. The predicted and observed peak concentrations for total PCB and Aroclor 1242 were in good agreement.

149. After the turning point, the no-desorption ($K_d = 0$) simulations were in better agreement with the observed elution curves than simulations made using slope-derived distribution coefficients. Simulations using point-derived distribution coefficients (not shown) indicated that after the turning point is reached, the PCB concentrations in permeameter leachate would remain at the peak value for hundreds of pore volumes. Thus, slope-derived distribution coefficients for PCB desorption after the turning point are in better agreement with the observed data than point-derived distribution coefficients, and a no-desorption model is in better agreement with observed data after the turning point than a desorption model using slope-derived distribution coefficients.

150. As previously discussed, the tendency of peak concentrations to persist depends on the distribution coefficients applicable after the turning point. Qualitatively, the observed PCB elution curves after the turning point are in agreement with the sequential batch leach data because PCB concentrations in permeameter leachates decrease after reaching peak values. Quantitatively, the agreement is not good after the turning point because distribution coefficients from the sequential batch leach tests indicate that peak concentrations should have persisted longer. The differences between batch and permeameter PCB data after peak values are reached suggest fundamental differences in PCB desorption for these tests.

Source term modeling for anaerobic metals

151. The integrated approach could not be applied to anaerobic metals leaching for several reasons. Cadmium, lead, and zinc anaerobic elution curves did not show the peaks that the sequential batch leach tests indicated should have developed. Although the anaerobic permeameter data for chromium, copper, and nickel were consistent with anaerobic sequential batch leach data, the apparent correlation of peak development with conductivity elution was not verified in the subsequent study of factors affecting desorption properties of New Bedford Harbor sediment (Appendix A). The sequential batch leach tests described in Appendix A showed that the nonconstant partitioning of metals was not necessarily related to conductivity changes. Thus, correlation of selected metal leaching with conductivity elution would be strictly empirical. A deterministic approach to source term modeling of metals leaching from New

Bedford Harbor sediment could not be developed from the data obtained in this study.

Application of Results to CDF Evaluation

152. Part of the evaluation of CDF alternatives for New Bedford Harbor sediment involves estimation of the quantity and quality of water that seeps through dikes and foundation materials after filling has been completed. Seepage of contaminated pore water is generally referred to as leaching. To estimate losses by leaching, information is needed on leachate flow and quality. This report provides information on leachate quality. Leachate flow, which is dependent on site-specific hydraulic gradients and characteristics of the dike and foundation materials, is not addressed in this report.

153. The leachate data in this report fall into two major categories according to leaching conditions (anaerobic and aerobic leach tests) and two subcategories according to type of test (batch and permeameter leach tests). The aerobic and anaerobic leach tests were designed to provide information on leaching potential for different oxidation-reduction conditions. In general, the batch and permeameter leach tests were not intended to simulate fundamentally different conditions. The aerobic permeameter tests, however, more closely simulated anaerobic leaching of previously oxidized dredged material. Thus, the permeameter aerobic leaching tests should not be used to evaluate aerobic leaching of oxidized dredged material. In addition, anaerobic leach data showed significant differences between batch and permeameter leach tests. According to one of several possible explanations discussed earlier, these differences are possibly associated with differences in the aggregation of sediment solids. Since the method of dredging affects particle aggregation, batch and permeameter leach tests may simulate leaching for different methods of dredging and disposal. The batch tests more closely simulate contaminant leaching for hydraulic dredging and disposal than permeameter tests.

154. Neither hydraulic nor mechanical dredging adds sufficient oxygen to overcome the sediment oxygen demand of polluted sediments. As a result, the dredged material in a CDF is anaerobic, except for a surface crust that develops as the CDF dewaters by evaporation and seepage. The oxidized crust may eventually be several feet thick, but, in general, oxidized crust never represents a significant portion of the vertical dredged material profile in

fine-grained dredged material. The aerobic leach data, therefore, have limited applicability to estimating contaminant loss by leaching from a filled CDF unless the site is completely oxidized.

155. If the CDF is not capped with clean material, the aerobic sequential batch leach data describe leachate quality for flow through an oxidized crust. These data are provided in Tables 20 and 27 for metals and PCBs, respectively. The aerobic permeameter data describe leaching if the crust is flooded and anaerobic conditions are reestablished. These data are provided in Figures 41-48 for metals and Figures 49-51 for total PCB, Aroclor 1248, and Aroclor 1254, respectively. The PCB congener-specific concentrations are provided in Table 33.

156. Since the batch tests are a closer physical model of the agitation provided by hydraulic dredging than the permeameter tests, anaerobic sequential batch leach data should be used to estimate leachate quality for anaerobic seepage through the bottom and dikes of a CDF containing hydraulically dredged New Bedford Harbor material. For PCBs, the conductivity-K_d relationships developed using anaerobic batch leach tests conducted with DDI water can be used to estimate PCB concentrations as rainfall infiltrates the dredged material and displaces saline pore water. This will involve using appropriate field pore water velocity and dispersion to simulate conductivity elution, as well as Equations 10 and 8 and the coefficients provided in Table 35 to calculate PCB concentrations as a function of pore volumes displaced. A consolidation model can be run to account for reduction in porosity and hydraulic conductivity as the dredged material consolidates.

157. Leachate flow will be greatest during initial dewatering by drainage of excess pore water and should substantially decrease after the drainable water has been released. Since the conductivity of the drainable water released during seepage consolidation should be relatively constant, the contaminant concentrations in the first cycle of the anaerobic sequential batch leach tests should be used to estimate leachate quality as the site dewaters by drainage of pore water initially present. These data are provided in Tables A4 and A11. After infiltration begins to make a significant contribution to leachate flow, the effects of conductivity washout on contaminant leachate concentrations should be taken into account. This approach will couple the peak PCB concentrations with lowest flow. The tendency for peak

concentration to persist should be modeled using the slope-derived distribution coefficients provided in Table 37.

158. An approach similar to the one recommended for PCBs can be used to estimate metals concentrations as infiltration displaces saline pore water, although the conductivity-metal relationships will have to be developed by the user. The user should realize the limitations of extrapolations that do not have a deterministic foundation. An alternative would be to use metal concentrations in the anaerobic sequential batch leach tests conducted with DDI water as a direct indication of leachate quality. In this case, each cycle in the sequential batch leach tests represents passage of approximately 4 pore volumes.

PART V: SUMMARY AND CONCLUSIONS

Summary

159. State-of-the-art batch and column leach tests were conducted on anaerobic and aerobic New Bedford Harbor sediment. Batch testing included kinetic tests to determine the time required for dissolved contaminant concentrations to stabilize in batch tests, liquid-to-solids ratio tests to determine the appropriate liquid-to-solids ratio to use in batch tests, and sequential batch leach tests to obtain desorption isotherms and determine distribution coefficients. Column leach tests were conducted in divided-flow permeameters designed to minimize wall effects. Desorption isotherms from sequential batch leach tests and elution curves from permeameter leach tests were used in an integrated approach to obtain information on contaminant release characteristics of New Bedford Harbor sediment.

160. Kinetic tests showed that a 24-hr shaking time was sufficient to attain steady-state contaminant leachate concentrations for most metals and all PCBs. A liquid-to-solids ratio of 4:1 (by weight) was determined to be appropriate for conducting batch leach tests on New Bedford Harbor sediment. Dissolved PAHs were below the detection limit in all batch and permeameter leachates analyzed for PAHs.

161. Anaerobic PCB desorption isotherms showed nonconstant partitioning (negative slopes) to a critical value referred to in this report as the turning point. After the turning point, PCB desorption tended to follow classical, linear partitioning. Sequential leaching with saline water showed that the nonconstant partitioning portion of the PCB desorption isotherms was associated with changing conductivity and, hence, salinity.

162. The shape of observed PCB elution curves from anaerobic permeameter leach tests agreed with the shape of elution curves predicted on the basis of the desorption isotherms. The PCB concentrations in the permeameter tests were significantly lower than PCB concentrations in batch leach tests. Several explanations for concentration differences were discussed, including loss of contaminants by adsorption to container walls and particle disaggregation effects related to differences in hydraulic regimes in batch and column testing.

163. Polychlorinated biphenyl elution in permeameters up to the turning point could be modeled using conductivity-PCB distribution coefficient correlations developed primarily from sequential batch leach tests and modified for apparent permeameter distribution coefficients.

164. After the turning point, models of PCB desorption using batch distribution coefficients showed that slope-derived distribution coefficients were more successful in reproducing observed PCB elution curves than single-point distribution coefficients. Models based on no desorption, however, were in better agreement with observed PCB elution after the turning point than models that included desorption.

165. Anaerobic metal desorption isotherms also showed nonconstant partitioning, and some metals showed a turning point followed by classical, linear partitioning. Sequential leaching with saline water showed that nonconstant partitioning of metals was apparently independent of conductivity.

166. The shape of observed metal elution curves from anaerobic permeameter leach tests agreed with the shape of elution curves expected on the basis of batch desorption isotherms for some metals, but for other metals there was no agreement. For some metals, concentrations in permeameter leachate were in good agreement with concentrations in batch leachate, and for other metals, concentrations in permeameter leachate were lower than concentrations in batch leachate.

167. Sequential batch leach tests with aerobic sediment indicated that large quantities of nickel and zinc will be present in leachate from aerobic sediment. Because aerobic permeameter leach tests did not entirely satisfy aerobic leach testing objectives, aerobic batch and permeameter data were not compared.

168. The leachate data in this report provide the basis for predicting leachate quality under anaerobic and aerobic conditions in a confined disposal facility for dredged material from New Bedford Harbor. Contaminant concentrations as water infiltrates and displaces pore water can be estimated using correlations and data provided in this report as follows:

- a. For hydraulically dredged and disposed sediment, information from anaerobic sequential batch leach tests should be used to develop estimates of leachate quality.
- b. Conductivity-distribution coefficient correlations provide reliable estimates of PCB concentrations as saline pore water is displaced by infiltration. Simulation of conductivity

elution in the CDF will be required if the conductivity-distribution coefficient correlations are used.

c. Metal concentrations can be estimated using an approach similar to the one recommended for PCBs, or the leachate data in this report can be used as a direct indication of leachate quality.

Conclusions

169. A diversity of chemical interactions related to the chemical complexity of New Bedford Harbor sediment influence interphase transfer of contaminants from sediment solids to water. To some extent, these interactions are affected by fluid mechanics. As a result, there are numerous multicomponent sediment-water interactions, possibly dependent on the hydraulic regime in which the interactions take place, that make it impossible to determine a single set of intrinsic desorption parameters that describe both batch and permeameter leach tests. Determination of a unique set of intrinsic desorption coefficients does not appear possible for New Bedford Harbor sediment. Specific conclusions are provided below:

a. The PAHs do not leach in detectable amounts from New Bedford Harbor sediment.

b. Desorption of PCBs and metals from New Bedford Harbor sediment does not follow classical partitioning theory. The assumption of equilibrium-controlled, linear desorption with constant partitioning is not generally applicable to modeling leaching of contaminants from New Bedford Harbor sediment.

c. Correlation of PCB distribution coefficients with conductivity is a useful tool for making broad generalizations about PCB leaching from New Bedford Harbor sediment. Conductivity-distribution coefficient correlations provide reliable models for predicting PCB elution up to a critical point referred to in this report as the turning point.

d. Interphase transfer of metals from New Bedford Harbor sediment solids to water is more complicated than PCB interphase transfer. A sound theoretical basis for deterministic modeling of metal elution from New Bedford Harbor sediment is not available.

e. There remain many unanswered questions about the ability of currently available theory to model multicomponent interactions that are dependent on prior elution history.

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Table 1

Experimental Sequence for Determining Appropriate Shaking Times in New Bedford Kinetic Testing

Step 1	PLACE SEDIMENT IN APPROPRIATE CENTRIFUGE TUBE (STAINLESS STEEL OR POLYCARBONATE), ADD SUFFICIENT DEOXYGENATED-DISTILLED WATER TO MAINTAIN WATER-TO-SEDIMENT RATIO OF 4:1.
Step 2	PLACE CENTRIFUGE TUBES FOR METALS HORIZONTALLY ON SHAKER AND SHAKE AT 160 CYCLES PER MINUTE. PLACE CENTRIFUGE TUBES FOR ORGANIC CONTAMINANTS IN ROTARY MIXER AND TURN AT 40 REVOLUTIONS PER MINUTE.
Step 3	REMOVE TUBES (ENOUGH FOR TRIPLICATE SAMPLES FOR ORGANICS AND QUADRUPLICATE SAMPLES FOR METALS) FROM SHAKER AT APPROPRIATE INTERVALS: 1, 2, AND 7 DAYS FOR ORGANIC CONTAMINANTS, AND 1, 2, 4, AND 7 DAYS FOR METALS.
Step 4	CENTRIFUGE FOR 30 MINUTES AT 6,500 × g FOR ORGANICS AND 9,000 × g FOR METALS.
Step 5	FILTER CENTRIFUGED LEACHATE THROUGH A 0.45-μm PORE SIZE MEMBRANE FILTER FOR METALS, AND THROUGH A WHATMAN GF/D GLASS-FIBER PREFILTER AND A GELMAN AE GLASS-FIBER FILTER FOR 1-μm NOMINAL PORE SIZE FOR ORGANICS.
Step 6	ACIDIFY LEACHATE FOR ORGANIC ANALYSIS WITH HCl AND LEACHATE FOR METALS WITH ULTREX NITRIC ACID. STORE LEACHATE FOR ORGANIC ANALYSIS IN ACETONE-RINSED GLASS BOTTLES AND LEACHATE FOR METALS ANALYSIS IN PLASTIC BOTTLES.

Table 2

Test Sequence for Determining the Appropriate Liquid-to-Solids Ratio for Use During Batch Testing Procedures

Step 1	PLACE SEDIMENT IN APPROPRIATE CENTRIFUGE TUBES: 250-ml POLYCARBONATE FOR METALS AND 450-ml STAINLESS STEEL FOR ORGANIC CONTAMINANTS. ADD WATER TO EACH TUBE TO BRING FINAL WATER-TO-SEDIMENT RATIO TO 4:1, 10:1, 20:1, 30:1, 40:1, 50:1, AND 100:1. FOR AEROBIC SEDIMENT, THE 20:1 AND 40:1 WATER-TO-SEDIMENT RATIO TESTS WERE DELETED.
Step 2	MIXTURES FOR METAL ANALYSIS WERE THEN SHAKEN HORIZONTALLY AT 160 CYCLES PER MINUTE FOR 24 HR. MIXTURES FOR ORGANIC CONTAMINANT ANALYSIS WERE PLACED IN A ROTARY MIXER AND TURNED AT 40 REVOLUTIONS PER MINUTE FOR 24 HR.
Step 3	CENTRIFUGE FOR 30 MIN AT 6,500 × g FOR ORGANICS AND 9,000 × g FOR METALS.
Step 4	FILTER LEACHATE THROUGH 0.45-µm MEMBRANE FILTERS FOR METALS OR THROUGH A WHATMAN GD/F GLASS-FIBER PREFILTER FOLLOWED BY PASSAGE THROUGH A GELMAN AE GLASS-FIBER FILTER OF 1.0-µm NOMINAL PORE SIZE FOR ORGANICS.
Step 5	ACIDIFY LEACHATE FOR ORGANIC ANALYSIS WITH HCl AND LEACHATE FOR METALS ANALYSIS WITH ULTREX NITRIC ACID. STORE LEACHATE FOR ORGANIC ANALYSIS IN ACETONE-RINSED GLASS BOTTLES AND LEACHATE FOR METALS ANALYSIS IN PLASTIC BOTTLES.

Note: The anaerobic integrity of the sample was maintained during sample addition to centrifuge tubes, shaking, centrifugation, and filtration.

Table 3

Test Sequence for Sequential Batch Leaching of Anaerobic New Bedford Sediment for Metals and Organic Contaminant Analysis

Step 1	LOAD SEDIMENT INTO APPROPRIATE CENTRIFUGE TUBES: 250-ml POLYCARBONATE FOR METALS AND 450-ml STAINLESS STEEL FOR ORGANIC CONTAMINANTS. ADD SUFFICIENT WATER TO EACH TUBE TO BRING FINAL WATER-TO-SEDIMENT RATIO TO 4:1. SUFFICIENT STAINLESS STEEL TUBES MUST BE LOADED TO OBTAIN ENOUGH LEACHATE FOR ANALYSIS.
Step 2	GO THROUGH STEPS 2, 3, AND 4 IN TABLE 2, SETTING ASIDE A SMALL AMOUNT OF LEACHATE PRIOR TO ACIDIFICATION FOR ANALYSIS OF pH AND CONDUCTIVITY.
Step 3	RETURN TO STEP 2 AFTER REPLACING LEACHATE REMOVED IN THE INITIAL SET OF CENTRIFUGE TUBES WITH DEOXYGENATED-DISTILLED WATER. REPEAT THE ENTIRE PROCEDURE THE DESIRED NUMBER OF TIMES.

Notes: Testing sequence is the same for aerobic sediments except that anaerobic integrity is not maintained.

Table 4

Concentration of Metals in New Bedford Sediment (Dry Weight Basis)

Metal	Concentration, mg/kg
As	8.66 (0.24)*
Cd	35.4 (0.25)
Cr	754 (9)
Cu	1,730 (21)
Pb	2,013 (239)
Hg	2.59 (0.03)
Ni	122 (1.8)
Se	<0.49
Zn	3,017 (22)

* Standard error in parentheses.

Table 5

Concentration of PAH Compounds in Replicate Anaerobic and Aerobic New Bedford Sediment

Compound	Concentration, mg/kg	
	Anaerobic	Aerobic*
Naphthalene	<4.6	<2.5
Acenaphthylene	<4.6	<2.5
Acenaphthene	<4.6	<2.5
Fluorene	<4.6	<2.5
Phenanthrene	9.6 (0.3)**	8.8 (0.1)
Anthracene	<4.6	<2.5
Fluoranthene	8.7 (0.1)	15.6 (0.1)
Pyrene	7.1 (0.3)	13.5 (0.4)
Chrysene	7.5 (0.6)	8.9 (0.3)
Benzo (A) Anthracene	7.5 (0.6)	8.3 (0.1)
Benzo (B) Fluoranthene	11.8 (1.3)	12.0 (0.8)
Benzo (K) Fluoranthene	11.8 (1.3)	12.0 (0.8)
Benzo (A) Pyrene	7.6 (0.1)	6.4 (0.4)
Indeno(1,2,3-C D)Pyrene	<4.6	<2.5
Dibenzo(A H)Anthracene	<4.6	<2.5
Benzo(G H I)Perylene	<4.6	<2.5

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* After 3 months of exposure to air (see text for details).

** Standard error in parentheses.

Table 6

Total Sediment Concentrations of PCBs (Triplicate Analyses) in New Bedford Sediment (Dry Weight Basis)

Parameter*	Sediment Concentration, mg/kg dry weight Anaerobic	 Aerobic
PCB Congeners		
C7	0.56 (0.01)*	0.32 (0.000)
C8	165.7 (3.79)	84.5 (0.50)
C28	153.0 (5.29)	73.0 (3.0)
C44	84.1 (3.52)	30.0 (1.0)
C49	28.0 (0.85)	14.0 (1.0)
C50	153.0 (5.29)	75.0 (3.0)
C52	176.7 (9.29)	75.0 (3.0)
C70	59.2 (3.29)	23.0 (2.0)
C77	146.7 (3.36)	<1
C82	24.3 (1.21)	<1
C87	8.2 (0.41)	35.4 (2.4)
C97	22.9 (1.13)	18.5 (3.5)
C101	70.4 (4.29)	31.0 (4.0)
C105	36.7 (0.88)	19.0 (1.0)
C118	29.6 (1.31)	15.0 (2.0)
C136	17.1 (0.53)	14.0 (2.0)
C138	25.1 (0.61)	15.0 (2.0)
C143	24.7 (0.88)	4.3 (2.1)
C153	56.7 (3.07)	13.0 (7.1)
C155	50.0 (1.0)	37.0 (3.0)
C167	19.2 (2.75)	4.0 (2.0)
C180	7.94 (1.64)	1.7 (0.1)
C185	<1	<1
Aroclors		
A1242	887 (67)	721 (39)
A1254	662 (62)	450 (30)
Total PCB	2,167 (34)	1,250 (80)

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* Standard error in parentheses.

Table 7

PCB Congener Identification Key Used in This Report

IUPAC* Number	Compound
C7	2,4-dichlorobiphenyl
C8	2,4'-dichlorobiphenyl
C28	2,4,4'-trichlorobiphenyl
C44	2,2',3,5'-tetrachlorobiphenyl
C49	2,2',4,5'-tetrachlorobiphenyl
C50	2,2',4,6-tetrachlorobiphenyl
C52	2,2',5,5'-tetrachlorobiphenyl
C70	2,3',4',5-tetrachlorobiphenyl
C77	3,3',4,4'-tetrachlorobiphenyl
C82	2,2',3,3',4-pentachlorobiphenyl
C87	2,2',3,4,5'-pentachlorobiphenyl
C97	2,2',3',4,5-pentachlorobiphenyl
C101	2,2',4,5,5'-pentachlorobiphenyl
C105	2,3,3',4,4'-pentachlorobiphenyl
C118	2,3',4,4',5-pentachlorobiphenyl
C136	2,2',3,3',6,6'-hexachlorobiphenyl
C138	2,2',3,4,4',5'-hexachlorobiphenyl
C143	2,2',3,4,5,6'-hexachlorobiphenyl
C153	2,2',4,4',5,5'-hexachlorobiphenyl
C155	2,2',4,4',6,6'-hexachlorobiphenyl
C167	2,3',4,4',5,5'-hexachlorobiphenyl
C180	2,2',3,4,4',5,5'-heptachlorobiphenyl
C185	2,2',3,4,5,5',6-heptachlorobiphenyl

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* International Union of Pure and Applied Chemists.

Table 8

Interstitial Water Metal, PCB, and TOC Concentrations* in Anaerobic and Aerobic New Bedford Sediment

Parameter	Anaerobic Sediment	Aerobic Sediment
As	<0.005	NT**
Cd	0.0002 (0.00003)	NT
Cr	0.012 (0.001)	NT
Cu	0.009 (0.001)	NT
Pb	<0.001	NT
Ni	0.014 (0.005)	NT
Zn	0.035 (0.003)	NT
C7	0.00057 (0.00046)	0.0002 (0.00001)
C8	<0.00001	<0.00001
C28	0.054 (0.002)	0.067 (0.0037)
C44	0.014 (0.0006)	0.017 (0.0007)
C49	0.0048 (0.0002)	0.006 (0.0003)
C50	0.048 (0.0018)	0.058 (0.0026)
C52	0.031 (0.0012)	0.039 (0.002)
C70	0.011 (0.0006)	0.013 (0.0007)
C77	<0.00001	<0.00001
C82	0.0053 (0.0008)	<0.00001
C87	0.012 (0.0005)	0.002 (0.00007)
C97	0.0055 (0.0002)	0.007 (0.0003)
C101	0.013 (0.0006)	0.016 (0.0007)
C105	<0.00001	<0.00001
C118	0.010 (0.0006)	0.013 (0.0007)
C136	0.003 (0.0001)	0.004 (0.0001)
C138	0.0044 (0.0001)	0.006 (0.0002)
C143	0.005 (0.0002)	0.007 (0.0003)
C153	0.0097 (0.0002)	0.013 (0.0006)
C155	0.009 (0.0003)	0.011 (0.0007)
C167	0.0011 (0.0001)	0.0012 (0.00006)
C180	0.0013 (0.00007)	0.0016 (0.00007)
A1242	0.380 (0.015)	0.487 (0.023)
A1254	0.193 (0.012)	0.253 (0.012)
TPCB	0.607 (0.028)	0.793 (0.032)
TOC	114.5 (9.3)	46.7 (0.03)

---

* Expressed in milligrams per litre (standard error in parentheses).

** Not tested.

Table 9

Release of Metals into Leachate As a Function of Shaking Time*

Metal	Time of Shaking, days			
	1	2	4	7
As	17 (0.7)	12 (2)	<0.01	<0.01
Cd	1.1 (0.4)	0.9 (0.5)	1.3 (0.1)	1.6 (0.2)
Cr	23 (2)	25 (5)	43 (3)	69 (6)
Cu	29 (1)	30 (4)	51 (3)	83 (21)
Pb	22 (4)	24 (1)	34 (1)	44 (3)
Ni	12 (1)	13 (2)	15 (1)	16 (1)
Zn	32 (4)	60 (22)	316 (242)	359 (241)

* Concentrations expressed in micrograms per litre (standard error in parentheses).

Table 10

Release of Organic Contaminants into Leachate As a Function of Shaking Time*

Parameter	Time of Shaking, Days		
	1	2	7
C7	0.00003 (0.00002)	0.00006 (0.000)	0.00002 (0.00002)
C8	0.012 (0.008)	0.028 (0.006)	0.021 (0.013)
C28	0.036 (0.008)	0.044 (0.001)	0.043 (0.012)
C44	0.017 (0.001)	0.016 (0.0008)	0.019 (0.002)
C49	0.006 (0.001)	0.005 (0.0001)	0.004 (0.001)
C52	0.053 (0.015)	0.036 (0.001)	0.038 (0.006)
C70	0.004 (0.00005)	0.004 (0.0001)	0.006 (0.0008)
C77	0.068 (0.009)	0.084 (0.009)	0.109 (0.015)
C87	0.0018 (0.0013)	0.0005 (0.00001)	0.0042 (0.002)
C97	0.009 (0.002)	0.007 (0.0006)	0.009 (0.001)
C101	0.014 (0.0006)	0.013 (0.0003)	0.014 (0.002)
C118	0.0024 (0.00005)	0.002 (0.00005)	0.002 (0.0004)
C136	0.001 (0.00004)	0.0009 (0.0001)	0.001 (0.0003)
C138	0.007 (0.001)	0.006 (0.001)	0.008 (0.0005)
C153	0.054 (0.018)	0.064 (0.021)	0.087 (0.007)
C155	0.0137 (0.0027)	0.0107 (0.0003)	0.012 (0.0024)
C167	0.0005 (0.00008)	0.00033 (0.00001)	0.0003 (0.00004)
C180	0.003 (0.002)	0.0004 (0.00001)	0.0004 (0.00005)
A1242	0.400 (0.036)	0.446 (0.020)	0.460 (0.070)
A1252	0.323 (0.041)	0.370 (0.000)	0.390 (0.079)
TPCB	0.810 (0.115)	0.726 (0.035)	0.830 (0.125)

* Concentrations expressed in milligrams per litre (standard error in parentheses).

Table 11

Summary Data for Steady-State Sediment Concentrations Versus Steady-State Leachate Concentrations for Metal Desorption at Varying Water-to-Sediment Ratios

Metal	r^2 Value	Probability <	Slope
As	ND*	ND	ND
Cd	0.892	0.0001	-36.22
Cr	0.673	0.0001	-17.59
Cu	0.587	0.003	-22.90
Pb	0.491	0.001	-16.84
Ni	0.567	0.0003	-49.89
Zn	0.438	0.003	-27.93

* Not defined.

Table 12

Summary Data for Steady-State Sediment Concentrations Versus Steady-State Leachate Concentrations for Metal Desorption from Aerobic New Bedford Sediment at Varying Water-to-Sediment Ratios

Metal	r^2 Value	Probability <	Slope
As	0.593	0.0008*	52.79
Cd	0.049	0.424	-9.84
Cr	0.532	0.002*	-67.34
Cu	0.536	0.002*	-68.08
Pb	0.184	0.111	-11.05
Ni	0.444	0.007*	4.32
Zn	0.095	0.263	5.21

* Statistically significant difference.

Table 13

Summary of Mean Anaerobic New Bedford Batch Leaching Results for Differing Water-to-Sediment Ratios for PCBs

Parameter	r^2	P <	Slope
C7	0.293	0.268	-51.08
C8	0.312	0.249	-44.07
C28	0.044	0.680	-19.40
C44	0.674	0.045*	-108.40
C49	0.271	0.289	-57.55
C52	0.178	0.404	-48.47
C70	0.305	0.256	-47.28
C77	0.263	0.289	-31.08
C87	0.739	0.028*	-25.20
C97	0.327	0.236	-75.64
C101	0.328	0.234	-71.15
C105	0.969	0.0003*	-84.37
C118	0.641	0.050*	-86.33
C136	0.593	0.073	-21.76
C138	0.842	0.010*	-112.36
C153	0.726	0.031*	-106.06
C155	0.752	0.025*	-116.30
C167	0.389	0.185	-36.2
C180	0.990	0.001*	-106.80
A1242	0.719	0.033*	-136.20
A1254	0.453	0.143	-112.44

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* Statistically significant relationship.

Table 14

Summary of Mean Aerobic New Bedford Batch Leaching Results for Differing Water-to-Sediment Ratios for PCBs

Parameter	r^2	P <	Slope
C7	0.986	0.0001*	-112.37
C8	0.364	0.049*	31.54
C28	0.530	0.003*	70.98
C44	0.561	0.002*	56.22
C49	0.705	0.0002*	78.29
C50	0.389	0.017*	65.97
C52	0.715	0.0001*	76.13
C70	0.237	0.078	63.55
C77	0.706	0.0002*	-137.09
C82	0.017	0.701	10.99
C87	ND**	ND	ND
C97	0.193	0.116	49.21
C101	0.499	0.005*	79.67
C105	0.014	0.734	2.63
C118	0.116	0.232	-50.91
C136	0.024	0.597	5.73
C138	0.511	0.004*	23.14
C143	0.010	0.740	-9.70
C153	0.087	0.304	16.41
C155	0.991	0.0001*	-110.82
C167	0.145	0.177	-12.04
C180	0.179	0.132	-18.87
C185	0.930	0.0001	-102.37
A1242	0.275	0.054	77.26
A1254	0.565	0.002*	-104.89
TPCB	0.520	0.004*	112.04

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* Statistically significant relationship.

** Not defined.

Table 15

Leachate pH Measured in New Bedford Sequential Batch Leachate Testing

Sequential Leach Number	Anaerobic	Aerobic
1	7.2 (0.01)*	6.2 (0.05)
2	7.3 (0.1)	3.7 (0.3)
3	7.1 (0.05)	2.1 (0.3)
4	7.6 (0.05)	4.2 (0.2)
5	7.4 (0.06)	5.7 (0.1)
6	6.7 (0.06)	5.7 (0.1)
7	6.5 (0.03)	--

* Standard error in parentheses.

Table 16

Steady-State Heavy Metal Sediment Concentrations* in Anaerobic New Bedford Sediment

	Sequential Leach Number						
Metal	1	2	3	4	5	6	7
As	8.62	8.61	8.60	8.56	8.53	8.51	8.51
Cd	39.40	35.38	35.34	35.27	35.24	35.19	35.16
Cr	753.9	753.5	752.5	751.1	750.4	749.5	748.8
Cu	1,729.9	1,729.0	1,727.4	1,718.3	1,714.3	1,710.0	1,707.4
Pb	2,012.5	2,012.5	2,011.5	2,009.9	2,009.2	2,008.2	2,007.9
Ni	122.0	121.9	121.7	121.4	121.2	121.0	120.8
Zn	3,016.7	3,015.4	3,010.9	3,003.9	2,999.8	2,995.1	2,987.8

* Expressed in milligrams per kilogram.

Table 17

Heavy Metal Concentrations* in Leachate from Anaerobic New Bedford Sediment

	Sequential Leach Number													
Metal	1		2		3		4		5		6		7	
As	10.3	(1.40)	1.30	(1.30)	4.30	(1.43)	9.30	(1.10)	7.30	(0.30)	4.80	(2.80)	0.00	(0.00)
Cd	0.22	(0.13)	4.32	(0.40)	9.22	(1.04)	14.6	(1.40)	10.8	(0.60)	12.4	(1.70)	8.40	(1.64)
Cr	16.8	(1.10)	103.0	(8.10)	261.0	(29.7)	356.5	(7.84)	173.8	(6.30)	225.3	(80.2)	160.5	(51.6)
Cu	27.5	(0.90)	222.5	(19.1)	394.8	(220.7)	285.0	(2.64)	1,006	(105.2)	1,058	(380.7)	656.0	(232.8)
Pb	15.5	(0.90)	100.0	(10.2)	272.3	(55.2)	398.5	(7.20)	173.0	(19.1)	236.3	(109.7)	71.0	(16.3)
Ni	11.0	(1.41)	22.0	(3.80)	43.0	(7.60)	65.5	(8.14)	59.5	(5.80)	49.5	(5.83)	52.3	(3.20)
Zn	70.8	(26.9)	339.0	(20.8)	1,118	(171.2)	1,750	(293.5)	1,014	(59.1)	1,173	(363.0)	1,828	(298.03)

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* Expressed in micrograms per litre (standard error in parentheses).

Table 18

Summary of Sequential Batch Leaching Sediment and Leachate Steady-State Relationships for Metals in Anaerobic New Bedford Sediment

Metal	r^2 Value	Probability <	Slope
As	0.002	0.929	0.450
Cd	0.393	0.0004*	-11.05
Cr	0.239	0.008*	-7.35
Cu	0.298	0.0026*	-6.37
Pb	0.154	0.04*	-5.09
Ni	0.463	0.0001*	-13.72
Zn	0.513	0.0001*	-10.15

* Statistically significant relationship.

Table 19

Steady-State Heavy Metal Concentrations* in Aerobic New Bedford Sediment

	Sequential Leach Number					
Metal	1	2	3	4	5	6
As	8.59	8.52	8.45	8.38	8.32	8.29
Cd	35.38	35.31	35.21	34.93	34.15	33.03
Cr	753.9	753.8	753.0	752.5	752.3	752.2
Cu	1,729.9	1,729.8	1,729.5	1,729.1	1,728.9	1,728.4
Pb	2,013.0	2,012.9	2,012.9	2,012.8	2,012.8	2,012.7
Ni	116.8	115.0	113.4	111.3	108.8	105.0
Zn	2,961.8	2,913.9	2,862.1	2,776.0	2,632.5	2,483.4

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* Expressed in milligrams per kilogram.

Table 20

Heavy Metal Concentrations* in Leachate from Aerobic New Bedford Sediment

Metal	Sequential Leach Number 1	2	3	4	5	6
As	0.018 (0.001)	0.017 (0.001)	0.017 (0.001)	0.019 (0.001)	0.014 (0.001)	0.009 (0.001)
Cd	0.006 (0.001)	0.017 (0.003)	0.024 (0.005)	0.072 (0.018)	0.195 (0.029)	0.279 (0.043)
Cr	0.037 (0.022)	0.020 (0.003)	0.205 (0.099)	0.124 (0.068)	0.033 (0.002)	0.039 (0.002)
Cu	0.019 (0.006)	0.040 (0.006)	0.070 (0.011)	0.089 (0.013)	0.047 (0.003)	0.129 (0.01)
Pb	0.010 (0.001)	0.015 (0.006)	0.010 (0.001)	0.011 (0.002)	0.012 (0.002)	0.017 (0.001)
Ni	1.30 (0.214)	0.448 (0.031)	0.405 (0.043)	0.524 (0.036)	0.619 (0.204)	0.949 (0.102)
Zn	13.8 (1.11)	12.0 (1.27)	12.9 (1.32)	21.5 (1.94)	35.9 (3.46)	37.3 (4.53)

* Expressed in milligrams pre litre (standard error in parentheses).

Table 21

Summary of Sequential Batch Leaching Sediment and Leachate Steady-State Relationships for Metals in Aerobic New Bedford Sediment

Metal	r^2 Value	Probability <	Slope
As	0.349	0.0023*	17.5
Cd	0.967	0.0001*	-7.9
Cr	0.111	0.111	-2.6
Cu	0.645	0.0001*	-10.6
Pb	0.114	0.106	-5.6
Ni	0.017	0.538	-1.5
Zn	0.900	0.0001*	-14.3

* Statistically significant relationship.

Table 22

Steady-State Sediment Organic Contaminant Concentrations* for New Bedford Sediment Following Anaerobic Leaching

Compound	Sequential Leach Number 1	2	3	4
C7	0.559	0.559	0.559	0.558
C8	165.59	165.27	164.67	164.24
C28	152.86	152.43	151.97	151.37
C44	84.07	83.94	83.66	83.48
C49	27.92	27.87	27.78	27.72
C52	176.61	176.38	175.94	175.61
C70	59.18	59.10	58.92	58.80
C77	146.53	145.98	144.98	144.21
C97	22.88	22.83	22.73	22.65
C101	70.34	70.21	69.97	69.79
C105	36.68	36.63	36.55	36.50
C118	29.59	29.57	29.52	29.49
C136	17.09	17.06	16.99	16.93
C138	25.02	24.97	24.89	24.83
C153	56.62	56.42	56.10	55.79
C155	49.98	49.88	49.67	49.52
C167	19.20	19.19	19.17	19.12
C180	7.93	7.92	7.89	7.88
A1242	885.98	881.76	872.56	866.02
A1254	661.25	658.66	653.67	649.99

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* Expressed in milligrams per kilogram, dry weight (standard error in parentheses).

Table 23

Steady-State Organic Contaminant Leachate Concentrations* for Anaerobic New Bedford Sediment Following Anaerobic Leaching

Compound	Sequential Leach Number			
	1	2	3	4
C7	0.05 (0.02)	0.11 (0.01)	0.21 (0.04)	0.15 (0.01)
C8	27.1 (11.8)	80.3 (5.4)	150.0 (28.8)	106.0 (9.4)
C28	34.0 (17.0)	106.6 (6.6)	116.6 (60.09)	150.0 (5.2)
C44	13.1 (4.8)	34.0 (2.5)	68.0 (13.2)	48.6 (5.3)
C49	19.4 (18.7)	11.6 (0.6)	21.6 (3.8)	15.6 (1.3)
C52	12.6 (9.2)	59.3 (3.8)	110.3 (20.5)	82.0 (8.0)
C70	3.7 (3.1)	20.6 (1.7)	44.3 (9.3)	31.0 (4.0
C77	42.3 (20.1)	136.6 (3.3)	250.0 (49.3)	193.3 (3.3)
C82	0.6 (0.4)	2.8 (0.1)	5.6 (1.1)	3.8 (0.3)
C87	0.26 (0.13)	3.7 (0.27)	6.4 (1.1)	7.0 (2.0)
C97	3.0 (2.6)	13.6 (1.2)	23.3 (2.9)	22.0 (3.7)
C101	6.9 (4.6)	31.3 (2.3)	60.6 (11.9)	45.6 (5.4)
C105	5.8 (5.6)	11.2 (1.0)	19.3 (2.9)	14.7 (1.3)
C118	0.8 (0.6)	4.9 (0.3)	12.5 (3.7)	7.2 (0.7)
C136	0.4 (0.2)	7.8 (6.1)	17.3 (3.9)	16.0 (3.0)
C138	12.0 (8.7)	11.3 (0.3)	20.0 (3.2)	16.0 (1.7)
C153	25.2 (24.3)	51.6 (2.9)	80.3 (38.5)	76.3 (0.1)
C155	5.3 (4.4)	25.3 (1.9)	51.3 (10.5)	38.0 (4.6)
C167	0.16 (0.12)	2.4 (0.8)	4.9 (1.3)	12.8 (8.7)
C180	0.1 (0.1)	3.5 (0.1)	6.8 (2.0)	4.0 (0.9)
A1242	253.3 (148.3)	1,056.6 (72.18)	2,300.0 (472.5)	1,633.3 (218.5)
A1254	187.0 (96.5)	646.6 (38.4)	1,246.6 (249.3)	920.0 (128.9)

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* Expressed in micrograms per litre (standard error in parentheses).

Table 24

Summary of New Bedford Anaerobic Sequential Leaching Results for PCBs

Parameter	r^2	$P <$	Slope
C7	0.535	0.007*	-8.72
C8	0.537	0.007*	-7.97
C28	0.671	0.001*	-8.26
C44	0.546	0.006*	-7.87
C49	0.181	0.160	-4.12
C52	0.577	0.004*	-7.72
C70	0.555	0.006*	-6.92
C77	0.575	0.004*	-8.06
C82	0.541	0.006*	-7.29
C87	0.737	0.0003*	-7.27
C97	0.673	0.001*	-8.38
C101	0.580	0.004*	-7.60
C105	0.450	0.017*	-7.71
C118	0.486	0.011*	-5.85
C136	0.579	0.004*	-5.98
C138	0.259	0.091	-5.94
C153	0.495	0.011*	-7.01
C155	0.575	0.004*	-7.35
C167	0.948	0.0001*	-5.06
C180	0.436	0.019*	-5.41
A1242	0.561	0.005*	-7.15
A1254	0.552	0.006*	-7.56

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* Statistically significant relationship.

Table 25

DOC Concentrations* in Anaerobic New Bedford Sequential Leachate

Sequential Leach Number			
1	2	3	4
43.3 (2.7)	43.0 (0.8)	54.7 (1.5)	41.0 (3.8)

* Expressed in milligrams per litre (standard error in parentheses).

Table 26

DOC Concentrations* in Anaerobic New Bedford Leachate at Differing Water-to-Sediment Ratios

Water-to-Sediment Ratio					
4:1	10:1	30:1	50:1	75:1	100:1
53.0 (2.3)	41.0 (4.2)	26.0 (4.2)	17.3 (0.3)	20.0 (1.2)	18.0 (2.7)

* Expressed in milligrams per litre (standard error in parentheses).

Table 27

Leachate Concentration and Single-Point Organic Contaminant Distribution Coefficient for Aerobic New Bedford Sediment

Parameter	Leachate Concentration*	K_d**
C7	0.00007 (0.00001)	4,903 (427)
C8	0.0158 (0.0009)	5,415 (305)
28	0.0252 (0.0016)	2,937 (181)
C44	0.008 (0.0005)	3,802 (238)
C49	0.0025 (0.0001)	5,612 (284)
C50	0.023 (0.0024)	3,430 (488)
C52	0.017 (0.0009)	4,454 (222)
C70	0.004 (0.0002)	6,033 (435)
C87	0.0009 (0.0005)	6,617 (4068)
C97	0.003 (0.0002)	6,275 (470)
C101	0.006 (0.0005)	5,349 (490)
C105	0.0033 (0.0011)	8,441 (2301)
C118	0.0025 (0.0004)	217 (36)
C136	0.003 (0.0005)	5,000 (724)
C138	0.004 (0.0008)	4,468 (1268)
C143	0.0018 (0.0004)	2,846 (551)
C153	0.006 (0.0013)	2,571 (472)
C155	0.003 (0.0001)	12,447 (598)
C167	0.0017 (0.0007)	4,605 (1527)
C180	0.0016 (0.0003)	1,241 (230)
C185	0.0006 (0.0001)	3,100 (1143)
A1242	0.146 (0.011)	5,039 (358)
A1254	0.069 (0.006)	6,727 (571)
TPCB	0.262 (0.019)	4,863 (334)

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* Expressed in milligrams per litre (standard error in parentheses).

** Expressed in litres per kilogram (standard error in parentheses).

Table 28

Operating Variables for Permeameter Leach Tests

Permeameter Type	Permeability 10^{-6} cm/sec Initial	Final	Average Flow ml/day
Anaerobic metals	1.6	0.016	15.5
Anaerobic organics	3.7	0.021	17.9
Aerobic metals	1.3	0.071	20.4
Aerobic organics	1.9	0.045	23.7

Table 29

Aroclor and Total PCB Concentrations* in Leachate from Anaerobic Organics Permeameters

Pore Volume	A1016	A1221	A1232	A1242	A1248	A1254	A1260	Total PCB
				Replicate 1				
0.66	<0.0002	<0.0002	<0.0002	0.0052	<0.0002	0.0056	<0.0002	0.0108
1.80	<0.0002	<0.0002	<0.0002	0.0018	<0.0002	0.0020	<0.0002	0.0048
2.78	<0.0002	<0.0002	<0.0002	0.0004	<0.0002	0.0003	<0.0002	0.0011
3.81	<0.0002	<0.0002	<0.0002	0.0034	<0.0002	0.0002	<0.0002	0.0054
4.85	<0.0002	<0.0002	<0.0002	0.0120	<0.0002	0.0070	<0.0002	0.0180
5.91	<0.0002	<0.0002	<0.0002	0.0057	<0.0002	0.0022	<0.0002	0.0079
6.74	<0.0002	<0.0002	<0.0002	0.0028	<0.0002	0.0005	<0.0002	0.0033
				Replicate 2				
0.63	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	0.0009	<0.0002	0.0023
1.72	<0.0002	<0.0002	<0.0002	0.0005	<0.0002	0.0002	<0.0002	0.0008
2.64	<0.0002	<0.0002	<0.0002	0.0021	<0.0002	<0.0002	<0.0002	0.0022
3.57	<0.0002	<0.0002	<0.0002	0.0113	<0.0002	0.0024	<0.0002	0.0120
4.47	<0.0002	<0.0002	<0.0002	0.0061	<0.0002	0.0011	<0.0002	0.0072
				Replicate 3				
0.52	<0.0002	<0.0002	<0.0002	0.0008	<0.0002	0.0007	<0.0002	0.0031
1.55	<0.0002	<0.0002	<0.0002	0.0009	<0.0002	0.0008	<0.0002	0.0020
2.51	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
3.49	<0.0002	<0.0002	<0.0002	0.0120	<0.0002	0.0086	<0.0002	0.0160
4.47	<0.0002	<0.0002	<0.0002	0.0121	<0.0002	0.0023	<0.0002	0.0158
5.41	<0.0002	<0.0002	<0.0002	0.0102	<0.0002	0.0022	<0.0002	0.0128
6.76	<0.0002	<0.0002	<0.0002	0.0050	<0.0002	0.0012	<0.0002	0.0066

* Expressed in milligrams per litre.

Table 30a

PCB Congener Concentrations* in Leachate from Anaerobic Organics Permeameters

(Congeners C7-C97)

Sample Number	Sample Pore Volume ml	Congener											
		C7	C8	C28	C44	C49	C50	C52	C70	C77	C82	C87	C97
Anaerobic Organics - PN1													
1	0.66	<0.00001	<0.00001	<0.00001	0.00019	<0.00001	0.00006	0.00003	<0.00001	<0.00001	0.00016	0.00001	0.00011
2	1.80	<0.00001	<0.00001	0.00026	0.00014	0.00004	0.00038	0.00017	0.00014	<0.00001	0.00010	0.00003	0.00011
3	2.78	<0.00001	<0.00001	0.00030	0.00004	<0.00001	0.00037	0.00016	<0.00001	<0.00001	<0.00001	0.00015	<0.00001
4	3.81	<0.00001	<0.00001	0.00041	0.00020	0.00006	0.00040	0.00039	0.00004	0.00020	<0.00001	<0.00001	0.00001
5	4.85	<0.00001	<0.00001	0.00099	0.00059	0.00017	0.00110	0.00110	0.00033	0.00130	0.00012	0.00021	0.00032
6	5.91	<0.00001	0.00007	0.00071	0.00027	0.00005	<0.00001	0.00066	0.00015	0.00014	0.00011	0.00003	0.00008
7	6.74	<0.00001	<0.00001	0.00019	0.00008	0.00002	<0.00001	0.00022	<0.00001	<0.00001	<0.00001	<0.00001	0.00001
Anaerobic Organics - PN2													
1	0.63	<0.00001	0.00015	0.00002	0.00003	<0.00001	0.00001	<0.00001	0.00005	<0.00001	0.00016	0.00001	0.00003
2	1.72	<0.00001	0.00044	0.00007	0.00007	0.00002	0.00010	0.00004	0.00001	<0.00001	<0.00001	<0.00001	0.00001
3	2.64	<0.00001	0.00120	0.00034	0.00012	0.00005	0.00033	0.00028	<0.00001	0.00019	<0.00001	<0.00001	<0.00001
4	3.57	<0.00001	0.00035	0.00051	0.00028	0.00007	0.00044	0.00087	0.00005	<0.00001	<0.00001	0.00001	0.00006
5	4.47	<0.00001	0.00043	0.00006	0.00016	0.00004	<0.00001	0.00046	0.00005	0.00011	<0.00001	<0.00001	0.00002
Anaerobic Organics - PN3													
1	0.52	<0.00001	0.00015	0.00006	0.00003	<0.00001	0.00005	0.00005	0.00003	<0.00001	0.00017	0.00007	0.00001
2	1.55	<0.00001	0.00063	0.00013	0.00009	0.00002	0.00019	0.00008	0.00004	<0.00001	0.00003	0.00006	0.00004
3	2.51	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00001
4	3.49	<0.00001	0.00260	0.00130	0.00066	0.00017	0.00140	0.00110	0.00044	0.00210	0.00023	0.00040	0.00097
5	4.47	<0.00001	0.00043	0.00117	0.00031	0.0007	<0.00001	0.00021	0.00012	<0.00001	<0.00001	0.00003	0.00007
6	5.41	<0.00001	0.00047	0.00106	0.00029	0.00008	<0.00001	0.00079	0.00015	0.00023	<0.00001	0.00002	0.00006
7	6.76	<0.00001	0.00043	0.00056	0.00016	0.00003	<0.00001	0.00043	0.00006	<0.00001	<0.00001	0.00001	0.00004

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* Expressed in milligrams per litre.

Table 30b

PCB Congener Concentrations* in Leachate from Anaerobic Organics Permeameters

(Congeners C101-C185)

Sample Number	Sample Pore Volume ml	Congener C101	C105	C118	C136	C138	C143	C153	C155	C167	C180	C185
Anaerobic Organics - PN1												
1	0.66	<0.00001	0.00009	0.00018	0.00033	<0.00001	0.00023	<0.00001	<0.00001	<0.00001	0.00018	<0.00001
2	1.80	0.00014	<0.00001	0.00010	0.00011	0.00016	0.00008	0.00020	0.00011	0.00007	0.00006	<0.00001
3	2.78	<0.00001	<0.00001	0.00012	<0.00001	0.00008	<0.00001	0.00010	<0.00001	<0.00001	<0.00001	<0.00001
4	3.81	<0.00001	0.00007	<0.00001	0.00003	<0.00001	<0.00001	<0.00001	0.00007	<0.00001	0.00004	0.00005
5	4.85	0.00073	0.00019	0.00030	0.00022	0.00017	0.00015	0.00046	0.00056	0.00020	0.00014	0.00011
6	5.91	0.00023	<0.00001	0.00011	0.00007	0.00006	0.00011	0.00015	<0.00001	<0.00001	0.00005	<0.00001
7	6.74	0.00003	<0.00001	<0.00001	0.00001	0.00001	<0.00001	0.00005	<0.00001	<0.00001	0.00001	<0.00001
Anaerobic Organics - PN2												
1	0.63	0.00006	0.00005	0.00015	<0.00001	0.00011	<0.00001	<0.00001	0.00006	<0.00001	<0.00001	<0.00001
2	1.72	<0.00001	<0.00001	0.00002	<0.00001	0.00002	<0.00001	0.00001	0.00001	0.00003	<0.00001	<0.00001
3	2.64	<0.00001	<0.00001	<0.00001	0.00002	<0.00001	<0.00001	<0.00001	0.00005	<0.00001	<0.00001	<0.00001
4	3.57	0.00025	<0.00001	0.00002	0.00005	0.00004	<0.00001	0.00014	0.00020	0.00003	0.00001	0.00002
5	4.47	0.00012	<0.00001	0.00003	0.00003	0.00003	<0.00001	0.00009	<0.00001	<0.00001	0.00001	<0.00001
Anaerobic Organics - PN3												
1	0.52	0.00003	0.00007	<0.00001	<0.00001	0.00014	<0.00001	<0.00001	0.00004	<0.00001	<0.00001	0.00012
2	1.55	0.00003	0.00017	0.00005	0.00015	0.00003	0.00003	<0.00001	0.00004	<0.00001	<0.00001	<0.00001
3	2.51	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
4	3.49	0.00092	0.00050	0.00040	0.00034	0.00032	0.00020	0.00067	0.00054	0.00021	0.00005	0.00006
5	4.47	0.00028	0.00013	0.00006	<0.00001	0.00005	0.00001	0.00020	<0.00001	<0.00001	0.00002	0.00001
6	5.41	0.00022	<0.00001	0.00013	0.00006	0.00005	0.00001	0.00167	<0.00001	<0.00001	0.00001	0.00001
7	6.76	0.00013	<0.00001	0.00006	0.00003	0.00005	<0.00001	0.00009	<0.00001	<0.00001	0.00002	0.00001

SEE TABLE 7 FOR PCB CONGENER IDENTIFICATION KEY

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* Expressed in milligrams per litre.

Table 31

pH Dependency of Initial Leachate Metal Concentration in Aerobic Metals Permeameters

Permeameter	pH	Cd	Fe	Mn	Ni	Zn
3	3.1	0.0113	320	7.19	23.7	1.61
1	4.4	0.0093	254	3.44	0.159	0.13
2	5.9	0.0014	169	2.64	1.198	1.17

Table 32

Aroclor and Total PCB Concentrations* in Leachate from Aerobic Organics Permeameters

Pore Volume	A1016	A1221	A1232	A1242	A1248	A1254	A1260	TPCB
				Replicate 1				
0.37	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
1.11	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
1.89	<0.0002	<0.0002	<0.0002	0.0012	<0.0002	0.0010	<0.0002	0.0026
2.69	<0.0002	<0.0002	<0.0002	0.0022	<0.0002	0.0003	<0.0002	0.0040
3.52	<0.0002	<0.0002	<0.0002	0.0066	<0.0002	0.0018	<0.0002	0.0074
4.27	<0.0002	<0.0002	<0.0002	0.0049	<0.0002	0.0033	<0.0002	0.0082
				Replicate 2				
0.42	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	0.0002	<0.0002	<0.0002
1.20	<0.0002	<0.0002	<0.0002	0.0006	<0.0002	0.0002	<0.0002	0.0011
1.95	<0.0002	<0.0002	<0.0002	0.0007	<0.0002	0.0007	<0.0002	0.0019
2.77	<0.0002	<0.0002	<0.0002	0.0015	<0.0002	0.0002	<0.0002	0.0016
3.58	<0.0002	<0.0002	<0.0002	0.0060	<0.0002	0.0007	<0.0002	0.0063
4.33	<0.0002	<0.0002	<0.0002	0.0053	<0.0002	0.0012	<0.0002	0.0065
5.03	<0.0002	<0.0002	<0.0002	0.0030	<0.0002	0.0003	<0.0002	0.0033
				Replicate 3				
0.41	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
1.20	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	0.0001
1.95	<0.0002	<0.0002	<0.0002	0.0014	<0.0002	0.0011	<0.0002	0.0018
2.70	<0.0002	<0.0002	<0.0002	0.0058	<0.0002	0.0016	<0.0002	0.0068
3.45	<0.0002	<0.0002	<0.0002	0.0046	<0.0002	0.0010	<0.0002	0.0175
4.27	<0.0002	<0.0002	<0.0002	0.0052	<0.0002	0.0015	<0.0002	0.0067
5.06	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002

* Expressed in milligrams per litre.

Table 33a

PCB Congener Concentrations* in Leachate from Aerobic Organics Permeameters

(Congeners C7-C97)

Pore Volume	C7	C8	C28	C44	C49	C50	C52	C70	C77	C82	C87	C97
						Replicate 1						
0.37	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
1.11	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00004
1.89	<0.00001	<0.00001	0.00034	0.00005	0.00002	0.00020	0.00009	0.00007	0.00003	0.00005	0.00004	<0.00001
2.69	<0.00001	0.00026	0.00024	0.00008	0.00002	0.00010	0.00023	0.00005	0.00026	<0.00001	0.00002	0.00004
3.52	<0.00001	0.00070	0.00058	0.00017	0.00004	0.00046	0.00048	0.00007	<0.00001	<0.00001	0.00002	0.00007
4.27	<0.00001	0.00003	0.00050	0.00016	0.00003	<0.00001	0.00041	0.00016	0.00018	0.00012	0.00002	0.00005
						Replicate 2						
0.42	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
1.20	<0.00001	0.00048	0.00005	0.00007	0.00001	0.00002	0.00008	<0.00001	<0.00001	<0.00001	<0.00001	<0.00007
1.95	<0.00001	0.00082	0.00015	<0.00001	0.00001	0.00012	<0.00001	<0.00001	0.00026	0.00004	0.00003	<0.00001
2.77	<0.00001	<0.00001	0.00018	0.00009	0.00003	0.00013	0.00016	0.00003	<0.00001	<0.00001	<0.00001	0.00002
3.58	<0.00001	0.00093	0.00038	0.00009	0.00002	<0.00001	0.00031	0.00003	<0.00001	<0.00001	0.00002	0.00003
4.33	<0.00001	0.00030	0.00063	0.00016	0.00003	<0.00001	0.00036	0.00010	0.00015	<0.00001	0.00002	0.00006
5.03	<0.00001	<0.00001	0.00021	0.00005	0.00001	<0.00001	0.00014	<0.00001	0.00009	<0.00001	<0.00001	<0.00001
						Replicate 3						
0.41	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
1.20	<0.00001	0.00042	<0.00001	<0.00001	<0.00001	<0.00001	0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00008
1.95	<0.00001	0.00050	0.00011	0.00004	<0.00001	0.00010	0.00007	0.00004	0.00015	<0.00001	<0.00001	0.00004
2.70	<0.00001	0.00048	0.00049	0.00010	0.00002	0.00049	0.00042	0.00009	0.00010	<0.00001	0.00006	0.00006
3.45	<0.00001	0.00038	0.00025	0.00006	0.00002	0.00025	0.00019	0.00002	<0.00001	0.00004	<0.00001	0.00002
4.27	<0.00001	0.00062	<0.00056	0.00015	0.00003	<0.00001	0.00034	0.00014	0.00018	<0.00001	0.00002	0.00005
5.06	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00002	<0.00001	<0.00001	<0.00001

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* Expressed in milligrams per litre.

Table 33b

PCB Congener Concentrations* in Leachate from Aerobic Organics Permeameters

(Congeners C101-C185)

Pore Volume	C101	C105	C118	C136	C138	C143	C153	C155	C167	C180	C185
Replicate 1											
0.37	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
1.11	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00005	<0.00001	<0.00001
1.89	0.00004	0.00016	0.00014	<0.00001	0.00008	0.00010	0.00016	0.00010	0.00006	0.00008	<0.00001
2.69	0.00028	0.00006	0.00003	<0.00001	0.00002	0.00006	0.00008	0.00015	<0.00001	0.00001	0.00002
3.52	0.00017	<0.00001	0.00010	0.00006	0.00006	0.00001	0.00015	0.00014	<0.00001	0.00002	<0.00001
4.27	0.00018	<0.00001	0.00010	0.00005	0.00005	0.00029	0.00021	0.00001	0.00007	<0.00001	<0.00001
Replicate 2											
0.42	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00001
1.20	<0.00001	0.00005	<0.00001	0.00002	0.00004	<0.00001	<0.00001	<0.00001	0.00001	<0.00001	<0.00001
1.95	<0.00001	0.00024	0.00005	0.00004	0.00001	0.00004	0.00019	0.00002	<0.00001	0.00004	<0.00001
2.77	0.00005	<0.00001	<0.00001	0.00001	<0.00001	0.00001	0.00002	0.00003	<0.00001	<0.00001	<0.00001
3.58	<0.00001	<0.00001	0.00003	0.00004	0.00003	<0.00001	0.00006	0.00001	<0.00001	0.00001	0.00002
4.33	0.00016	<0.00001	0.00009	0.00004	0.00003	<0.00001	0.00009	0.00001	<0.00001	0.00001	<0.00001
5.03	0.00001	<0.00001	0.00001	0.00001	0.00001	<0.00001	0.00003	0.00001	<0.00001	<0.00001	<0.00001
Replicate 3											
0.41	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00001
1.20	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00001
1.95	<0.00001	0.00005	<0.00001	0.00001	<0.00001	<0.00001	<0.00001	0.00001	<0.00001	<0.00001	<0.00001
2.70	0.00018	0.00009	0.00004	<0.00001	0.00004	0.00001	0.00012	0.00011	<0.00001	0.00001	<0.00001
3.45	0.00005	<0.00001	0.00001	0.00002	0.00002	<0.00001	0.00009	0.00008	0.00002	0.00001	<0.00001
4.27	0.00019	<0.00001	0.00013	0.00004	0.00006	0.00001	0.00015	<0.00001	<0.00001	<0.00001	<0.00001
5.06	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00001	<0.00001

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* Expressed in milligrams per litre.

Table 34

Peak Metal, Aroclor, and Total PCB Concentrations* in New Bedford Harbor Permeameter Leachates

Parameter	Anaerobic	Aerobic
Cadmium	0.0029	0.0113
Chromium	0.375	0.116
Copper	0.017	0.025
Iron	9.24	320
Manganese	2.94	7.19
Lead	0.01	0.012
Nickel	0.058	23.7
Zinc	0.14	1.61
Aroclor 1242	0.0121	0.0066
Aroclor 1254	0.0086	0.0033
Total PCB	0.018	0.0175

* Expressed in milligrams per litre.

Table 35

PCB-Conductivity Model Parameters for Equations 9 and 10

		Regression Parameters*		
PCB	A'	A	B	r^2
Total	11.888	6.175	0.181	0.970
A1242	11.228	5.742	0.189	0.924
A1254	11.913	6.196	0.162	0.910
C28	--	5.758	0.219	0.955
C118	--	6.062	0.209	0.826
C155	--	6.189	6.615	0.579

* Regression parameters are for anaerobic sequential batch leach tests using distilled-deionized water; see text for calculation of A' .

Table 36

Conductivity Simulation Parameters for Anaerobic Permeameters

Parameter	Permeameter Type	
	Metals	Organics
Darcy velocity, m/day	0.00205	0.00237
Effective porosity*	0.7661	0.7657
Longitudinal dispersivity, m	0.125	0.125
Retardation factor	1.4	1.4
Initial concentration	8.00 mmhos	8.00 mmhos
Concentration in water entering column	0.00 mmhos	0.00 mmhos
Column length, cm	14	28

* Mean of initial and final porosities.

Table 37

Distribution Coefficients After the Turning Point*

PCB	Point-Derived			Slope-Derived
	Cycle 5	Cycle 6	Cycle 7	
Total PCB	515	662	1,162	8.39
Aroclor 1242	294	371	722	7.46
Aroclor 1254	512	725	1,236	3.53

* From Tables A8 and A9 (expressed in litres per kilogram).

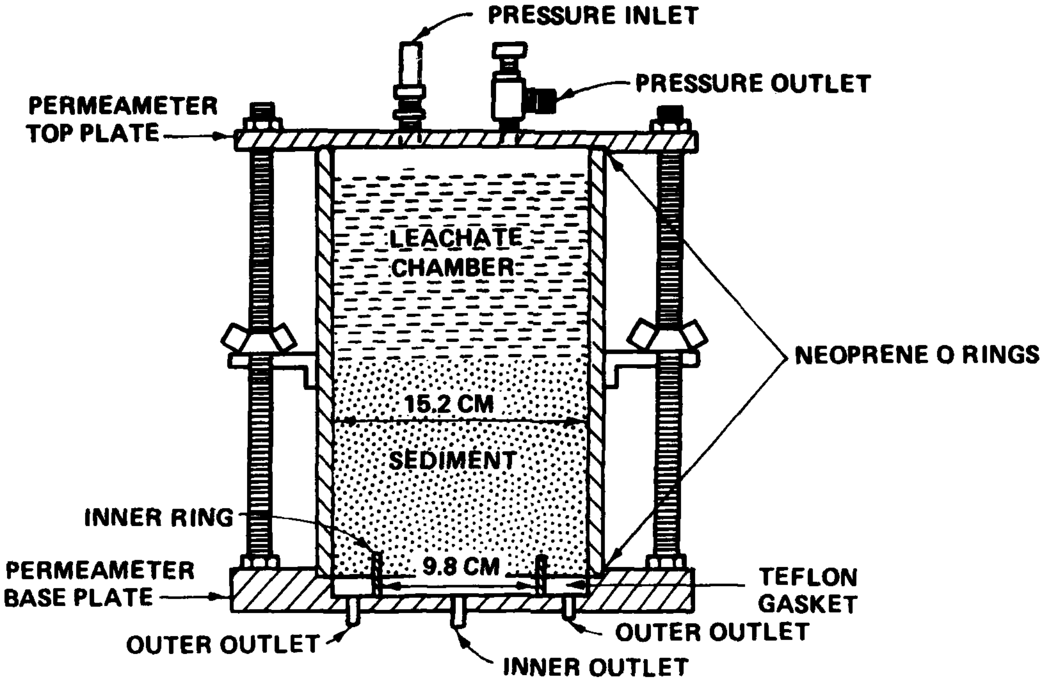

Figure 1. Divided-flow permeameter

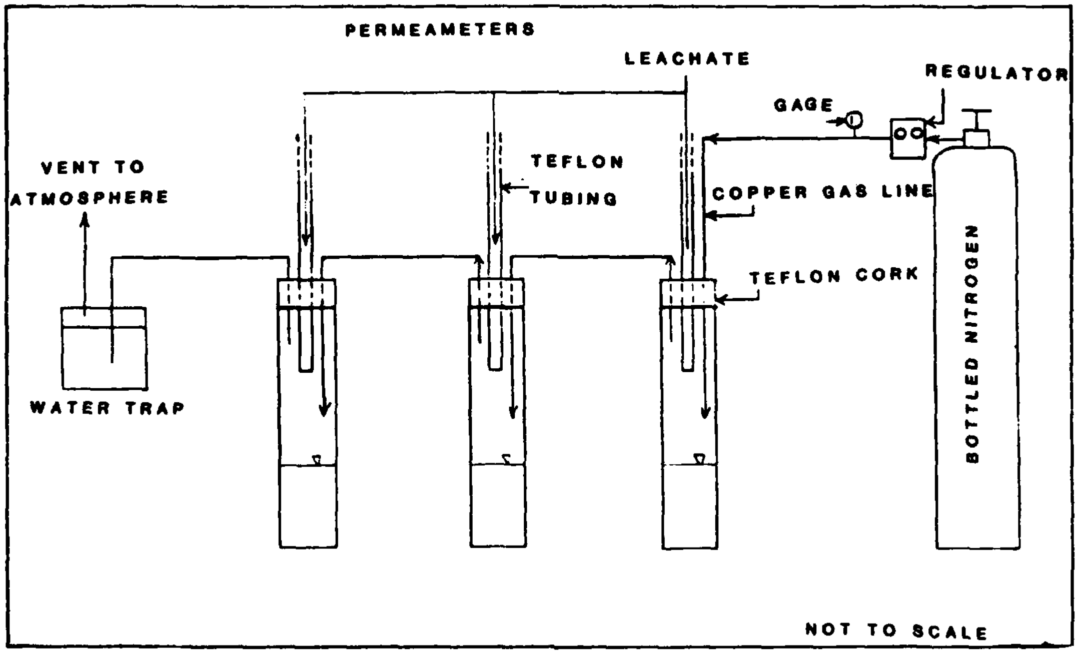

Figure 2. Isolation system for permeameter leachate

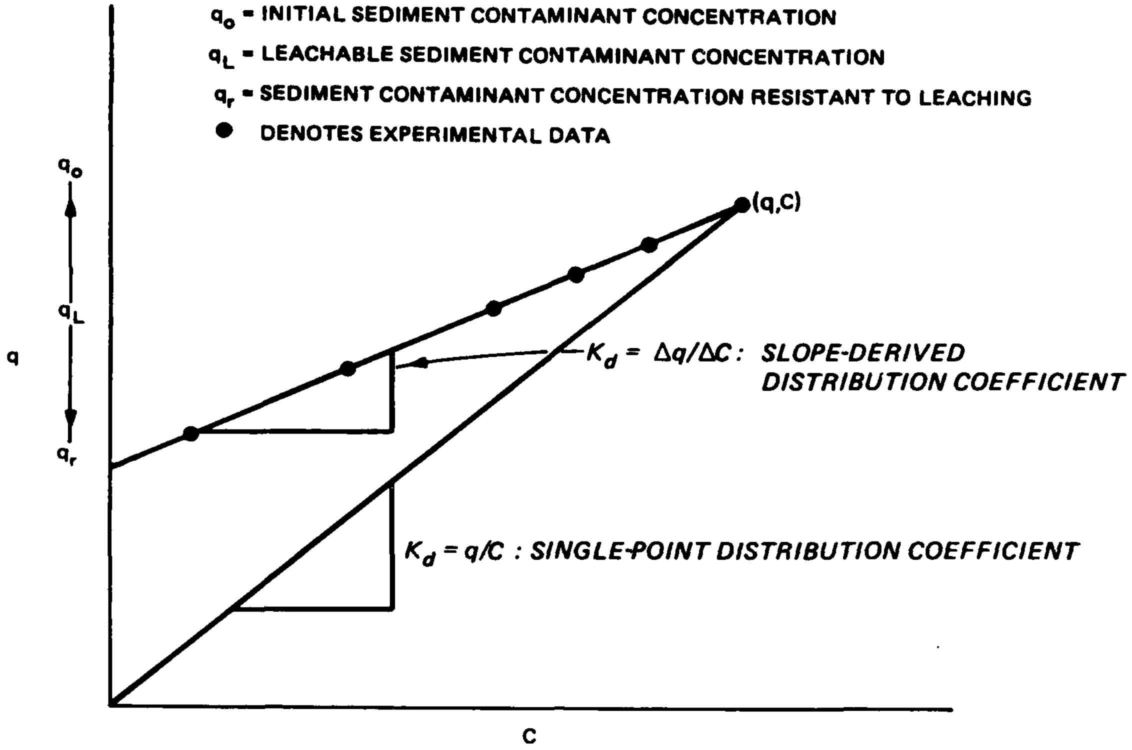

Figure 3. Ideal desorption isotherms for slope-derived and single-point distribution coefficients for constant partitioning

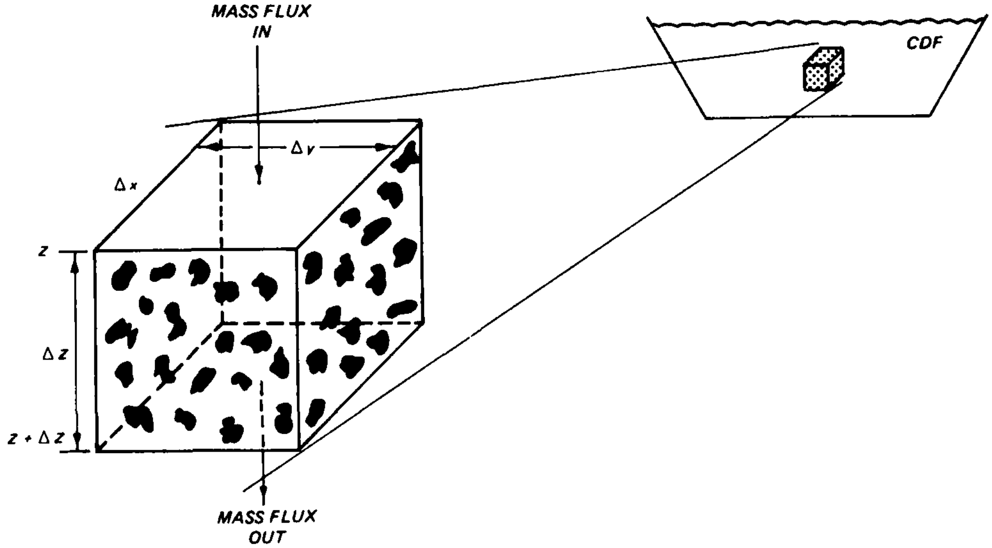

Figure 4. Representative element for dredged material in a confined disposal facility

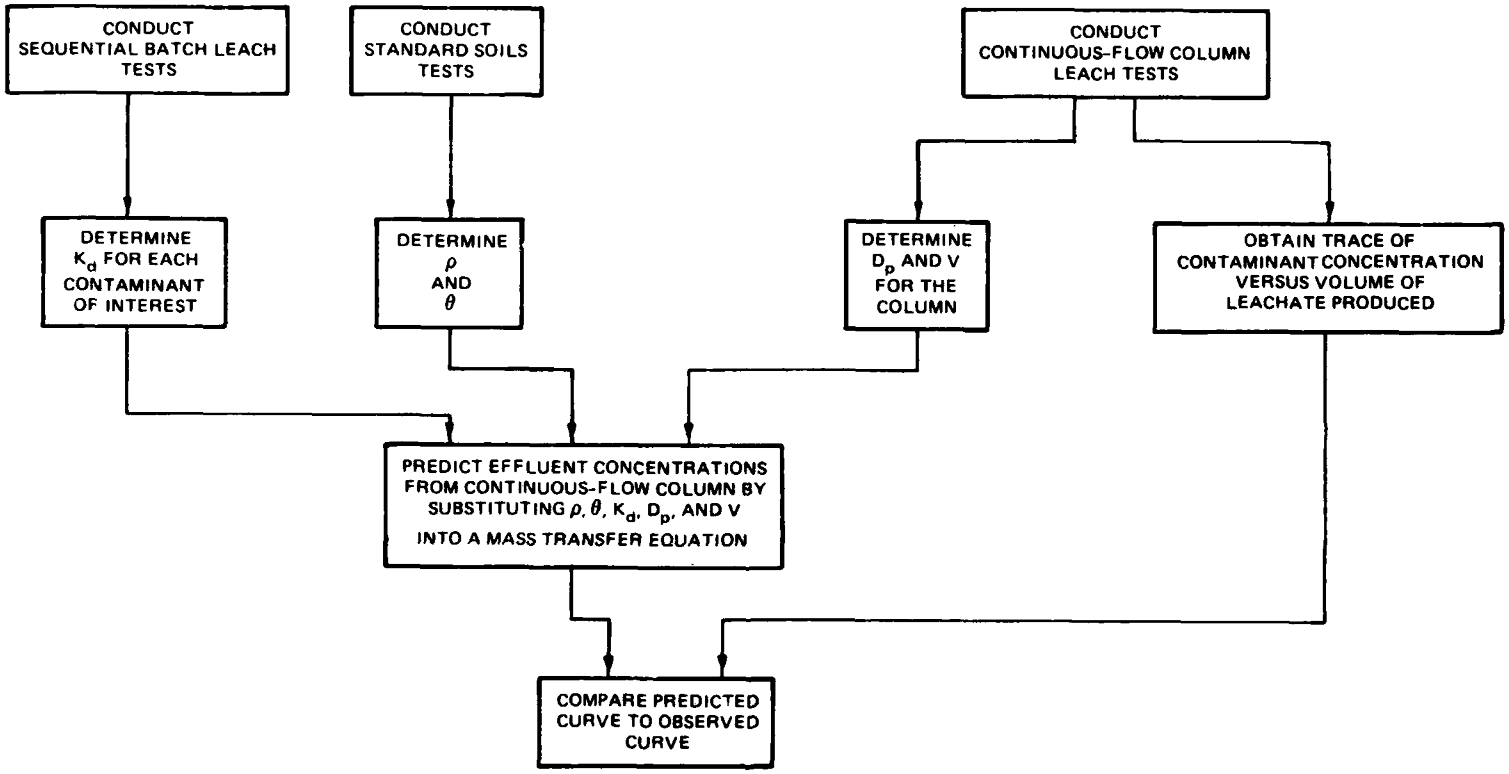

Figure 5. Schematic of integrated approach for examining the source term

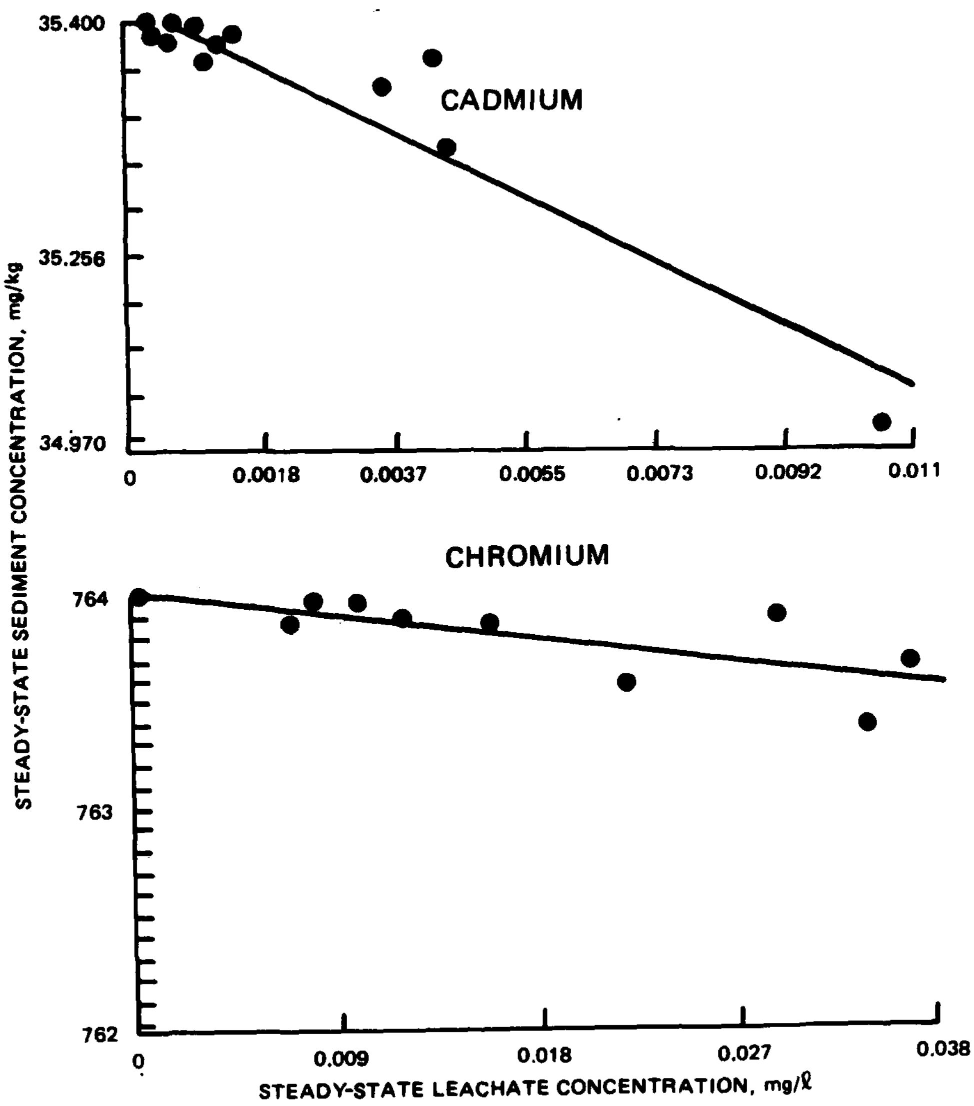

Figure 6. Desorption plots for Cd and Cr from anaerobic sediment-water ratio testing

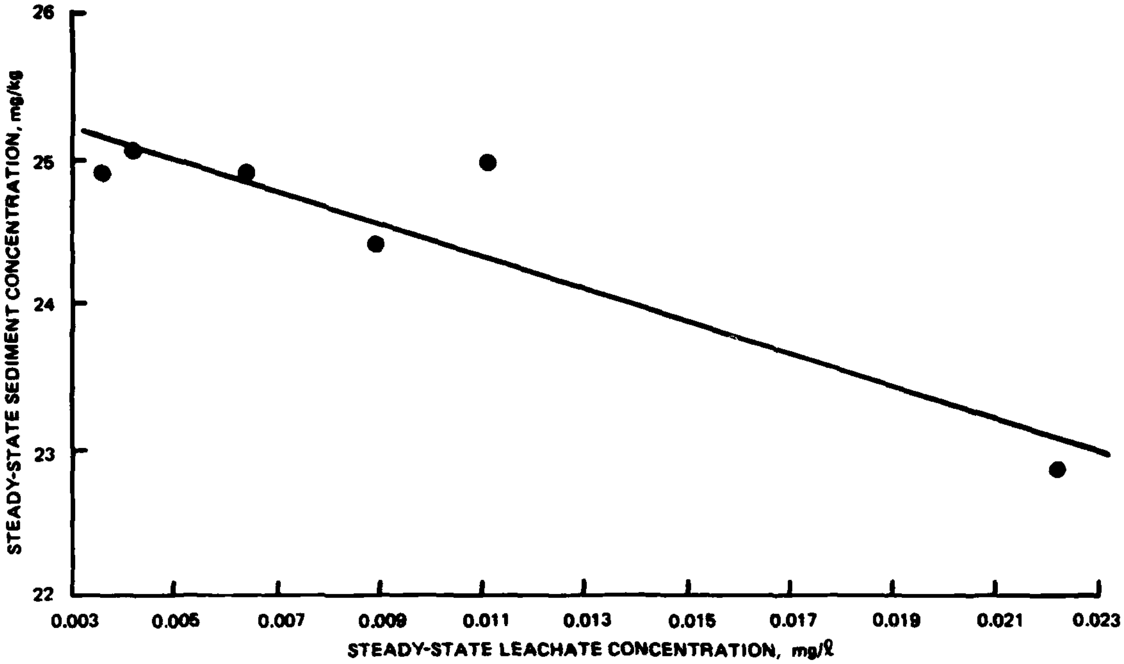

Figure 7. Desorption plot for congener 138 from anaerobic sediment-water ratio testing

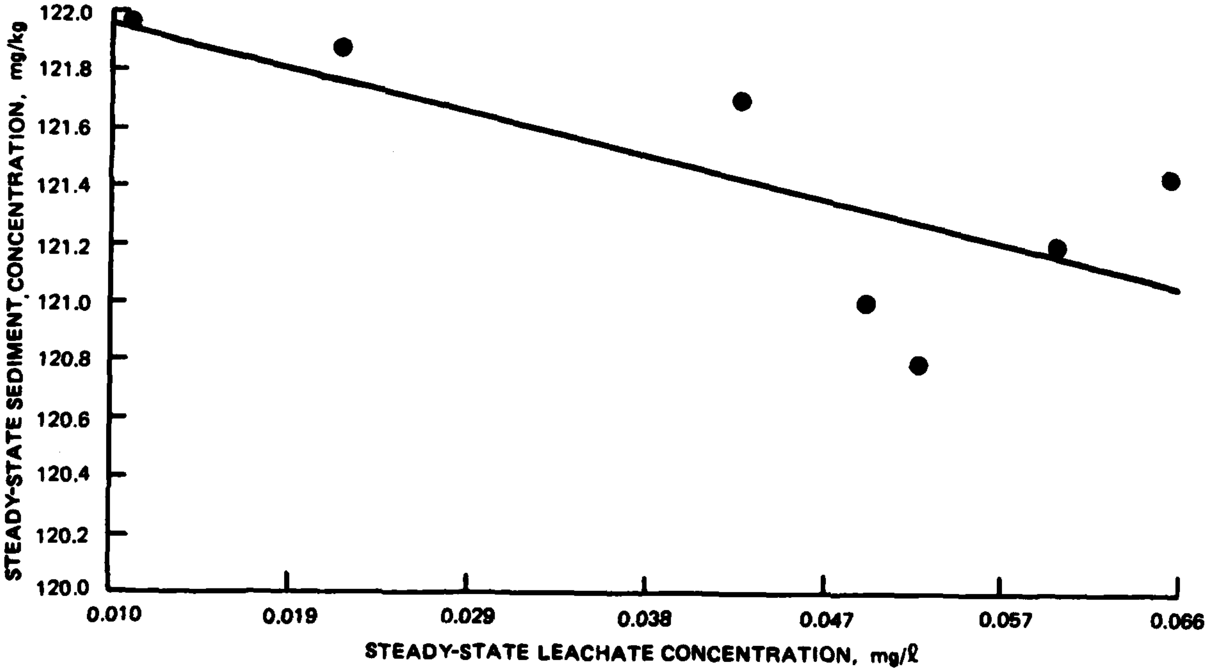

Figure 8. Desorption plot for Ni from anaerobic sequential batch testing

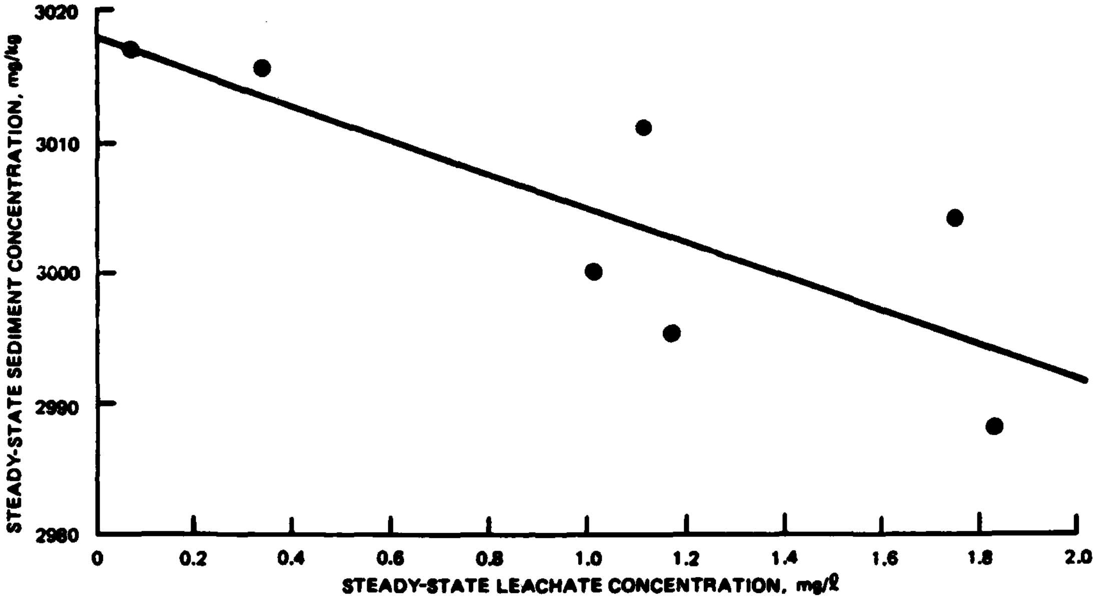

Figure 9. Desorption plot for Zn from anaerobic sequential batch testing

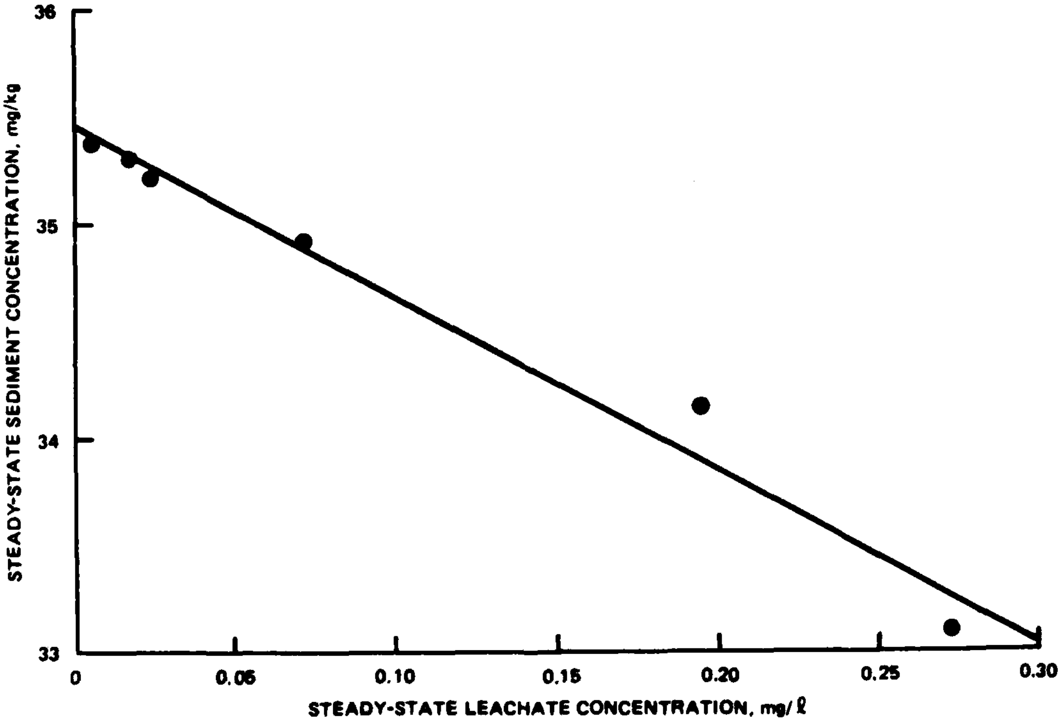

Figure 10. Desorption plot for Cd from aerobic sequential batch leaching

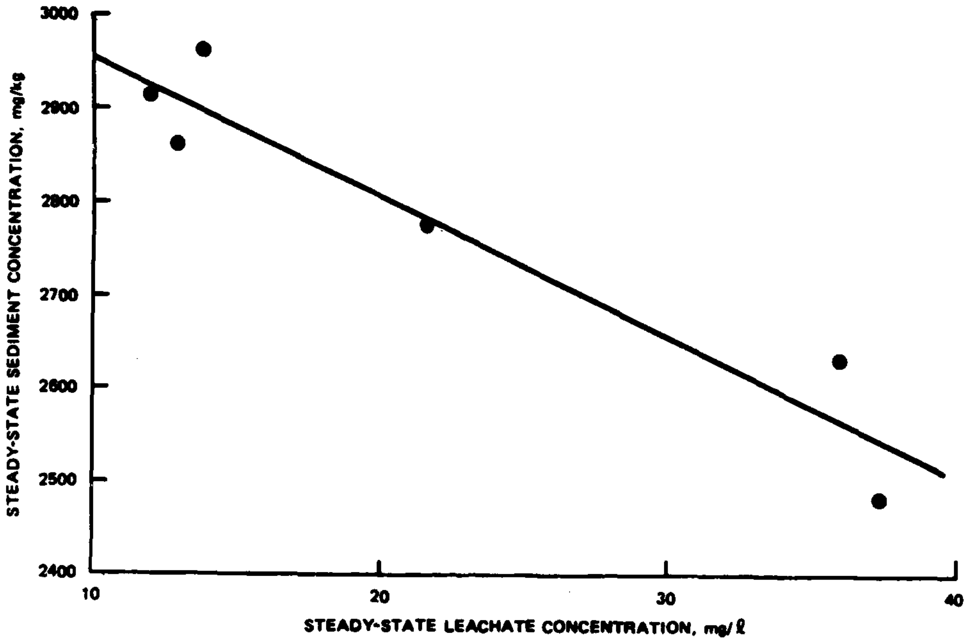

Figure 11. Desorption plot for Zn from aerobic sequential batch leaching

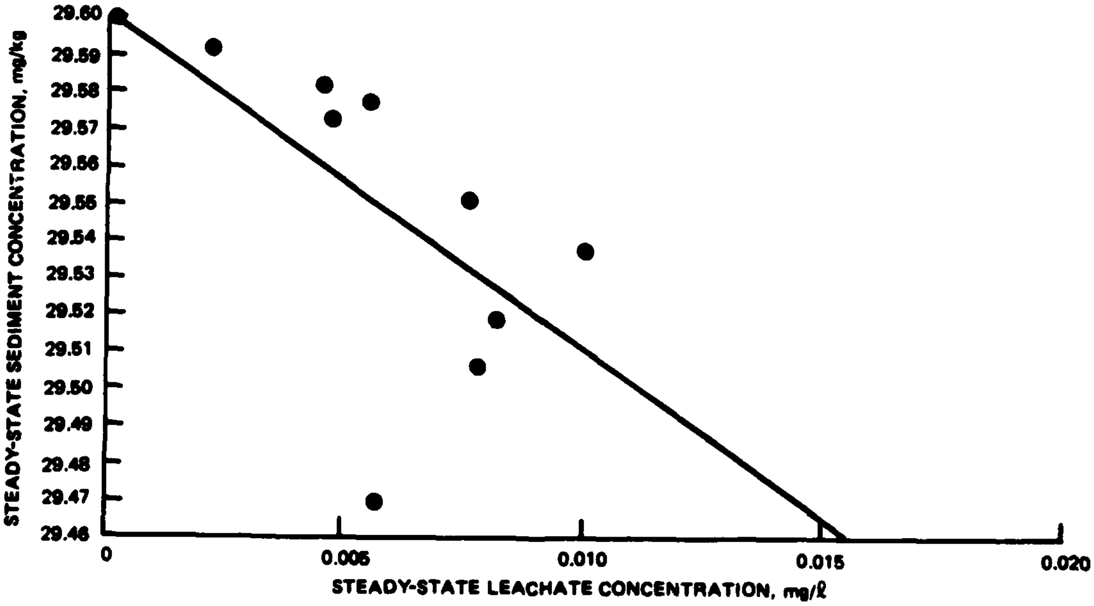

Figure 12. Desorption plot for PCB congener 118 from sequential batch testing

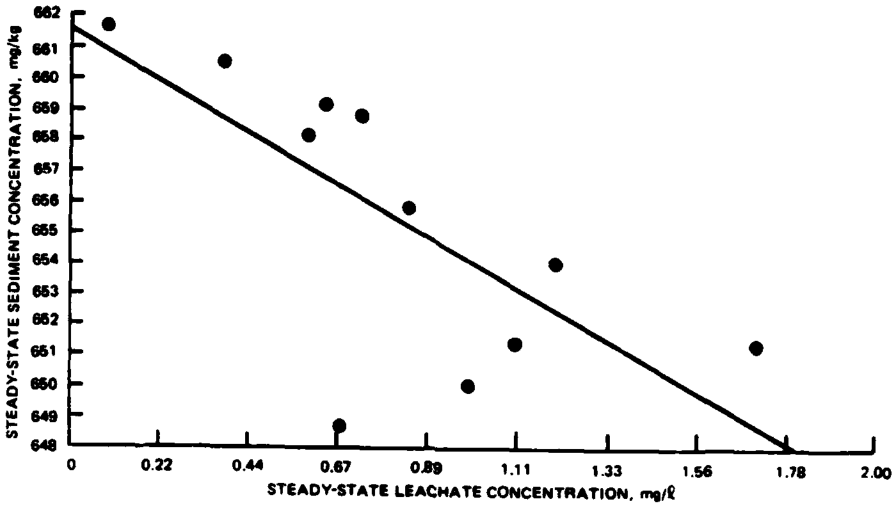

Figure 13. Desorption plot for Aroclor 1254 from sequential batch testing

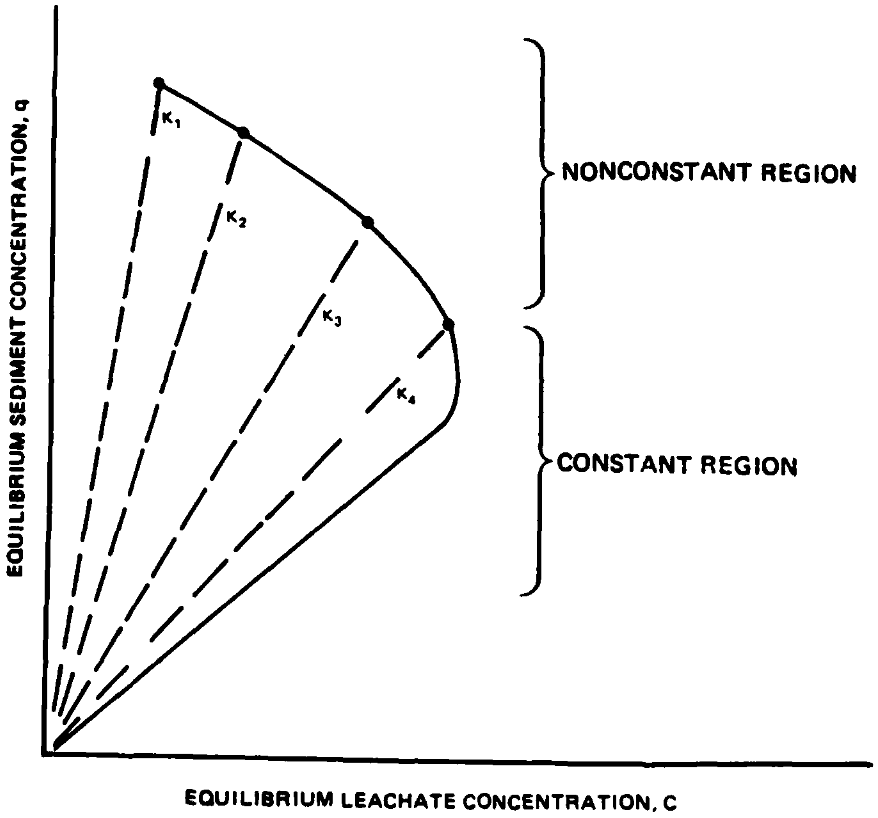

Figure 14. Isotherm demonstrating nonconstant and constant partitioning

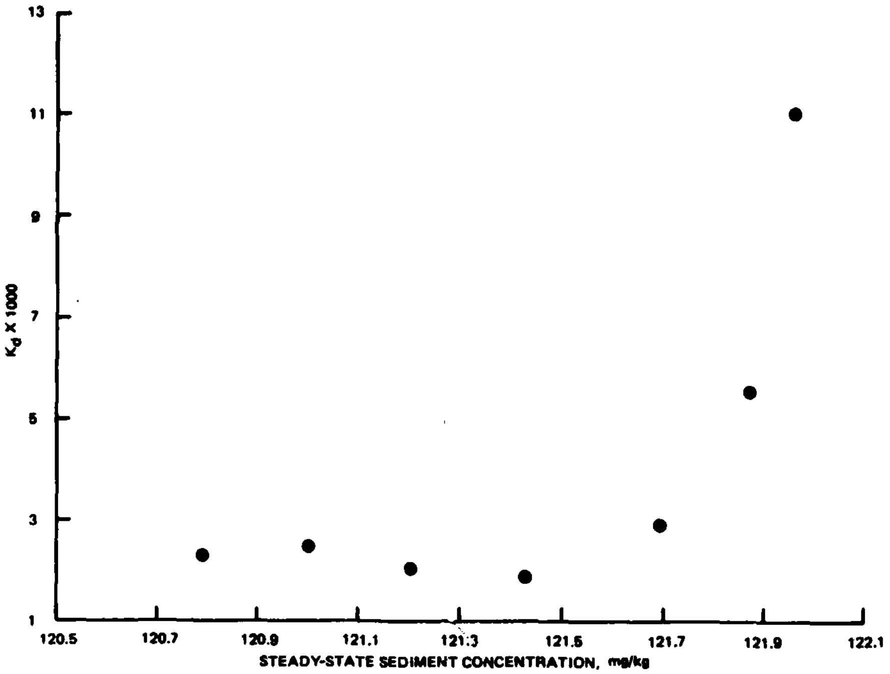

Figure 15. Single-point distribution coefficients for Ni during sequential batch leach tests as a function of steady-state sediment concentration

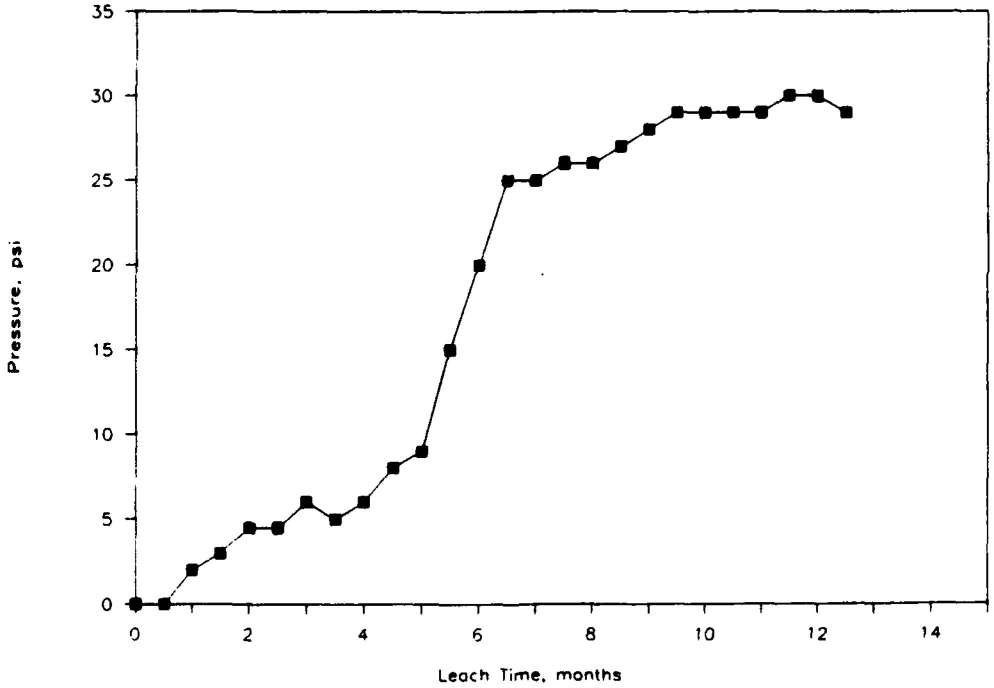

Figure 16. Pressures required to maintain constant flow in anaerobic metals permeameters (to convert pounds (force) per square inch to kilopascals, multiply by 6.894757)

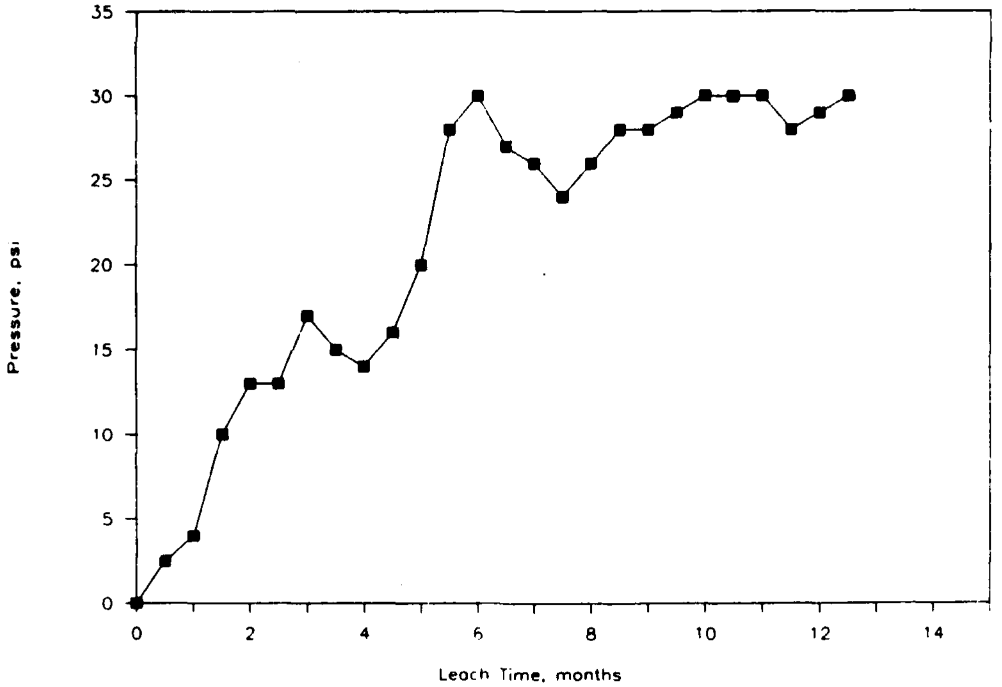

Figure 17. Pressures required to maintain constant flow in anaerobic organic permeameters (to convert pounds (force) per square inch to kilopascals, multiply by 6.894757)

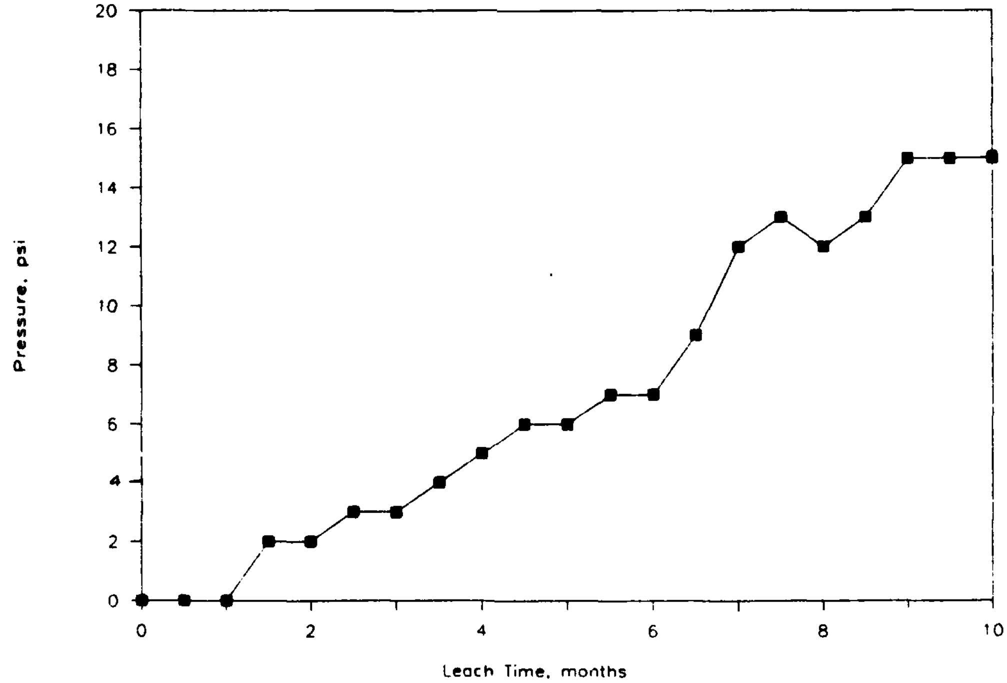

Figure 18. Pressures required to maintain constant flow in aerobic metals permeameters (to convert pounds (force) per square inch to kilopascals, multiply by 6.894757)

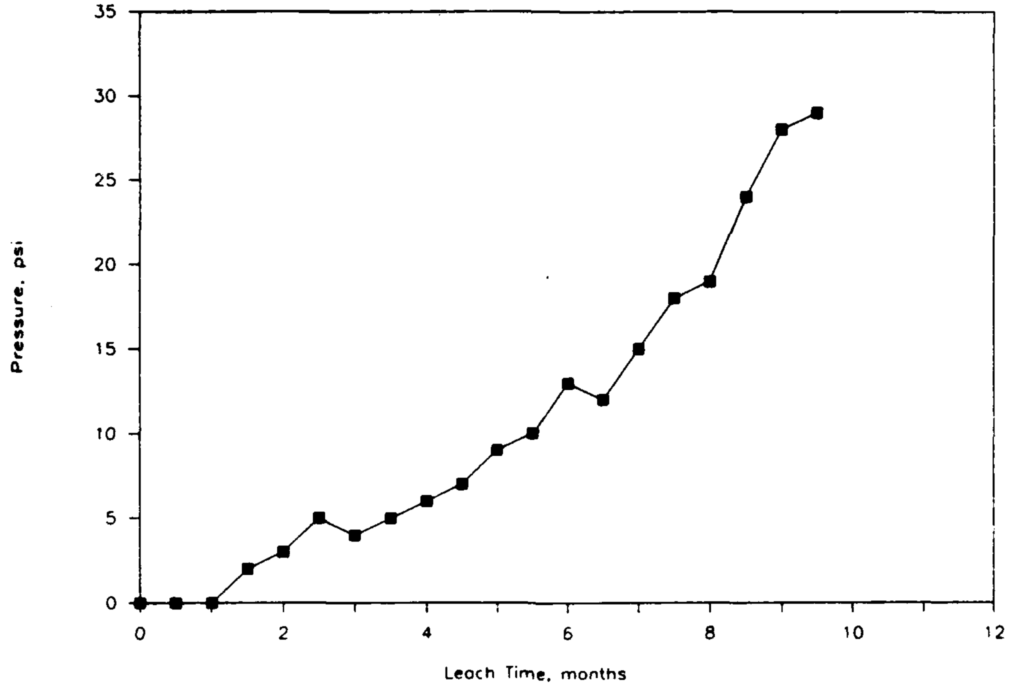

Figure 19. Pressures required to maintain constant flow in aerobic organic permeameters (to convert pounds (force) per square inch to kilopascals, multiply by 6.894757)

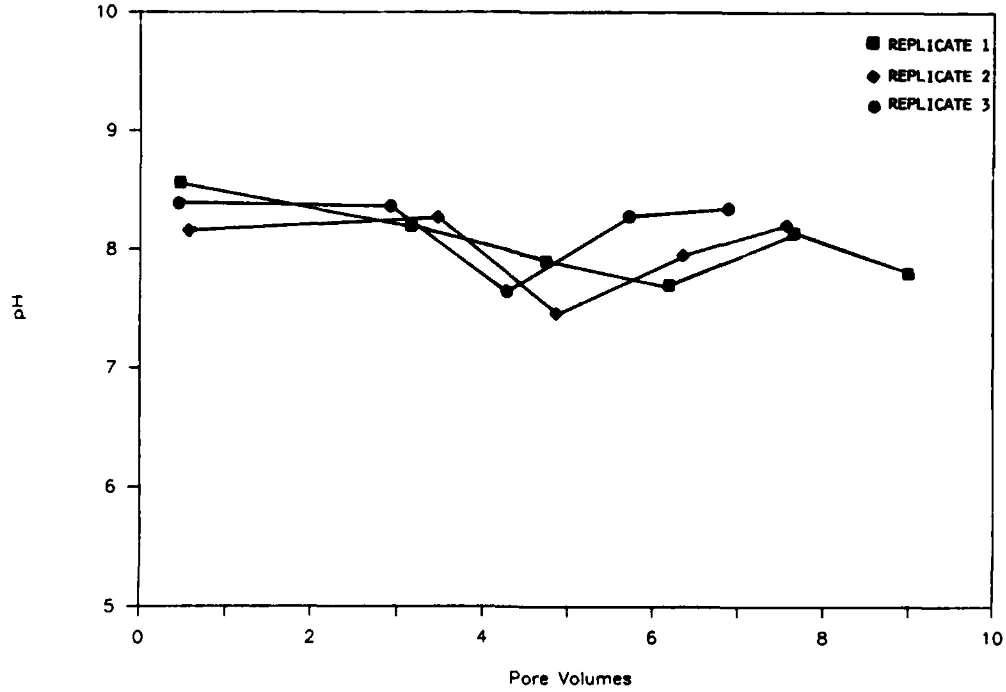

Figure 20. Values of pH in leachate from anaerobic metals permeameters

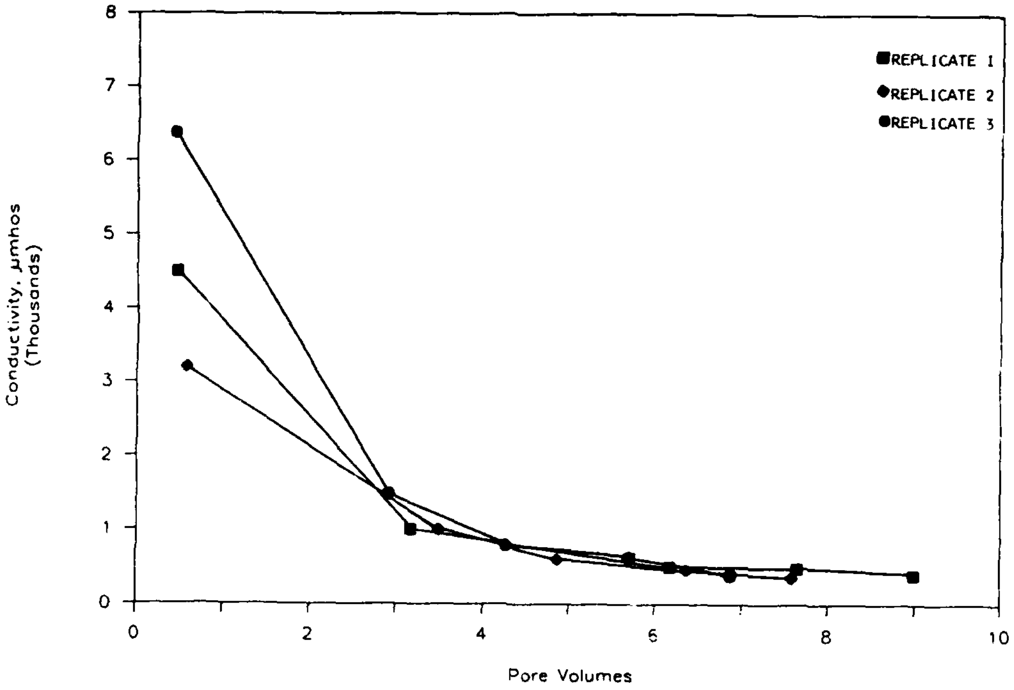

Figure 21. Conductivity in leachate from anaerobic metals permeameters

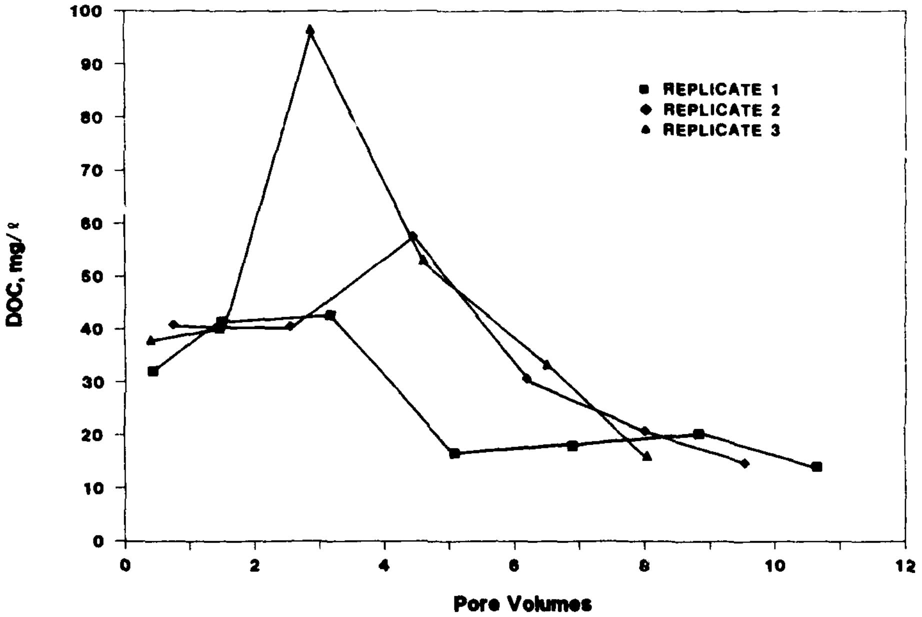

Figure 22. Dissolved organic carbon concentrations in leachate from anaerobic metals permeameters

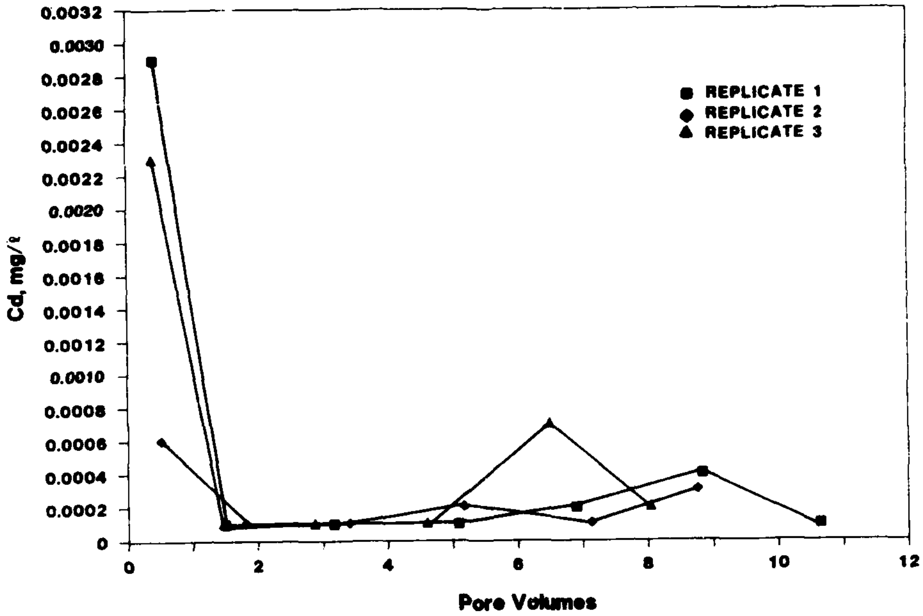

Figure 23. Cadmium concentrations in leachate from anaerobic metals permeameters

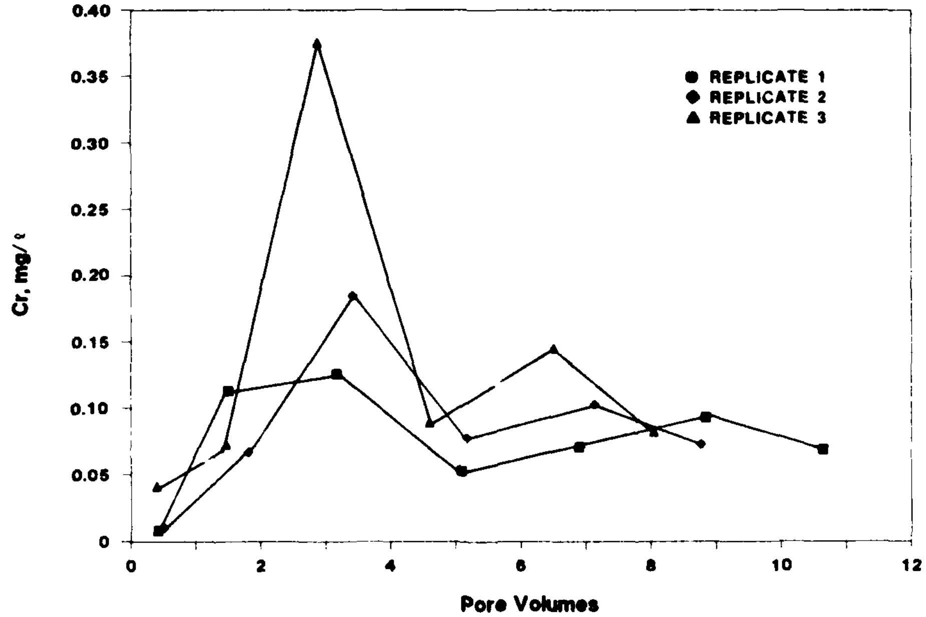

Figure 24. Chromium concentrations in leachate from anaerobic metals permeameters

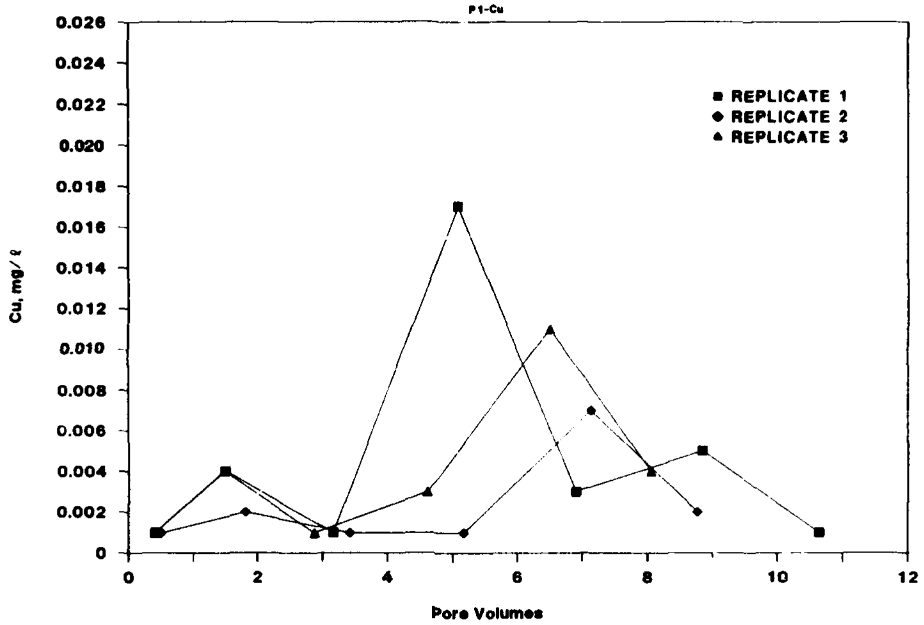

Figure 25. Copper concentrations in leachate from anaerobic metals permeameters

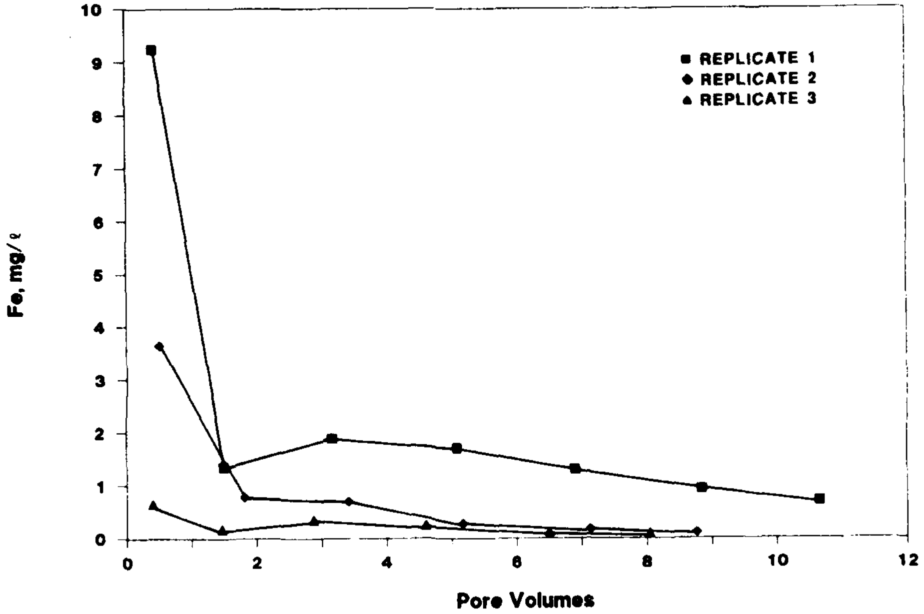

Figure 26. Iron concentrations in leachate from anaerobic metals permeameters

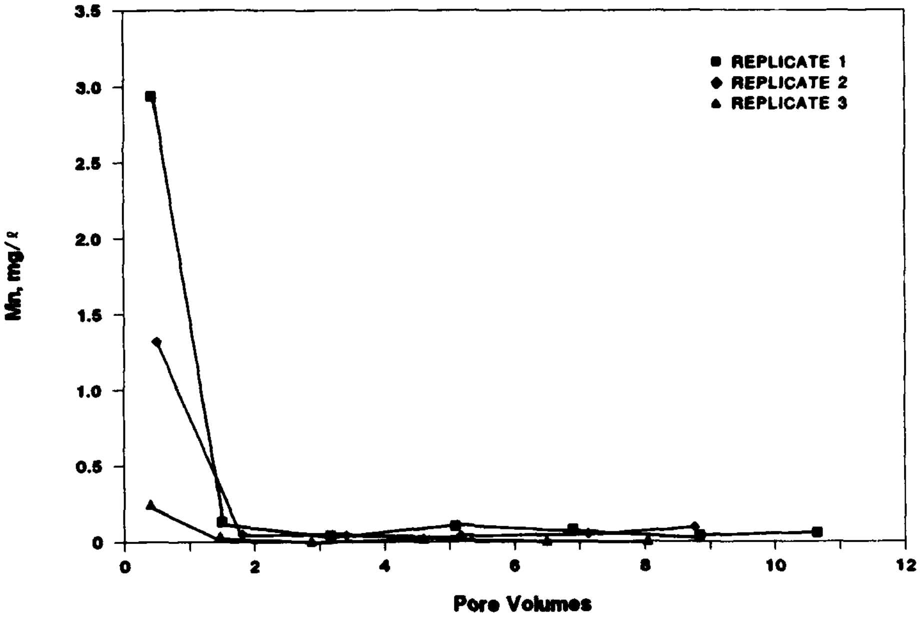

Figure 27. Manganese concentrations in leachate from anaerobic metals permeameters

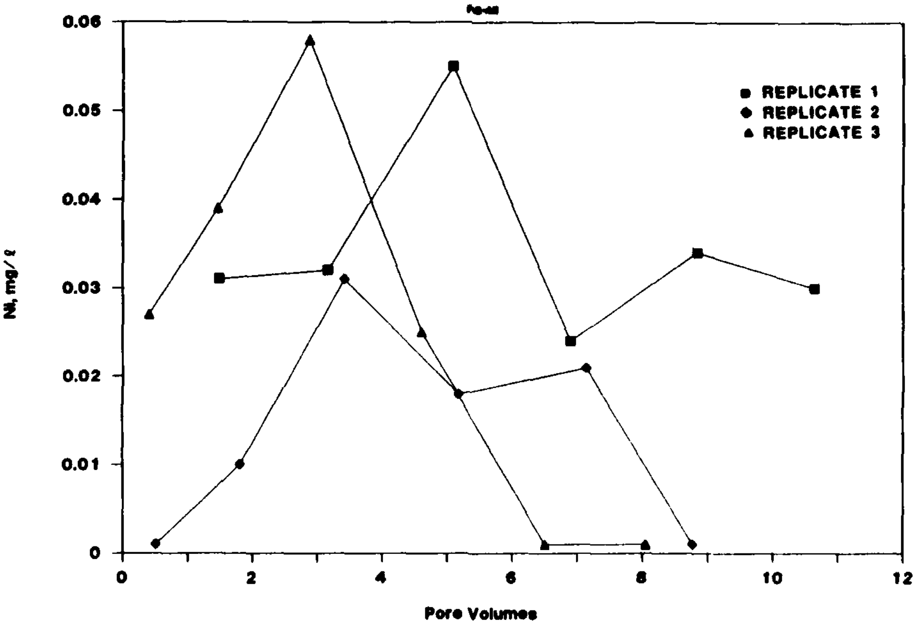

Figure 28. Nickel concentrations in leachates from anaerobic metals permeameters

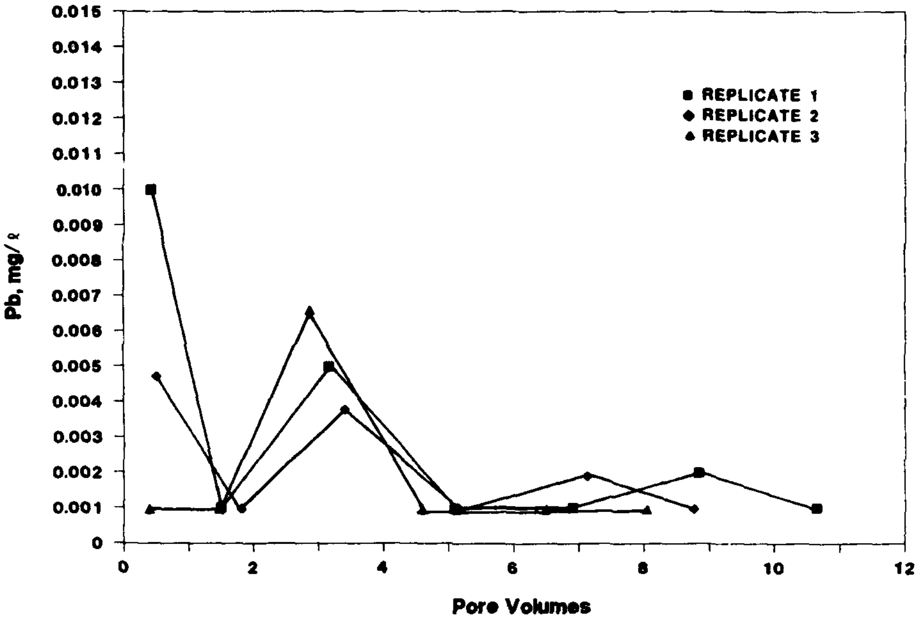

Figure 29. Lead concentrations in leachate from anaerobic metals permeameters

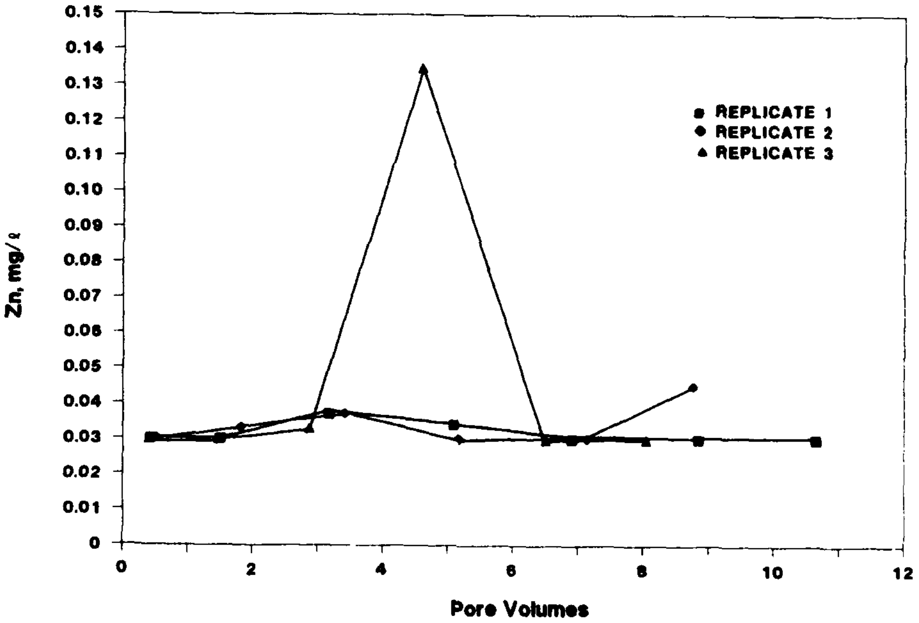

Figure 30. Zinc concentrations in leachate from anaerobic metals permeameters

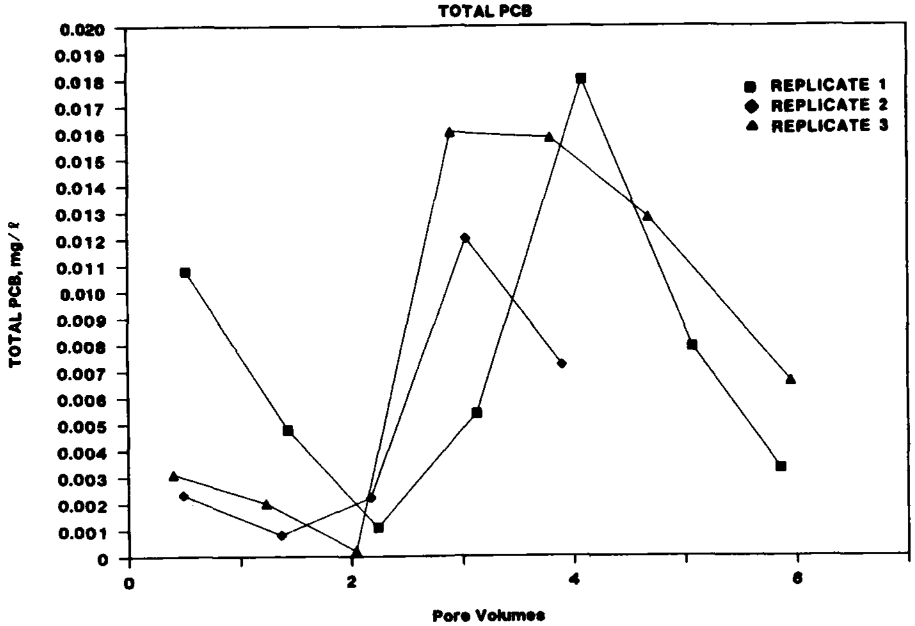

Figure 31. Total PCB concentrations in leachate from anaerobic organics permeameters

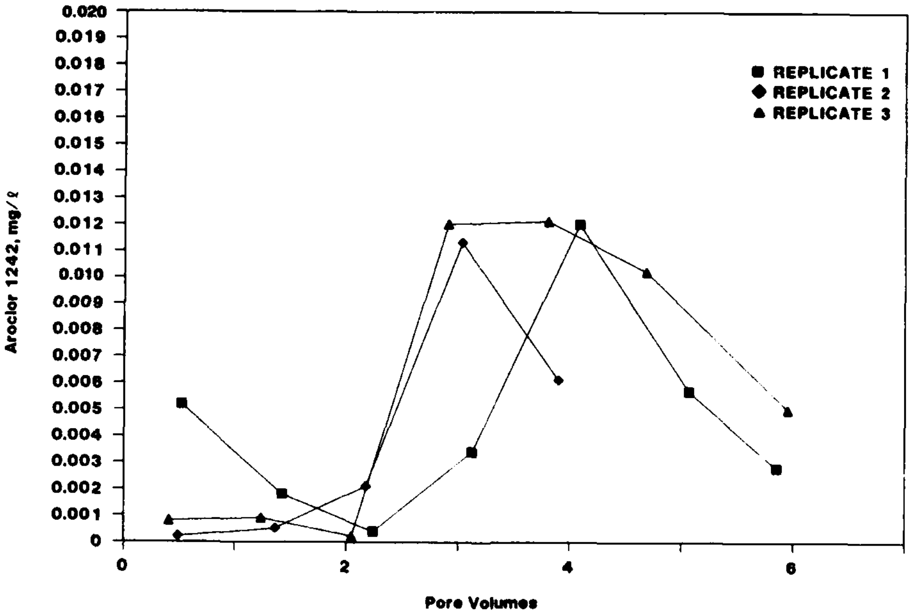

Figure 32. Aroclor 1242 concentrations in leachate from anaerobic organics permeameters

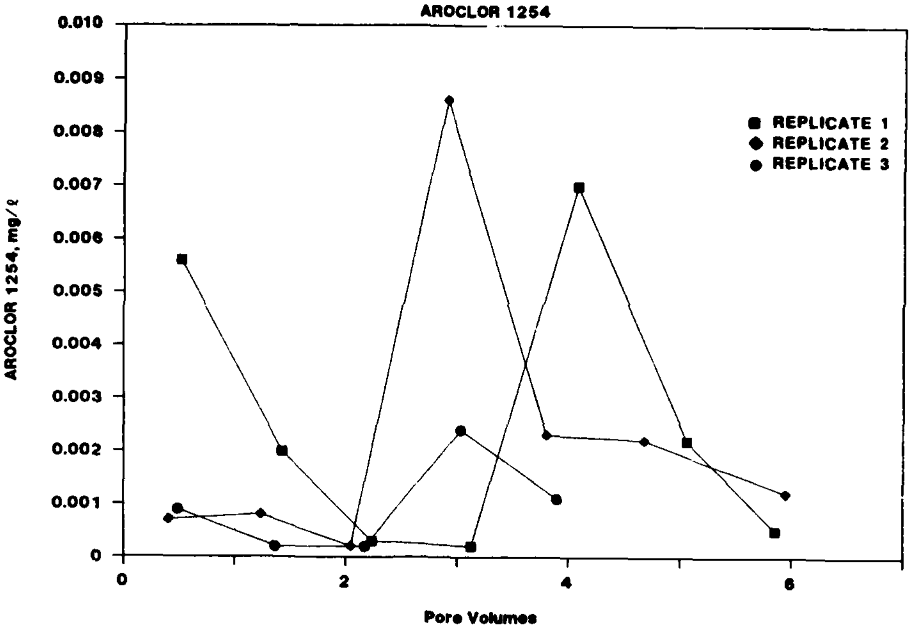

Figure 33. Aroclor 1254 concentrations in leachate from anaerobic organics permeameters

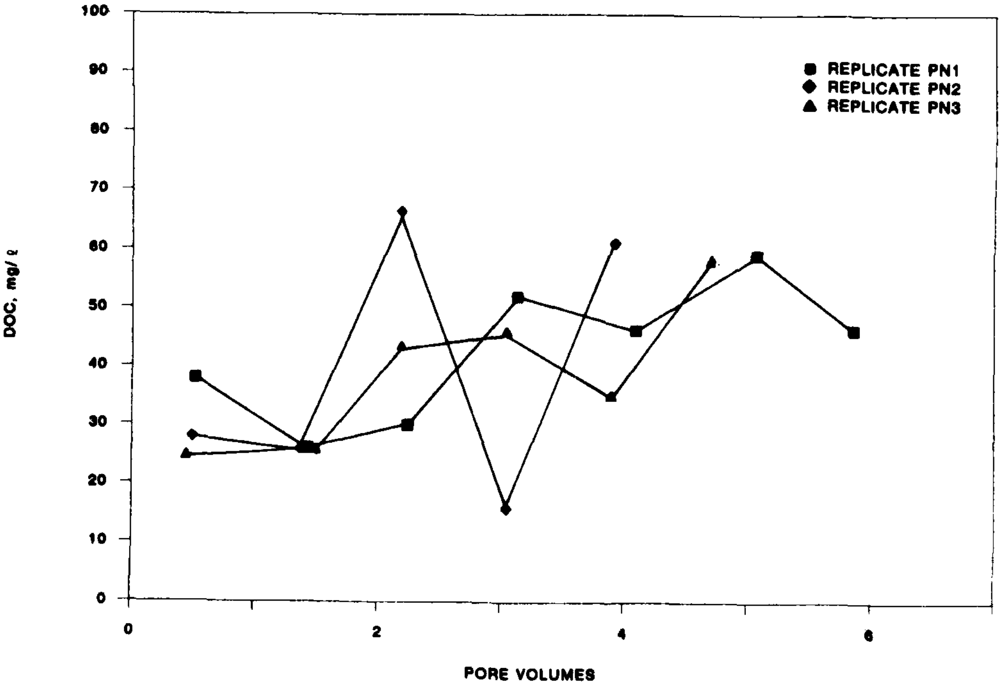

Figure 34. Dissolved organic carbon concentrations in leachate from anaerobic organics permeameters

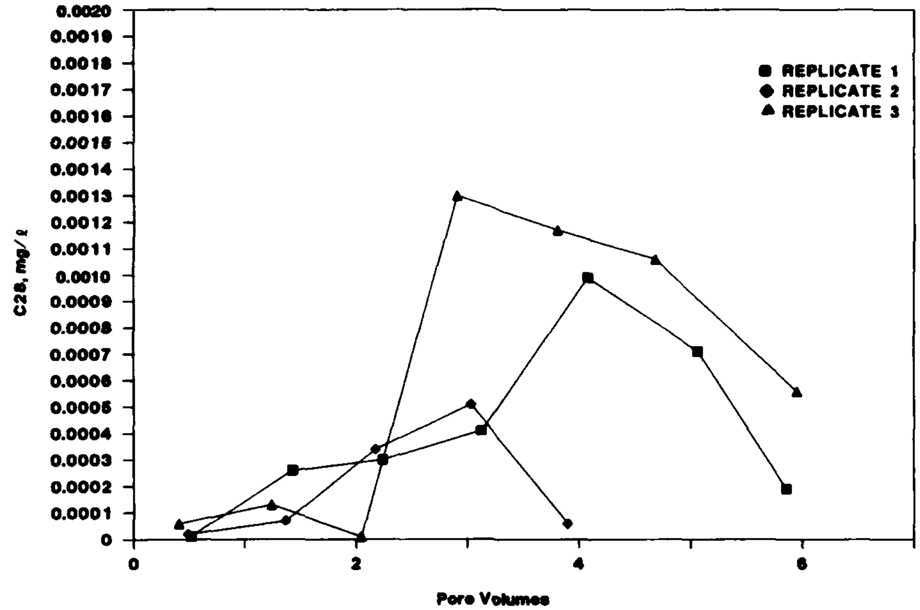

Figure 35. Congener C28 concentrations in leachate from anaerobic organics permeameters

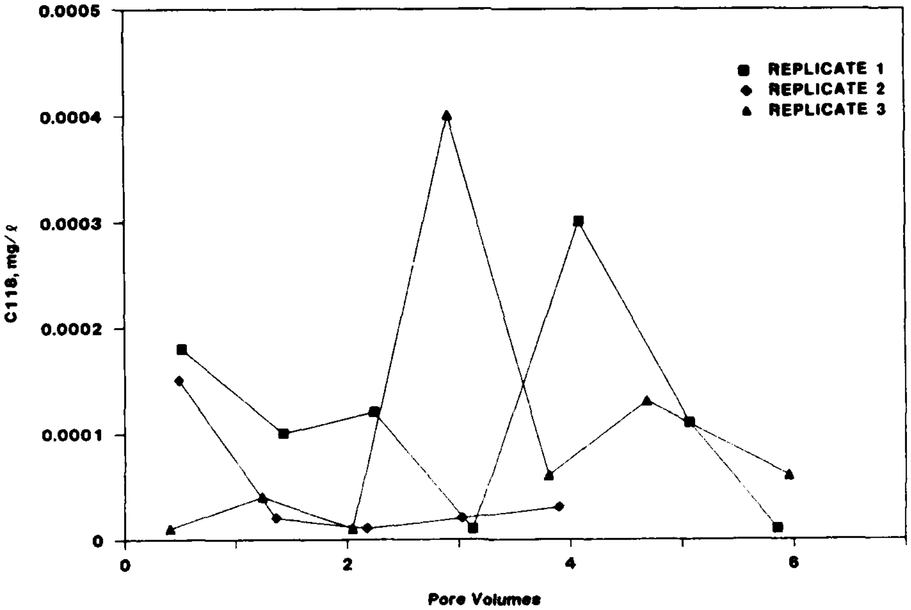

Figure 36. Congener C118 concentrations in leachate from anaerobic organics permeameters

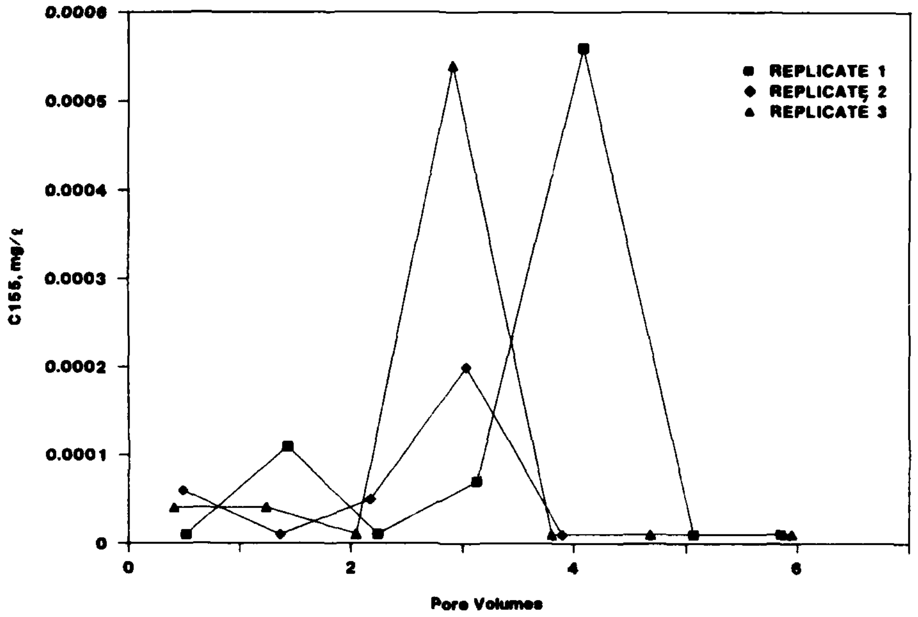

Figure 37. Congener C155 concentrations in leachate from anaerobic organics permeameters

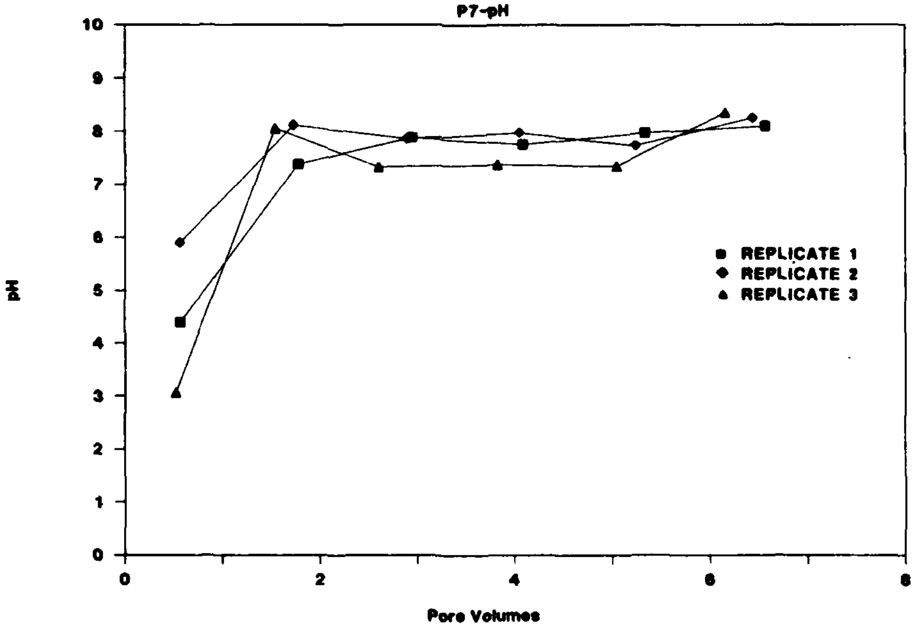

Figure 38. Values of pH in leachate from aerobic metals permeameters

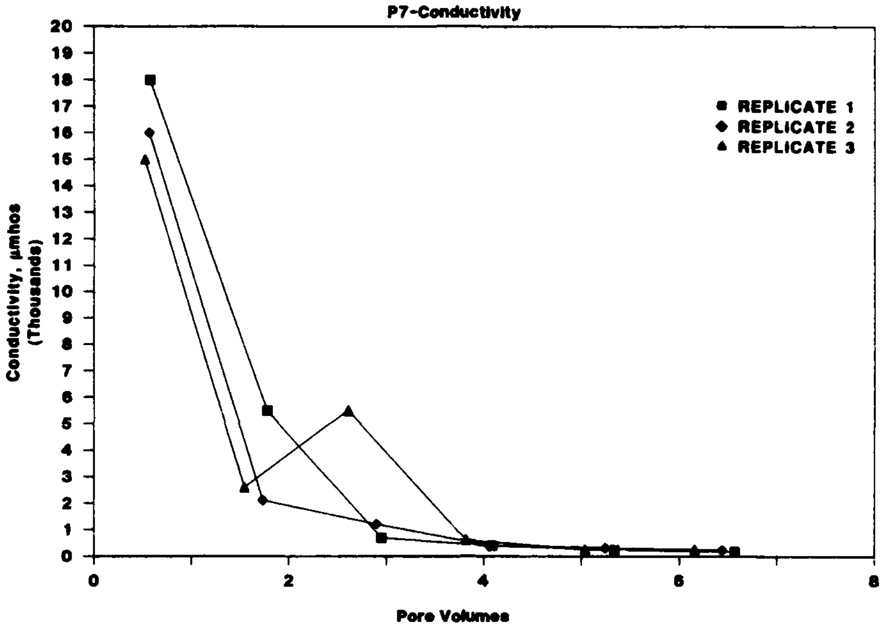

Figure 39. Conductivity in leachate from aerobic metals permeameters

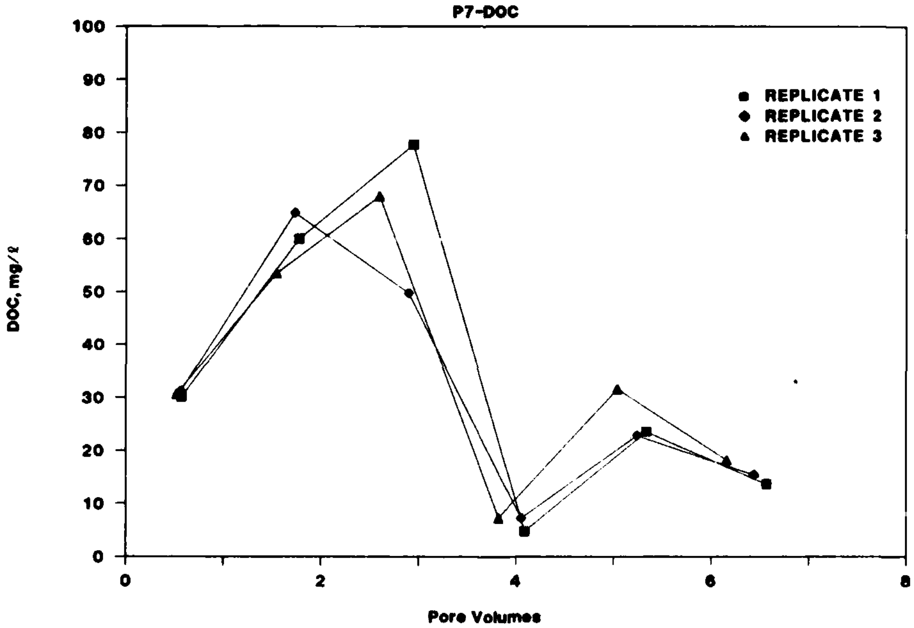

Figure 40. Dissolved organic carbon concentrations in leachate from aerobic metals permeameters

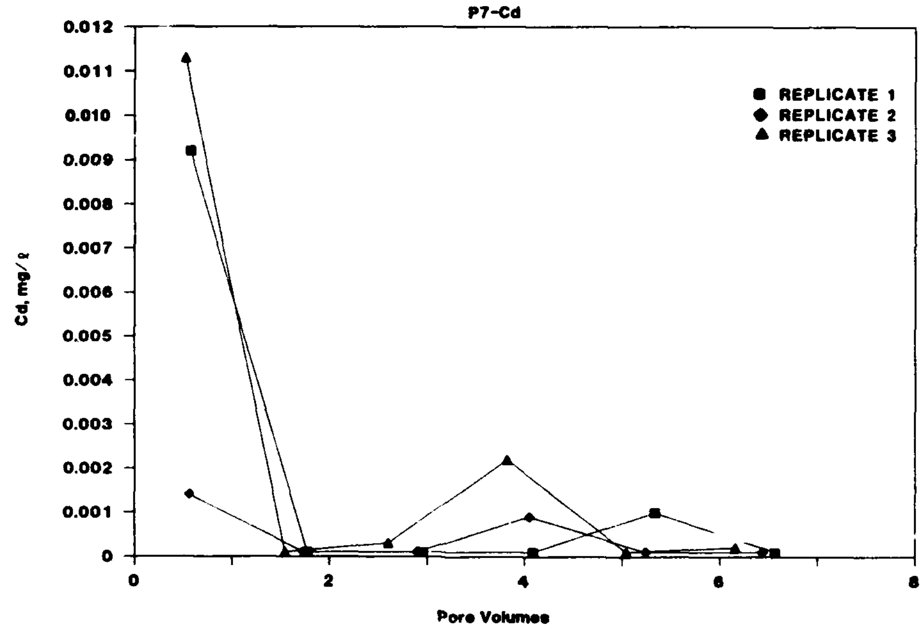

Figure 41. Cadmium concentrations in leachate from aerobic metals permeameters

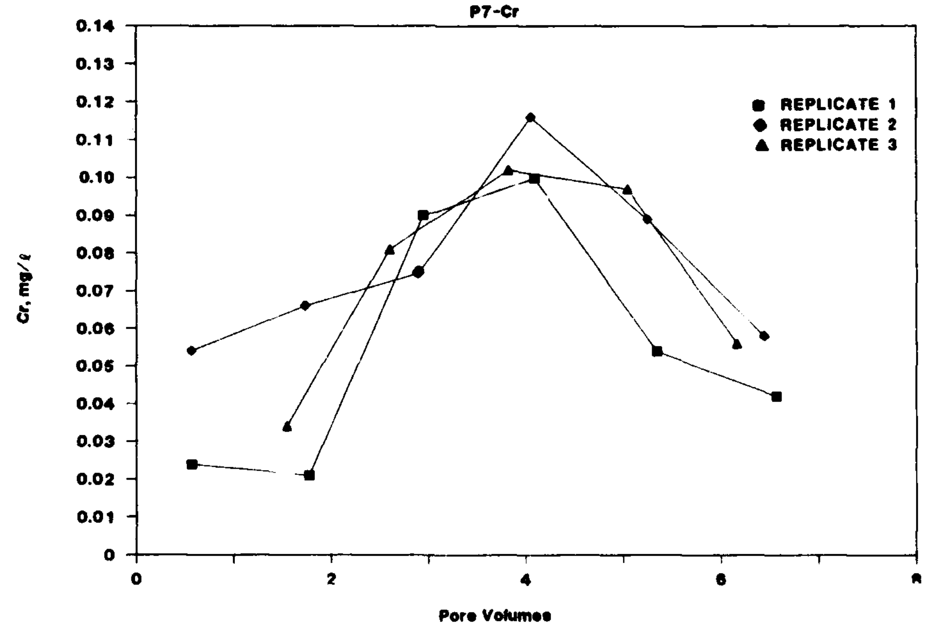

Figure 42. Chromium concentrations in leachate from aerobic metals permeameters

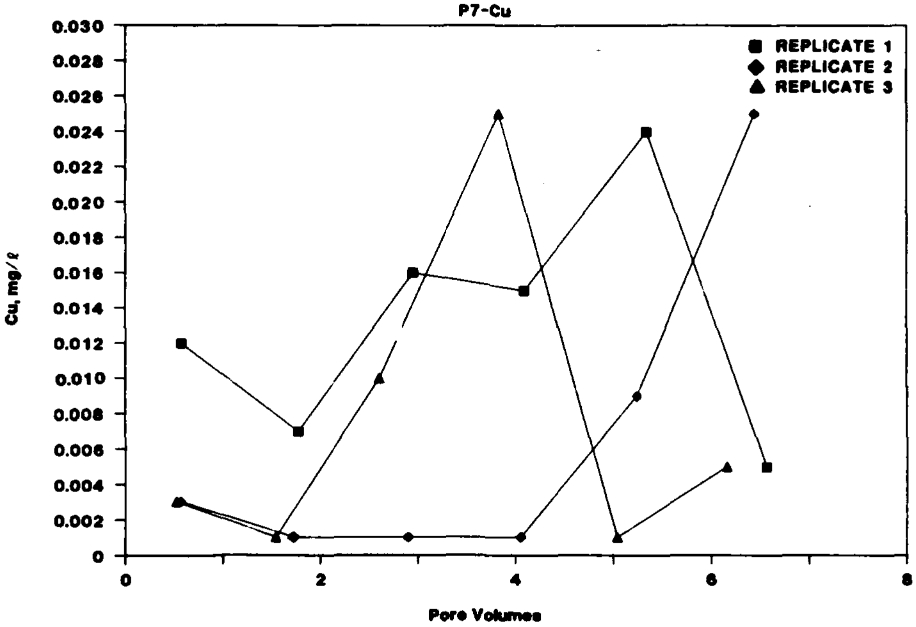

Figure 43. Copper concentrations in leachate from aerobic metals permeameters

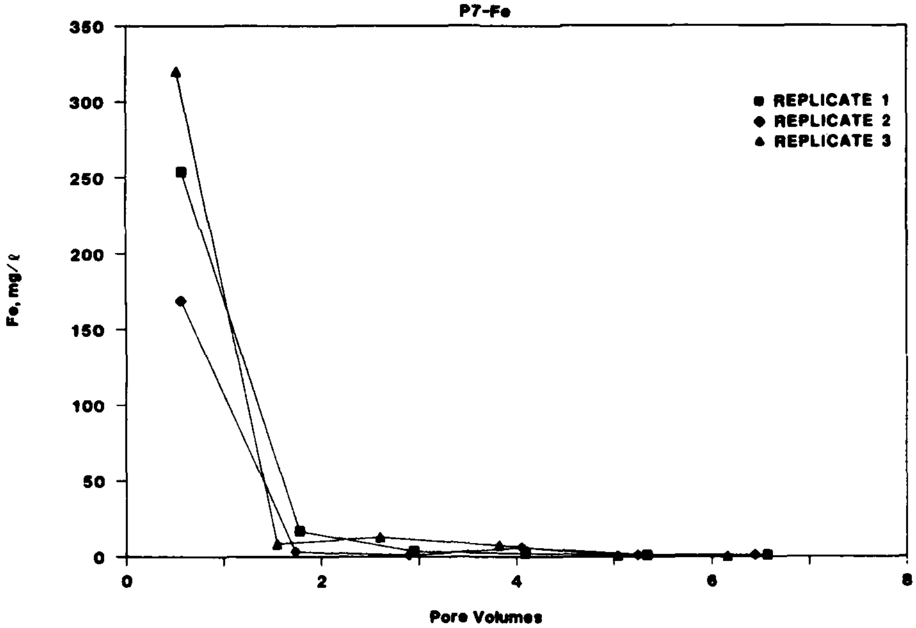

Figure 44. Iron concentrations in leachate from aerobic metals permeameters

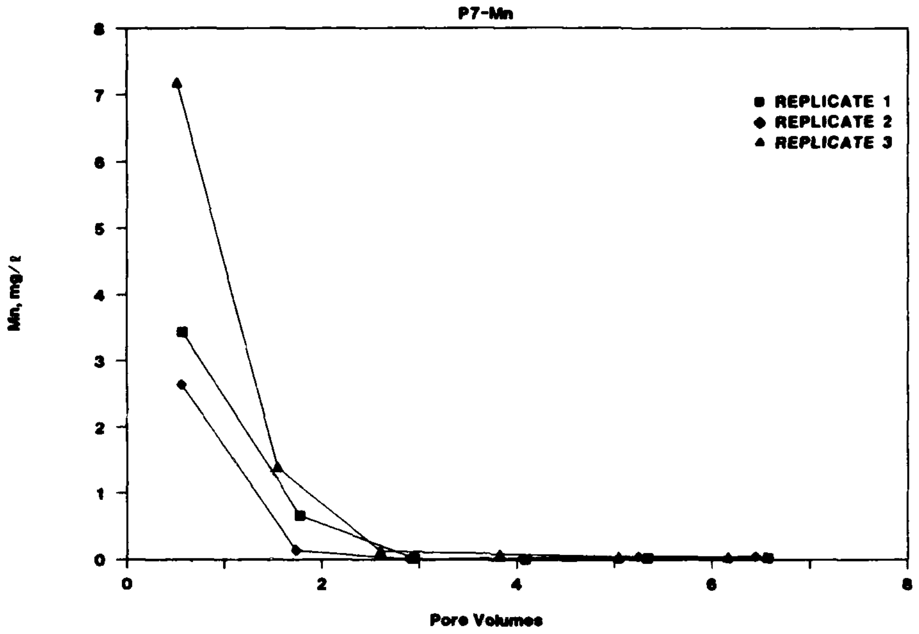

Figure 45. Manganese concentrations in leachate from aerobic metals permeameters

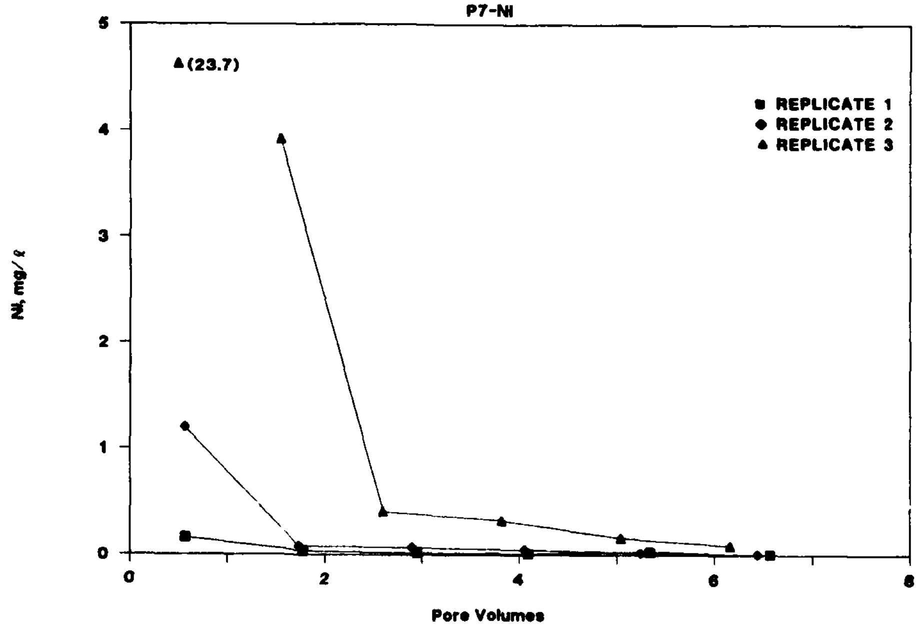

Figure 46. Nickel concentrations in leachate from aerobic metals permeameters

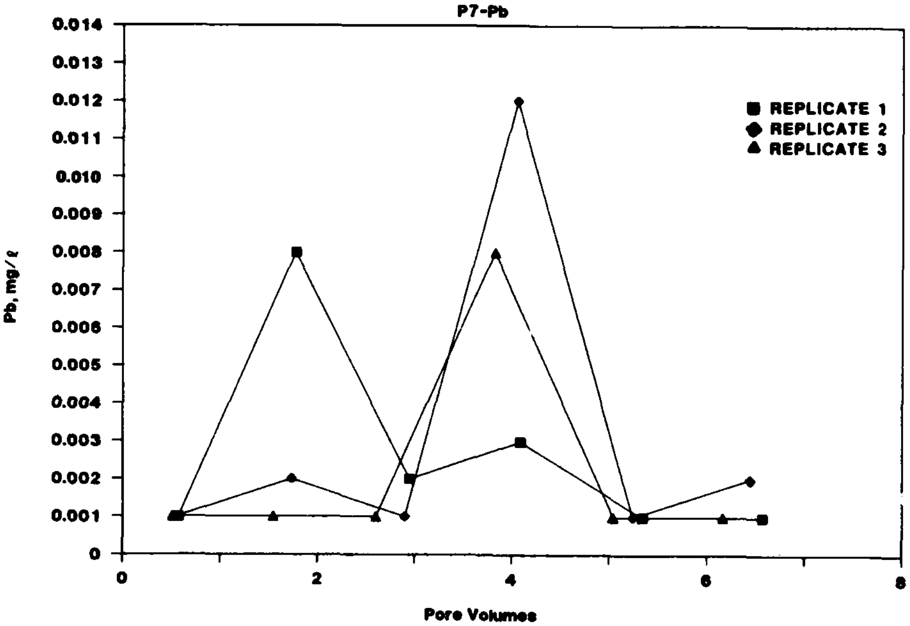

Figure 47. Lead concentrations in leachate from aerobic metals permeameters

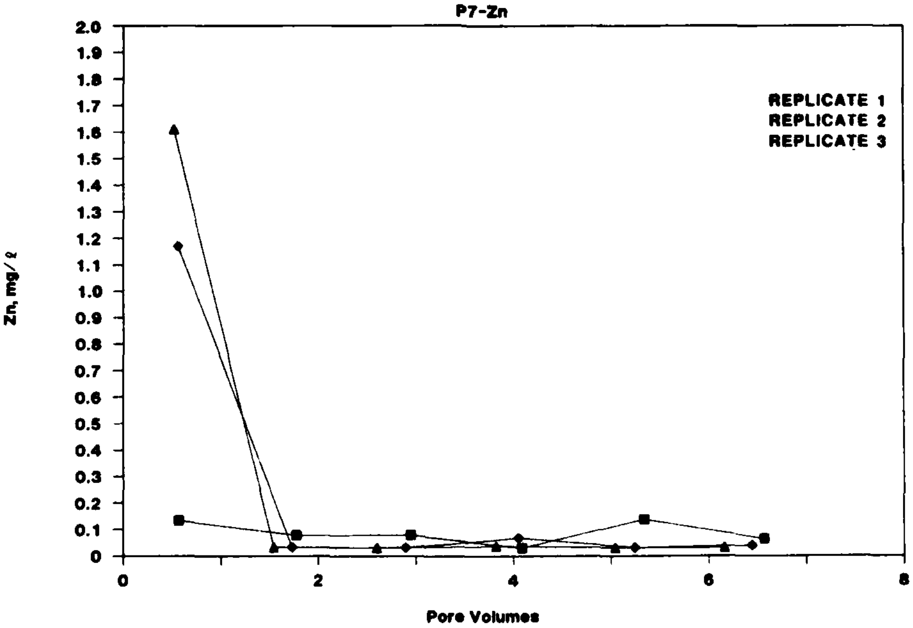

Figure 48. Zinc concentrations in leachate from aerobic metals permeameters

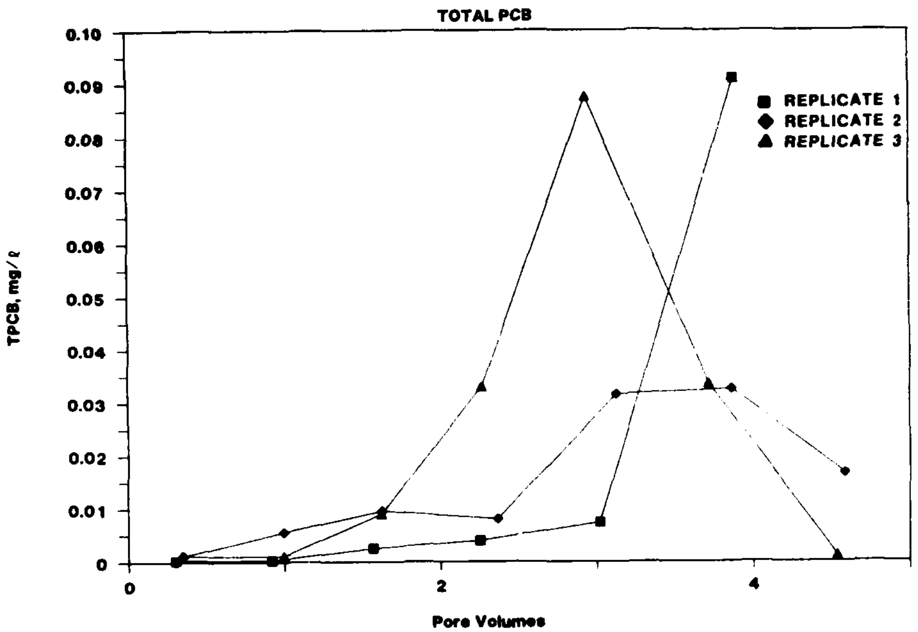

Figure 49. Total PCB concentrations in leachate from aerobic organics permeameters

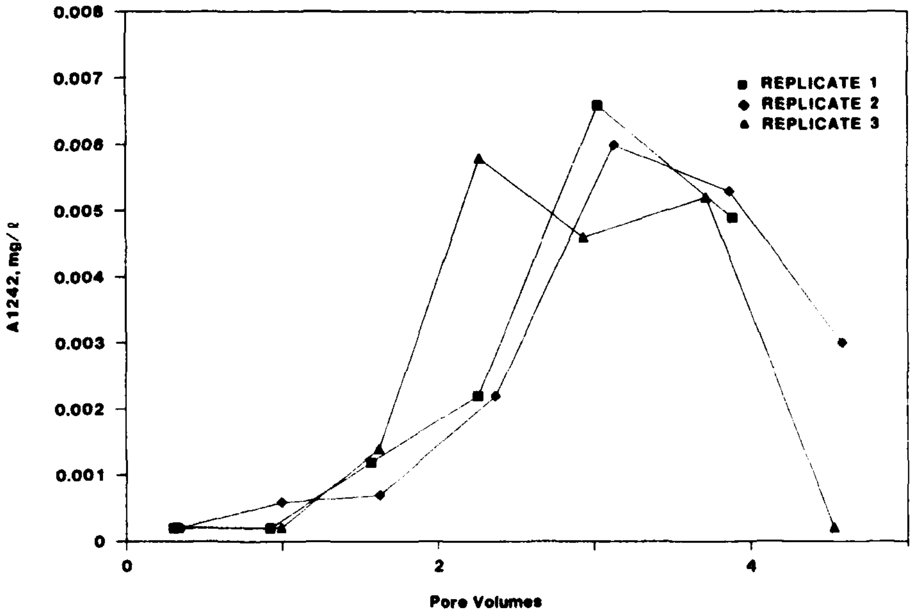

Figure 50. Aroclor 1242 concentrations in leachate from aerobic organics permeameters

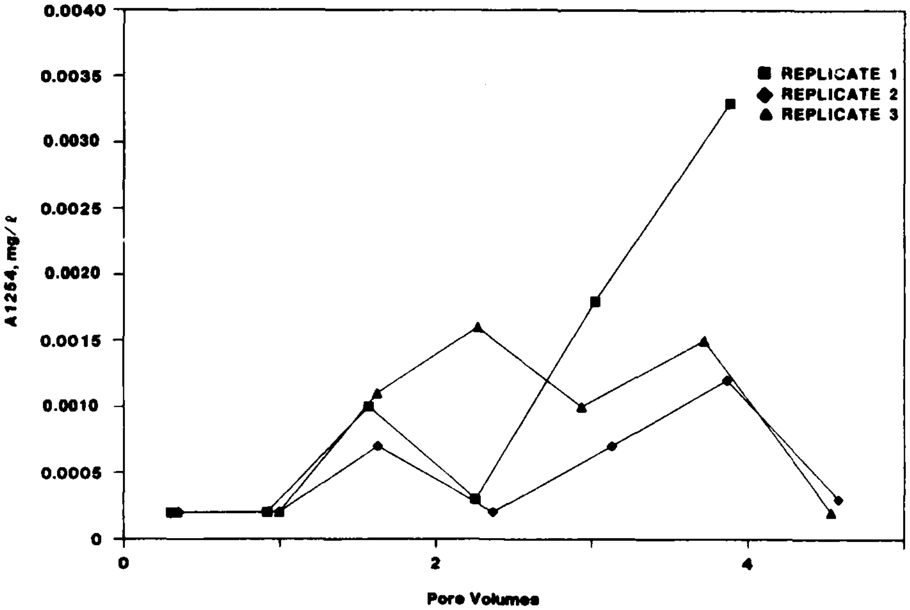

Figure 51. Aroclor 1254 concentrations in leachate from aerobic organics permeameters

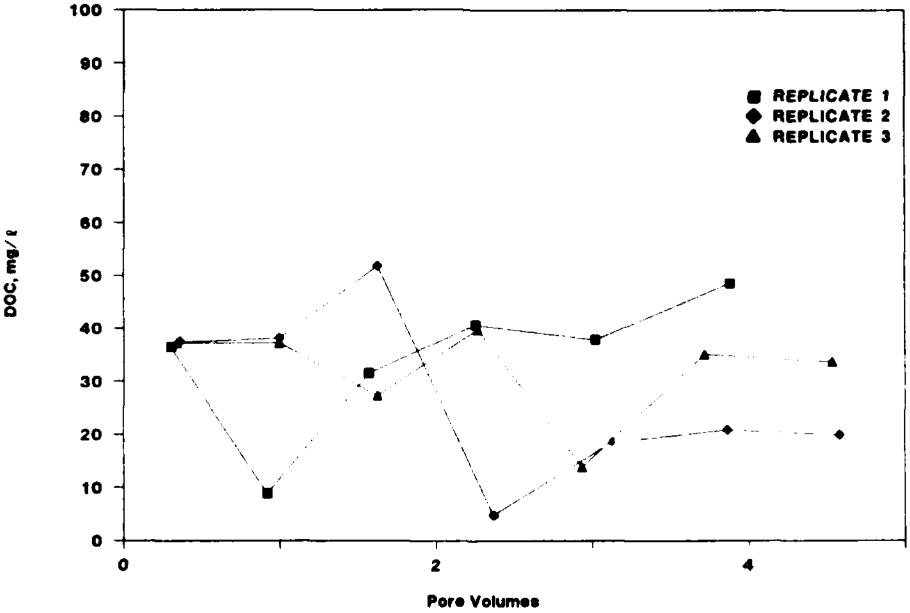

Figure 52. Dissolved organic carbon concentrations in aerobic organics permeameters

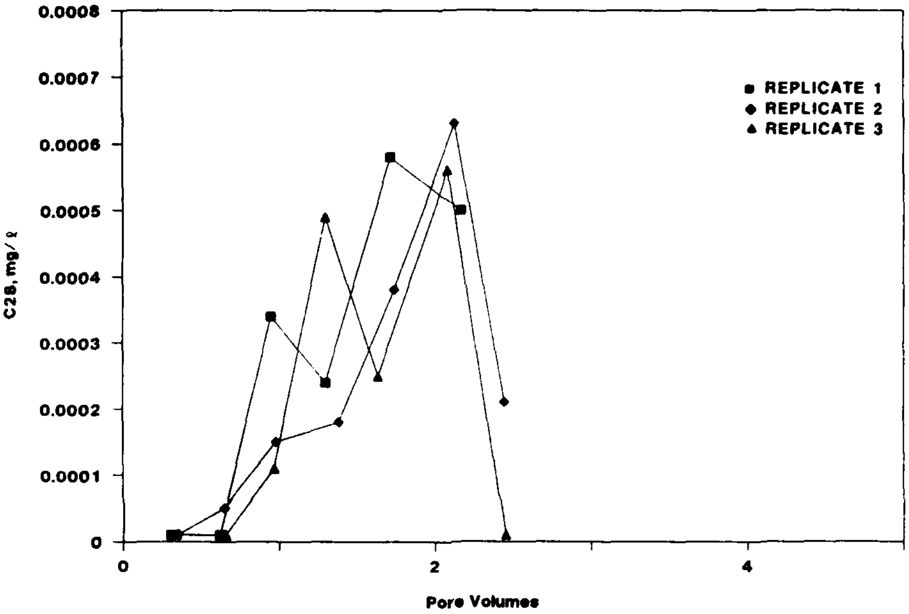

Figure 53. Congener C28 concentrations in leachate from aerobic organics permeameters

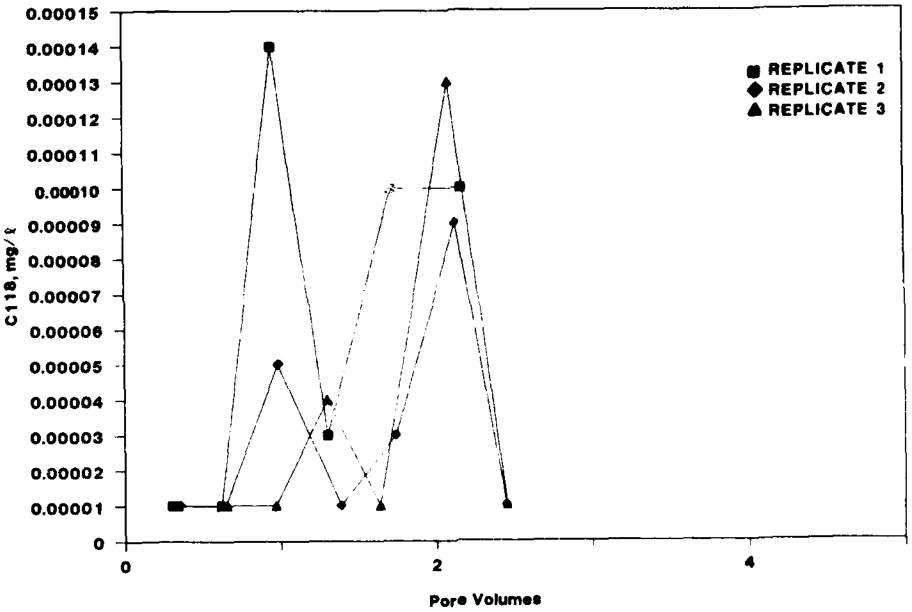

Figure 54. Congener C118 concentrations in leachate from aerobic organics permeameters

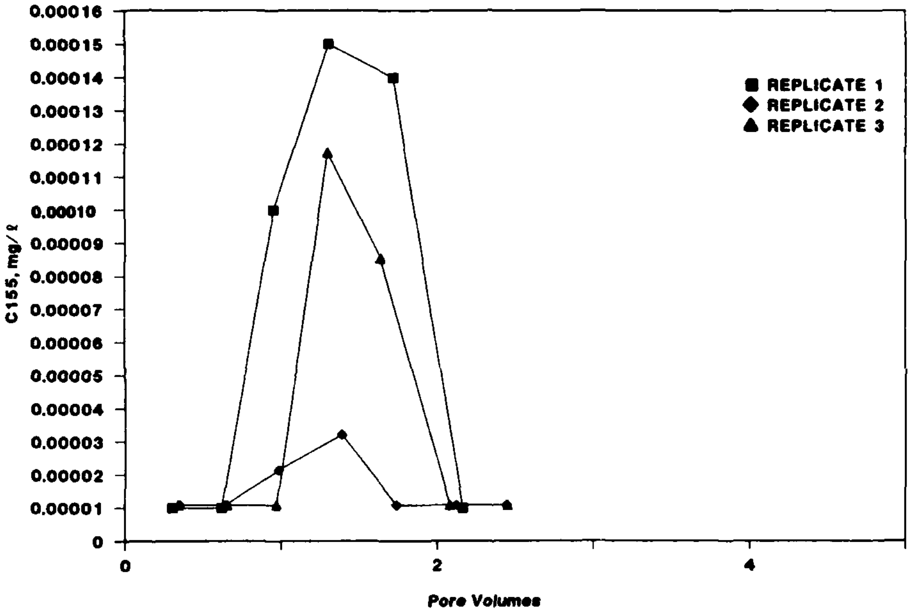

Figure 55. Congener C155 concentrations in leachate from aerobic organics permeameters

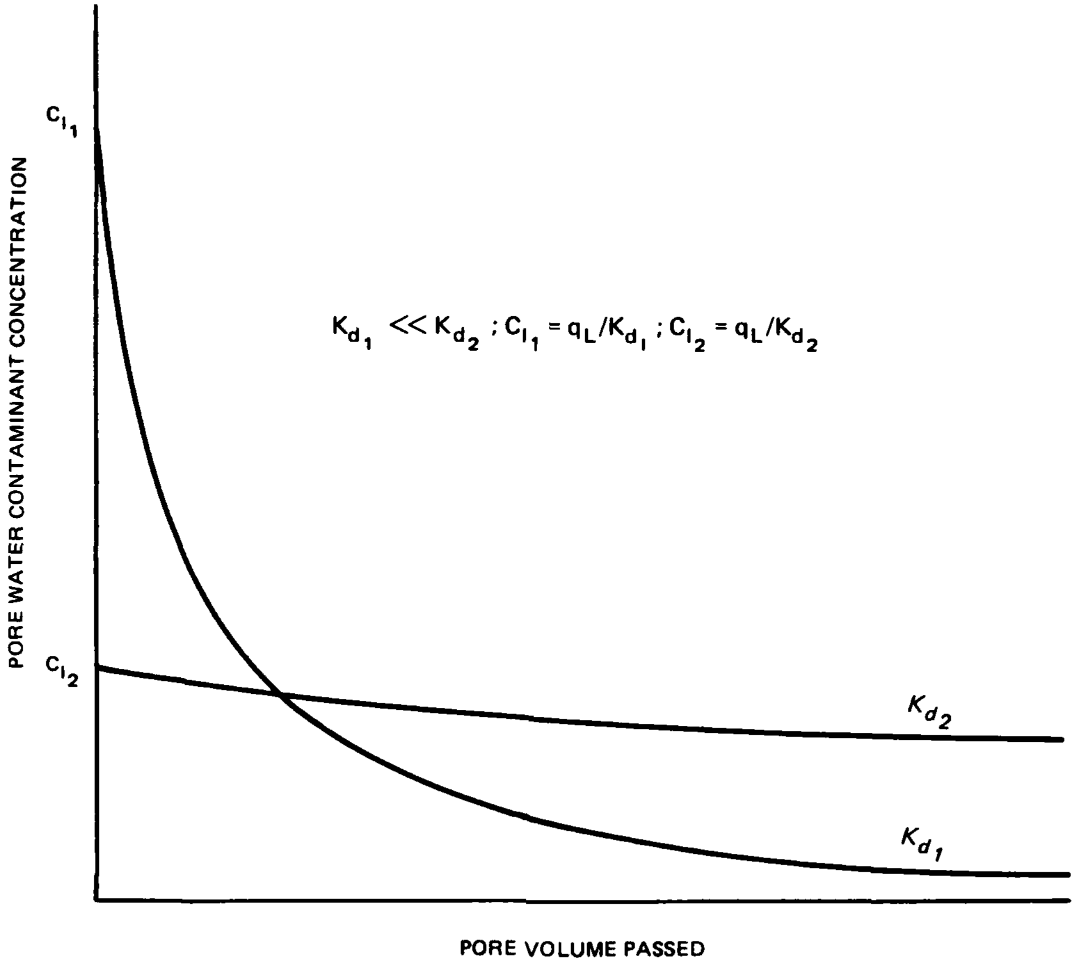

Figure 56. Dependency of contaminant persistence on K_d (from Environmental Laboratory 1987)

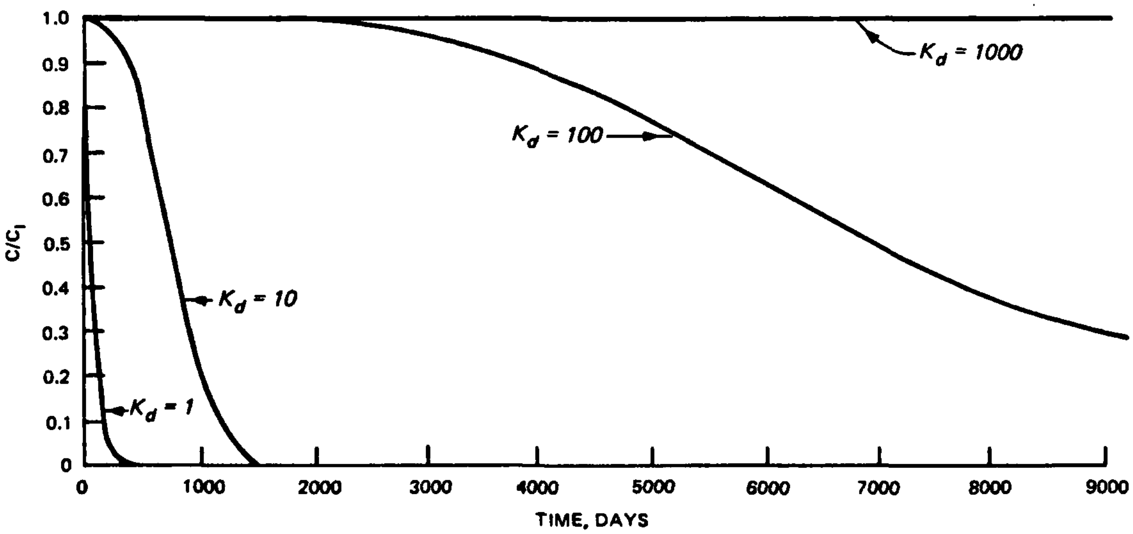

Figure 57. Fraction initial concentration remaining in permeameter leachate for various distribution coefficients (from Environmental Laboratory 1987)

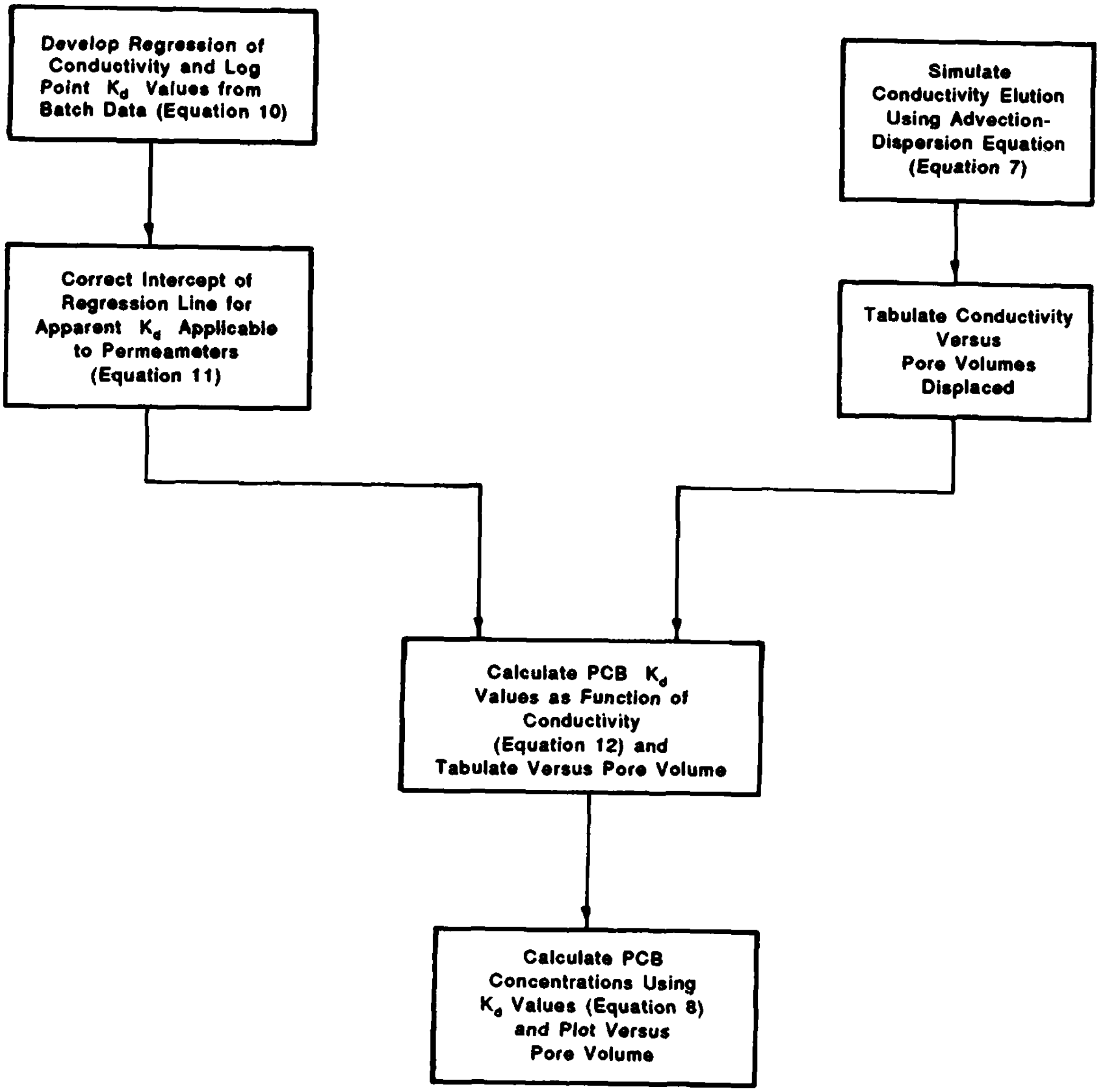

Figure 58. Procedure for simulating PCB elution in anaerobic permeameters during nonconstant partitioning

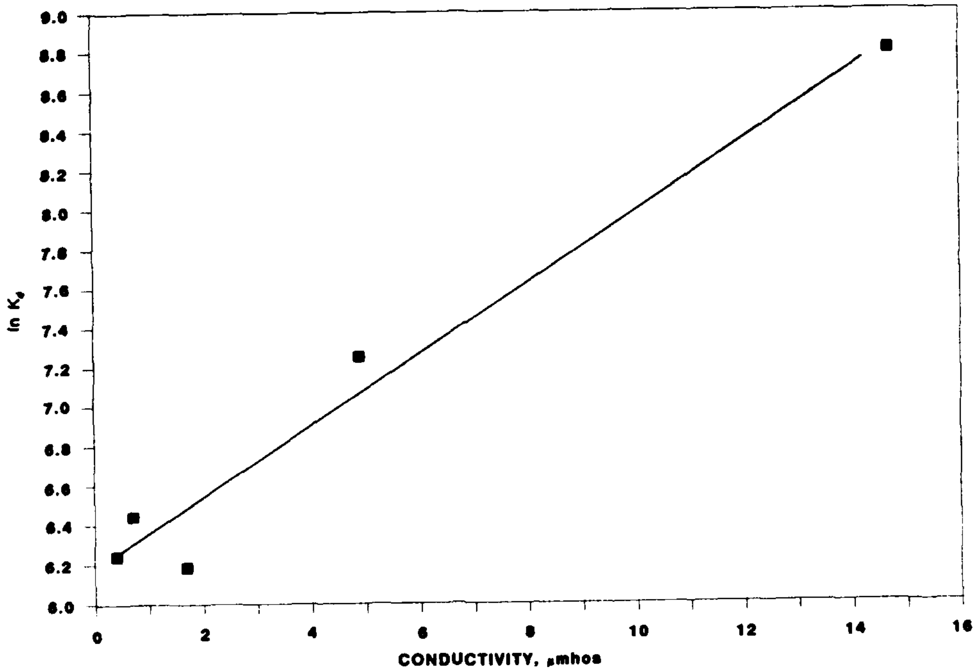

Figure 59. Distribution coefficient-conductivity relationship for total PCB in anaerobic sequential batch leach tests using DDI water

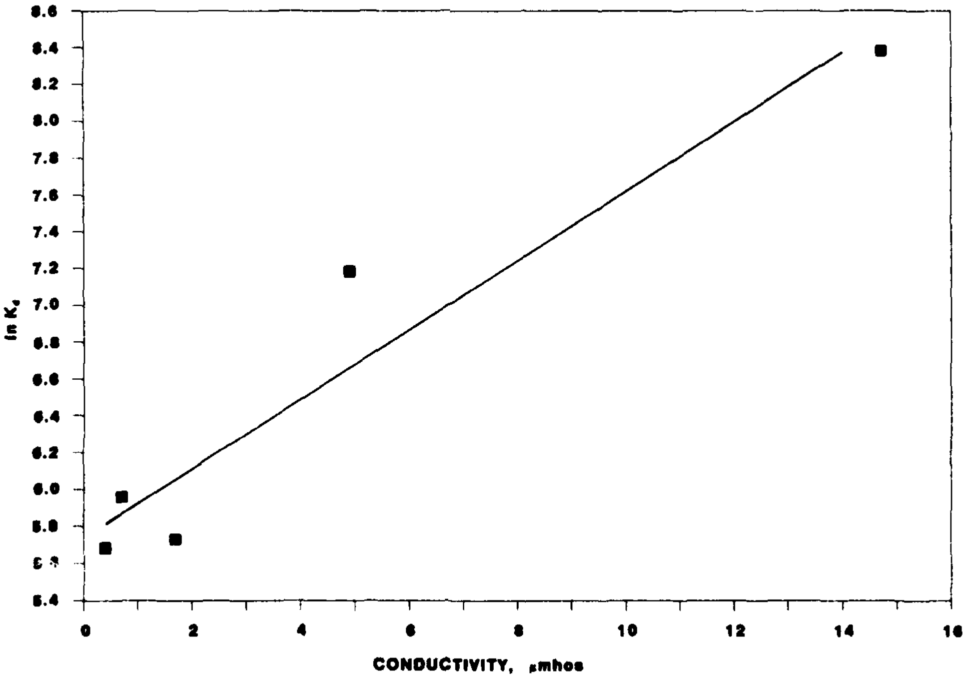

Figure 60. Distribution coefficient-conductivity relationship for Aroclor 1242 in anaerobic sequential batch leach tests using DDI water

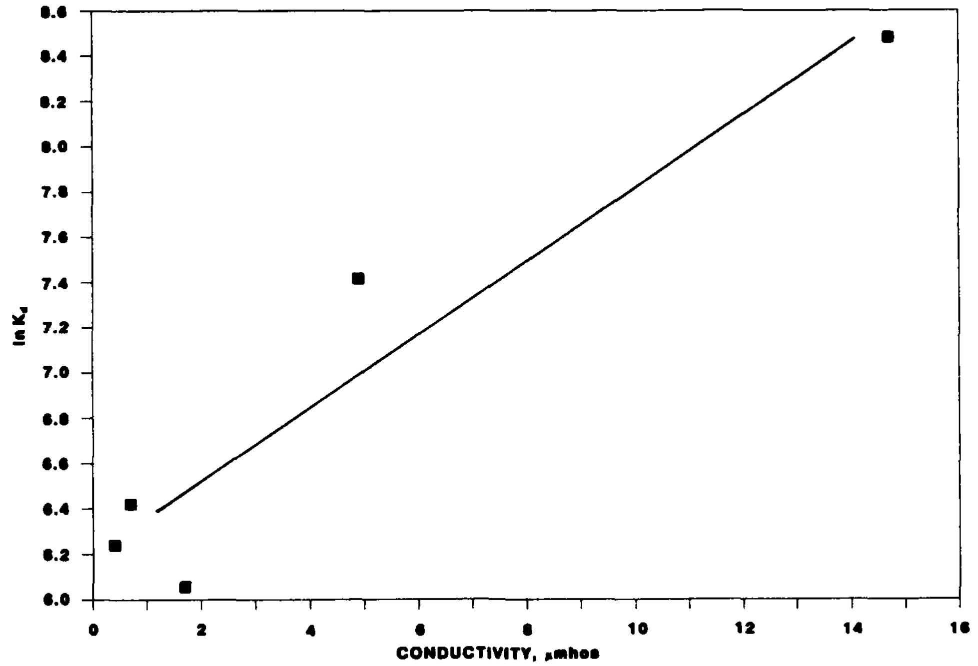

Figure 61. Distribution coefficient-conductivity relationship for Aroclor 1254 in anaerobic sequential batch leach tests using DDI water

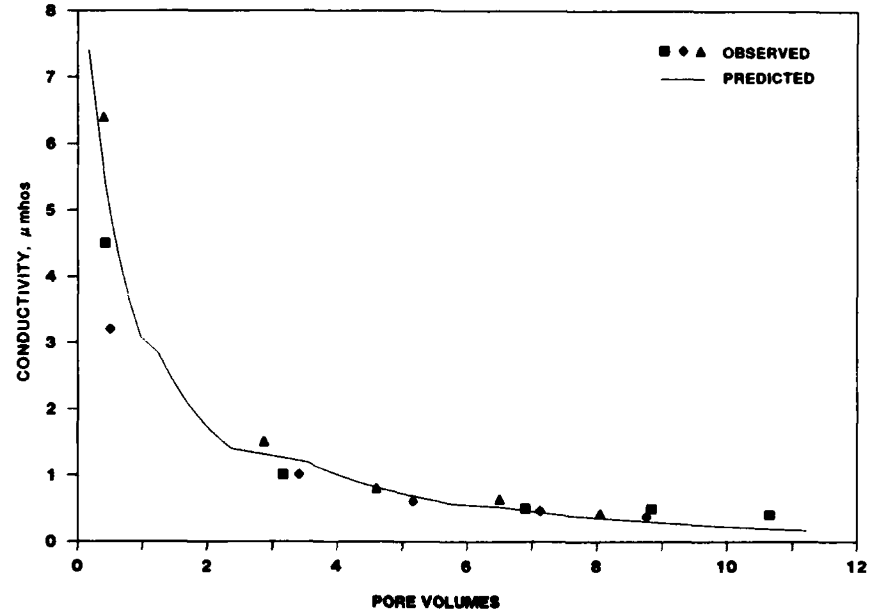

Figure 62. Predicted and observed conductivity elution curves for anaerobic metals permeameters

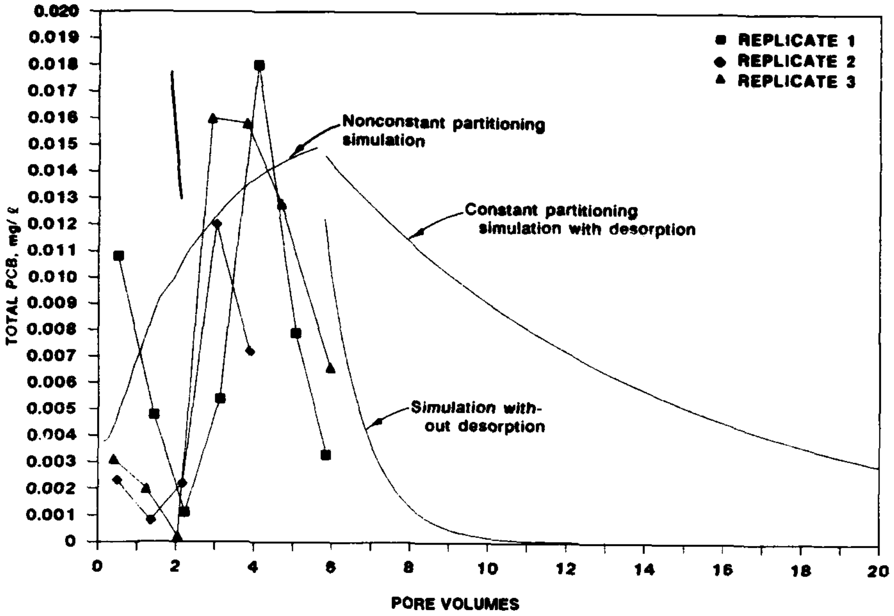

Figure 63. Simulated and observed elution curves for total PCB

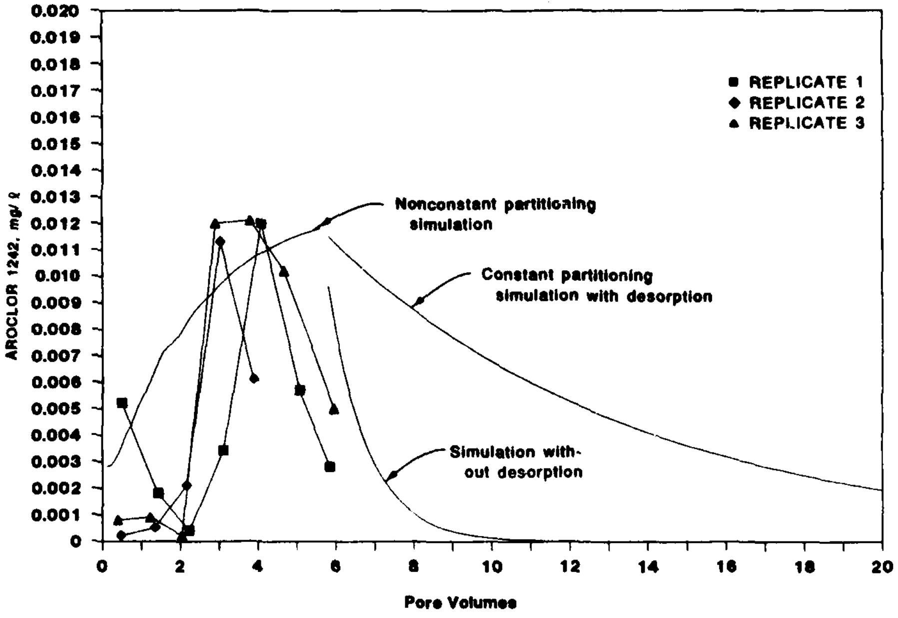

Figure 64. Simulated and observed elution curves for Aroclor 1242

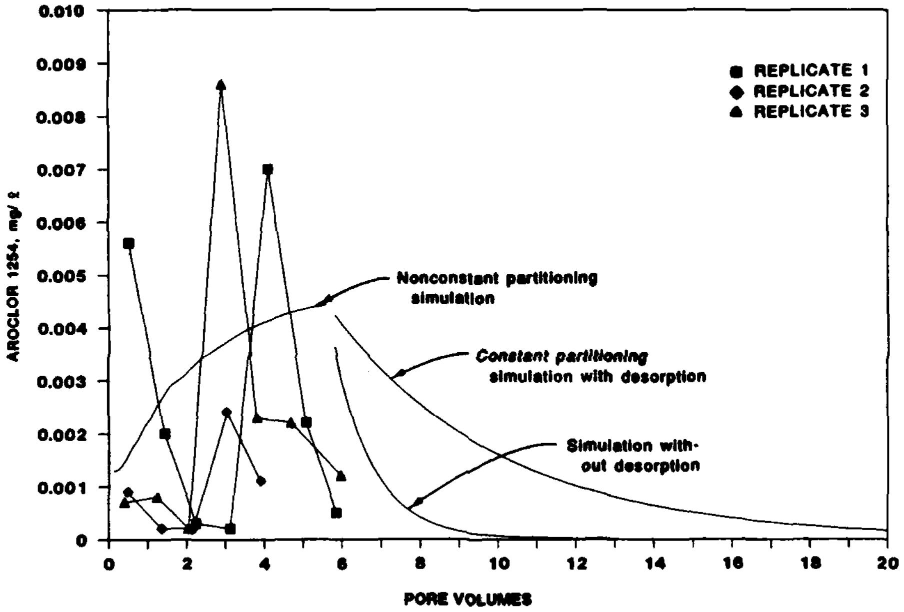

Figure 65. Simulated and observed elution curves for Aroclor 1254

APPENDIX A: INVESTIGATION OF FACTORS AFFECTING DESORPTION PROPERTIES OF NEW BEDFORD HARBOR SEDIMENT

Introduction

1. The equilibrium distribution of polychlorinated biphenyls (PCBs) between water and sediment is typically represented by a constant that is the ratio of the concentration in (or on) the sediment solids to the concentration in water (Thibodeaux 1979).* Hill, Myers, and Brannon (1988) present the essential aspects of the theory of these distribution coefficients as they apply to confined disposal facilities.

2. Previous leaching studies with sediments from Indiana Harbor, Indiana, and Everett Harbor, Washington, showed that sequential batch leaching is not always necessary to determine distribution coefficients for sediments (Environmental Laboratory 1987; Palermo et al., in preparation). Data from sequential batch leach tests plotted as a desorption isotherm tended to cluster around a central point, indicating that a single-cycle batch leach test could provide a good estimate of the distribution coefficient.

3. Because previous experience with PCB-contaminated sediments has suggested that distribution coefficients are constant and could be determined without sequential batch leaching, it was thought that sequential leaching of New Bedford Harbor sediment would not be necessary. As a check for deviation from previous results, a four-cycle sequential batch leach procedure was used for organic contaminants in New Bedford Harbor sediment.

4. The four-step leaching procedure presented in the main text gave results that were not consistent with previous experience or theory. Concentrations of PCB in the leachate increased at the beginning of leaching, contrary to expected results. Release of PCBs from New Bedford sediment could not be described by single distribution coefficients because the first portion of the isotherms showed nonconstant partitioning. Following the third leaching cycle, desorption isotherms began turning toward the vertical axis, a trend that would result in a classical desorption isotherm. Therefore, K_d values used to describe initial PCB leaching cannot be used to predict long-term PCB leaching from New Bedford sediment.

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* See References at the end of the main text.

5. Metal releases from anaerobic New Bedford sediment in batch tests also showed negative isotherms similar to those observed for PCBs when steady-state sediment and leachate concentrations were plotted. Metals, however, showed no indications of a turn toward the vertical axis in the desorption curve, even though metal leaching was taken through seven desorption cycles.

6. Results for metals and PCBs may be due to deviation from partitioning theory in highly contaminated Superfund sediments or may be particular to estuarine and marine sediments. Possible factors that could cause the results observed include (a) microbe-mediated transfer, (b) formation of microdroplets of PCB that remain in the leachate following centrifugation and filtration, and (c) destabilization of colloidal material and dispersion into leachate as the salinity decreased during successive leaching with distilled water. This appendix provides detailed descriptions and results of the tests used to examine the three factors listed above.

Methods and Materials

Microorganism enumeration in leachate

7. Microbes can possibly act as a carrier of PCB in leachate. To investigate the population dynamics of microbes in the leachate, microbial enumeration was carried out in leachate. Leachate was obtained for this portion of the study following procedures described for organic contaminants in sequential batch testing (see Part II of the main text). Seven leach cycles (a leach cycle consists of a batch test followed by centrifugation and replacement of removed water) were tested. In addition to the distilled water leachate, leachate was prepared for testing using 20 ppt saline water. The saline water was prepared in the laboratory using the method of Burkholder (1963). Leachate tests for microbial enumeration were conducted in triplicate.

8. Microorganisms were enumerated using a standard plate count method. Following filtration at the end of each leach cycle, a 10.0-ml sample was taken from each of the three replicate leachate samples and placed into an empty, sterile bottle. A 2.1-ml subsample was then taken from each bottle and, using appropriate aseptic technique, was carried through a dilution series from 10^0 to 10^{-9}. The remaining sample in each bottle was retained for the acridine orange (AO) examination described in the following section. The

diluent used was a sterile phosphate buffer (Butterfield's) containing 68 g of KH_2PO_4 per litre of glass-distilled water; the pH of the buffer was adjusted to 7.2 with 1N NaOH. Following placement into sterile 100-mm Petri plates, each dilution was mixed with sterile melted Standard Methods agar at 45° C using the pour plate technique. Plates were incubated 3 to 5 days at room temperature and then counted. The procedure was repeated daily for the seven cycles of the sequential leach tests.

PCB microdroplet investigation

9. To investigate the possibility that microdroplets of PCBs remained in the leachate following filtration, a hydrophobic surface-specific fluorescent dye was added to the leachate, followed by microscopic examination for microdroplets. Leachate for use in this test was prepared as described previously for the microbial investigation. Filtered leachates were examined using a modified version of the AO staining method of Hobbie, Daley, and Jasper (1977). A 4.0-ml subsample of each leachate sample tested was placed into a small clean test tube. To this was added 0.4 ml of 0.1-percent AO dye (freshly prepared). Following a 1-min incubation, the sample-dye mixture was filtered through a 0.2-μm, 47-mm-diam Nucleopore filter that had been prestained with Irgalan black dye. Filters were examined directly using Cargille immersion oil on a Zeiss Standard 18 microscope equipped with IV FL epifluorescence condenser, a 100-W halogen lamp, 455- to 500-bandpass filter, 510 beam splitter, and an LP 528 Barrier filter. When appropriate, results were recorded with a Zeiss camera back-attached to the tripod ocular tube on the microscope.

Leachate chemical testing

10. Metal and PCB analysis of leachate obtained using both saline and distilled water was conducted to investigate the effect of leaching solution ionic strength. Leachate for metals testing was obtained using seven leach cycles and the methods described for sequential leaching of metals in Part II of the main text. Saline leachate was obtained using the same method, except that the saline water previously described was used in place of distilled-deionized water. Saline and distilled water leachate for analysis of PCBs and dissolved organic carbon (DOC) were obtained as previously described in the microbial enumeration section of this appendix. Conductivity and pH analyses were conducted on these leachate samples as described in the main text. Sediment was also shaken in duplicate for a single leach cycle with a 5-percent

solution of sodium metaphosphate to determine if a dispersant would mobilize PCBs by breaking up flocculent material.

Analytical and statistical methods

11. Analytical methods used to chemically analyze leachate were identical to those described in the section on chemical analysis (see Part II of the main text). Statistical methods used were also identical.

Results and Discussion

12. Conductivity and pH values for saline and distilled water leachate from New Bedford Harbor sediments are summarized in Table A1. Conductivity values in the distilled water leachate showed a rapid decrease as leaching progressed. Conductivity of the saline water, as expected, remained relatively constant over the course of the leach tests. Leachate pH was somewhat higher in the distilled water leachate compared with the saline water leachate over the course of the test; the greatest difference measured occurred in the seventh leach cycle. The pH reported in Table A1 for distilled water leachate was consistently higher than distilled water leachate pH measured during previous testing (see Table 15 of the main text). Such a phenomenon, perhaps a result of sediment aging during storage, could possibly affect metal results, but should have little impact on PCB results.

Microorganism enumeration

13. The trends observed in numbers of microorganisms in the saline and distilled water leachate are presented in Figure A1. In distilled water leachate, total numbers of organisms began at levels of approximately 600 to 1,100 colony forming units per millilitre of leachate (CFUs/ml) following the first leach cycle. During the course of the leachate test, numbers of organisms rose steadily until peaking at approximately 1 million CFUs/ml following the fourth leach cycle, then declined by approximately two orders of magnitude in the remaining 2 days of leach testing. Numbers of organisms in the saline leachate varied over only one order of magnitude during the complete sequential leach cycle. Total numbers of organisms began at a level of approximately 400 CFUs/ml and rose to slightly more than 1,000 by the second day. Counts remained between 770 and 2,065 CFUs/ml during the next three leach cycles, following which numbers fell to approximately 500 CFUs/ml.

14. There was approximately 1,000 orders of magnitude difference between peak microorganism CFUs in the distilled water leachate and in the saline leachate. It cannot be determined with certainty if microbial population differences in the two media were due to release of microorganisms or to microbial growth during the test. It is highly improbable that a die-off of microorganisms occurred in the saline leach test. Examination of conductivity data in Table A1 indicates that at the end of the first leach cycle, conductivity in the distilled water leachate was approximately half that in the saline leachate. Conductivity values in the distilled water leachate reflect an approximate 100-percent dilution of interstitial water conductivity by distilled water. Therefore, interstitial water conductivity in New Bedford sediment before testing should be similar to that in the saline leachate. Microorganisms associated with the sediment should therefore not die off due to salinity shock. Lower conductivity regimes, however, may constitute better growth conditions for the microbial assemblage present in New Bedford sediment. Microbial growth of the magnitude observed may not be responsible for the increase in microorganisms. Concentrations of PCB did not increase during 7-day kinetic testing (Table 10, main text), although conductivity had been reduced by approximately 50 percent compared with interstitial water values. Such an increase would be expected if microorganism populations were increasing in the leachate and serving as a carrier for adsorbed PCB.

PCB microdroplet investigation

15. Examination of leachate with AO dye visually confirmed the increased number of microorganisms in the distilled water leachate as the leach cycle progressed. In conjunction with the increased number of microorganisms, a large increase in dye-sensitive (hydrophobic) material, presumably organic matter, was observed as the leach cycle progressed. No microdroplets of PCB or any other oil were observed. Various types of oil added to leachate and dispersed by shaking prior to AO examination formed perfectly spherical green microdroplets that wandered across the field of view of the microscope. No semblance of this appearance or behavior was observed in leachate that did not contain added oil.

Sequential leach testing

16. Metals. Steady-state sediment and leachate results are summarized in Tables A2 and A3, respectively, for distilled water and in Tables A4 and A5 for saline water. Distilled water leachate metal concentrations observed

during this study were generally lower for all metals tested than results of the earlier tests conducted with distilled water. A summary of linear regression relationships between steady-state sediment (q) and steady-state leachate (C) concentrations for the sequential leach test conducted with distilled water in the follow-on testing is presented in Table A6. As can be seen by comparing Table A6 with Table 18 of the main text, fewer significant statistical relationships existed between q and C in Table A6 than in Table 18. However, the slopes of the lines presented in Table A6, although differing in magnitude from those shown in Table 18, demonstrated similar trends (+ or - slopes), indicating that metal releases were behaving in a similar manner in both distilled water sequential leach tests.

17. Saline leachate metal concentrations were higher than concentrations observed in the distilled water leachate for arsenic and nickel. Results for other metals in the saline water leachate were either similar to or lower than metal concentrations in the distilled water leachate. Linear regression relationships between steady-state sediment (q) and steady-state leachate (C) concentrations for sequential leach tests conducted with saline water are presented in Table A7. Comparison of results summarized in Table A7 with those summarized in Table A6 indicates that leaching of anaerobic New Bedford sediment with saline water did not substantially improve the linear relationships between steady-state q and C values or change the direction (+ or - slope) of the isotherms obtained using distilled water.

18. Results for metals did not show any substantial differences between desorption isotherms for metals in New Bedford sediment as a function of leaching solution salinity. If metals had been associated with substances mobilized during distilled water leaching, then metal concentrations in distilled water leachate would have been considerably higher than in saline water leachate.

19. PCBs. Steady-state sediment and leachate results are summarized in Tables A8 and A9, respectively, for distilled water and in Tables A10 and A11 for saline water. Distilled water PCB leachate concentrations during this study were generally equal to or higher than PCB concentrations observed in the sequential batch leach tests conducted earlier with distilled water (Table 23). As can be seen by comparing Table A12, which presents a summary of PCB leaching results for PCBs conducted during this testing, with data

from previous sequential leaching with distilled water (Table 24 of the main text), trends in the data were in agreement and yielded similar slopes for both data sets.

20. The effect of distilled and saline water leaching on PCB leachate concentrations is illustrated in Figures A2 and A3 for total PCB and PCB congener C8, respectively. (Table 7 of the main text identifies the 23 congeners discussed in this report.) Leachate concentrations observed during distilled water leaching peaked during the third leach cycle, then began to decline. Leachate concentrations obtained using saline water did not change substantially during the course of the sequential leach testing. These data indicate that leaching of anaerobic New Bedford sediment with distilled water resulted in mobilization of PCBs, compared with leaching with saline water. The trends observed in PCB concentrations between distilled and saline water leachate were similar to those observed for enumeration of microorganisms (Figure A1) and DOC leachate results (Figure A4).

21. Both microorganisms and/or colloidal organic matter can act as carriers of PCB (Karickhoff 1985, Brownawell 1986). Since the organic matter in the microorganisms is contributing to DOC concentrations, it is impossible to separate the contributions of microorganisms and colloidal humic material to mobilization of PCB in distilled water leachates. However, the concentration of DOC and total PCB in the leachate was highly correlated ($r = 0.94$, $p < 0.05$), while the concentration of microorganism CFUs and total PCB in the leachate was not significant ($r = 0.47$). This indicates that leachate DOC concentration was more closely related to leachate concentration of total PCB than was leachate microorganism concentration.

22. There is an inverse relationship between the increase in leachate PCBs, DOC, and microorganisms and the decrease in leachate conductivity in the distilled water leach tests. These data strongly suggest that as conductivity in the distilled water leachate decreased, materials such as colloidal humic materials and microorganisms containing adsorbed PCB were destabilized, resulting in the mobilization of PCB into the leachate. This conclusion is strongly supported by results obtained by leaching New Bedford sediment with a 5-percent solution of sodium metaphosphate. Results of the sodium metaphosphate leach are summarized in Table A13, along with equivalent first-leach cycle PCB concentrations for distilled and saline water leachates. The data show no substantial differences between saline and distilled water PCB

leachate concentrations during the initial stages of leaching when conductivity in the distilled water leachate was sufficient to prevent colloid destabilization. However, when New Bedford sediment was leached with distilled water containing a dispersant, significantly higher PCB concentrations were observed in the leachate. In addition, when conductivity of the leachate did not decrease, as in the saline water tests, there was no mobilization of PCB or DOC or change in the level of microorganisms.

23. Leaching results for PCBs conducted with saline water are summarized in Table A14. These data indicate that not only were PCB concentrations lower in the saline water leachate, but the trends in the data had been reversed, resulting in positive slopes for most PCB compounds for which statistically significant relationships existed. Distribution coefficients (slopes) so obtained ranged from 3.96 ℓ/kg for congener 105 to 16.89 ℓ/kg for total PCB. These results indicate that the differences in ionic strength between the distilled water and saline leachates resulted in pronounced differences in the leaching behavior of PCBs. The change in conductivity during the distilled water sequential leach testing directly corresponded to the increased PCB concentrations noted in the leachate. If sediment in a confined disposal facility is leached by rainwater only, conductivity decreases and resulting PCB mobilization would be expected to occur. However, if the conductivity in leachate can be maintained at relatively high levels (20 ppt salinity), mobilization of PCBs noted in the distilled water leachate will not occur.

24. Nonconstant partitioning was observed in the distilled water leachate but did not appear to occur in the saline water leachate. As illustrated in Figure A5 for total PCB in saline water leachate, isotherms derived for PCBs using saline water demonstrated partitioning behavior consistent with current theory. The turn to the vertical axis for PCB desorption isotherms, postulated from previous studies with four leach cycles, did occur for some PCB compounds. A summary of New Bedford sequential distilled water leaching results for PCBs, with data from the area of nonconstant partitioning (day 1 and 2 leach cycle) removed, is presented as Table A15. The turn of the isotherm to the vertical axis is illustrated for total PCB in Figure A6. Increasing concentrations of PCB as sequential leaching progresses will therefore not occur indefinitely. The PCB concentrations will eventually decrease, and PCB desorption in most cases will follow constant partitioning.

25. A plot of K_d versus steady-state sediment total PCB concentrations in distilled and saline water leachate from anaerobic New Bedford sediment is presented as Figure A7. These data show that K_d values for total PCB in saline and freshwater leachates were similar following the first leach cycle (q = 2,166 mg/kg) but diverged radically thereafter. Single-point K_d values for distilled water leachate decreased rapidly, then stabilized at approximately 700 ℓ/kg. Distribution coefficients for total PCB in saline water leachate showed a steady increase as leaching progressed. The reasons for this behavior are not completely clear. However, the elevated levels of PCB and DOC in the leachate strongly suggest that the great majority of PCB in the leachate is associated with colloidal organic matter (Brownawell 1986). Saline leachate DOC concentrations did not vary greatly during the sequential leach cycles, but total PCB leachate concentrations decreased and single-point K_d values decreased. This indicates that as the saline water leach progressed, the character of the colloidal organic matter in the leachate may have changed. Colloidal matter released may have had less PCB associated with it, or colloidal material with adsorbed PCB may have constituted a decreasing share of the leachate DOC as leaching progressed. The freshwater leachate trends (Figure A7), in conjunction with data presented previously, indicate that colloidal organic matter and associated adsorbed PCB probably increased in the leachate, resulting in higher PCB and leachate DOC concentrations as well as a lower K_d .

Conclusions

26. Microdroplets of PCB were not responsible for the elevated concentrations of PCB in the distilled water leachate. Results of this study indicate that the deviation from partitioning theory of PCBs in the distilled water leachate was attributable to the conductivity decrease in the distilled water leachate. When the conductivity was held constant using saline water, PCBs were not mobilized into leachate. The increase in concentration of PCBs was accompanied by an increase in concentrations of microorganisms and DOC in the distilled water leachate. Although growth of microbial populations cannot be ruled out as a cause of increased microbial concentrations in distilled water leachate, it is highly probable that releases of microorganisms, PCBs, and DOC were caused by destabilization of colloidal humic materials in the

sediment. This is supported by results obtained when a dispersant was used as a leaching agent, resulting in significantly higher PCB leachate concentrations compared with those observed with either distilled or saline water.

27. Metal data did not show substantial differences in release patterns between distilled and saline water leachate. Metals released into the leachate were apparently not affected by the mobilization processes responsible for elevated PCB concentrations in the distilled water leachate.

Table A1

Conductivity and pH in Saline and Distilled Water for New Bedford Leachate

Sequential Leach Number	Conductivity*		pH**	
	Fresh Water	Saline Water	Fresh Water	Saline Water
1	14.7 (0.34)	28.6 (1.1)	7.7 (0.04)	7.2 (0.02)
2	4.9 (0.06)	29.3 (0.4)	7.8 (0.03)	6.9 (0.07)
3	1.7 (0.06)	29.9 (0.2)	7.8 (0.05)	7.7 (0.2)
4	0.7 (0.01)	29.2 (0.2)	7.7 (0.09)	7.1 (0.4)
5	0.4 (0.01)	29.3 (0.4)	7.7 (0.10)	7.2 (0.3)
6	0.4 (0.03)	30.3 (0.2)	7.3 (0.05)	6.4 (0.3)
7	0.4 (0.03)	30.0 (0.2)	7.6 (0.10)	6.4 (0.2)

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* Expressed in millisiemens (1 millisiemen = 1 millimho). Standard error is given in parentheses.

** Mean value (standard error).

Table A2

Steady-State Metal Sediment Concentrations* in Anaerobic New Bedford Sediment Leached with Distilled Water

Metal	Sequential Leach Number						
	1	2	3	4	5	6	7
As	8.61	8.59	8.59	8.57	8.57	8.57	8.56
Cd	35.39	35.38	35.37	35.37	35.37	35.37	35.37
Cr	753.97	753.85	753.82	753.79	753.61	753.59	753.58
Cu	1,729.94	1,729.57	1,729.55	1,729.53	1,728.75	1,728.68	1,728.68
Pb	2,012.94	2,012.87	2,012.87	2,012.87	2,012.82	2,012.80	2,012.80
Ni	122.00	121.85	121.85	121.81	121.81	121.76	121.45
Zn	3,016.60	3,016.22	3,016.22	3,016.18	3,015.08	3,014.38	3,004.99

* Expressed in micrograms per gram.

Table A3

Metal Concentrations* in Distilled Water Leachate from Anaerobic New Bedford Sediment

Metal	Sequential Leach Number						
	1	2	3	4	5	6	7
As	13.3 (0.7)	5.0 (2.0)	<5	<5	<5	<5	<5
Cd	3.2 (2.8)	1.9 (1.1)	0.3 (0.1)	<0.1	<0.1	<0.1	<0.1
Cr	6.3 (0.3)	32.3 (26.8)	6.3 (0.3)	6.7 (1.2)	46.3 (41.8)	4.7 (1.3)	1.3 (0.3)
Cu	15.0 (9.0)	92.3 (61.1)	5.7 (0.3)	5.7 (0.9)	193 (189)	18.3 (16.3)	1.3 (0.3)
Pb	16.0 (13.5)	15.3 (13.9)	1.3 (0.3)	<1	<1	6.0 (4.0)	<1
Ni	<1	<1	<1	<1	<1	<1	78 (6)
Zn	101 (51)	94 (69)	<30	<30	275 (236)	175 (36)	1,522 (730)

* Expressed in micrograms per litre (standard error in parentheses).

Table A4

Steady State Metal Sediment Concentrations* in Anaerobic New Bedford Sediment Leached with Saline Water

Metal	Sequential Leach Number 1	2	3	4	5	6	7
As	8.60	8.56	8.52	8.49	8.45	8.40	8.34
Cd	35.40	35.40	35.40	35.40	35.40	35.40	35.37
Cr	753.93	753.91	753.89	753.86	753.84	753.82	753.79
Cu	1,729.97	1,729.95	1,729.91	1,729.89	1,729.86	1,729.83	1,729.80
Pb	2,012.96	2,012.95	2,012.93	2,012.93	2,012.92	2,012.90	2,012.86
Ni	121.77	121.77	121.67	121.26	120.35	118.88	116.62
Zn	3,016.46	3,016.39	3,016.30	3,016.30	3,016.14	3,015.72	3,009.56

* Expressed in micrograms per gram.

Table A5

Metal Concentrations* in Saline Water Leachate from Anaerobic New Bedford Sediment

Metal	Sequential Leach Number 1	2	3	4	5	6	7
As	15.7 (0.3)	9.3 (0.7)	10.7 (2.4)	7.0 (0.6)	10.7 (1.9)	12.7 (2.6)	13.3 (0.9)
Cd	0.17 (0.07)	<0.1	<0.1	<0.1	<0.1	0.6 (0.09)	6.0 (5.7)
Cr	17.0 (4.7)	6.3 (1.2)	7.7 (2.7)	3.7 (0.3)	5.3 (0.3)	5.7 (0.3)	8.0 (1.2)
Cu	8.0 (2.1)	5.7 (0.3)	8.0 (3.1)	6.0 (0.00)	8.0 (0.6)	6.3 (0.9)	7.3 (0.9)
Pb	9.0 (1.2)	3.7 (1.5)	4.3 (1.9)	1.7 (0.3)	2.0 (0.6)	3.7 (0.9)	10.0 (6.5)
Ni	57 (30)	<1	27 (14)	103 (28)	227 (73)	366 (130)	565 (210)
Zn	90 (45)	<30	<30	<30	127 (91)	1,685 (1650)	670 (456)

* Expressed in micrograms per litre (standard error in parentheses).

Table A6

Summary of New Bedford Sequential Distilled Water Leaching Results for Metals in Follow-On Testing

Metal	r^2	P <	Slope
As	0.014	0.612	0.636
Cd	0.040	0.383	-1.89
Cr	0.129	0.109	-2.58
Cu	0.220	0.032	-2.94
Pb	0.103	0.156	-2.66
Ni	0.343	0.005	-3.91
Zn	0.959	0.0001	-4.81

Table A7

Summary of New Bedford Sequential Saline Water Leaching Results for Metals in Follow-On Testing

Metal	r^2	P <	Slope
As	0.024	0.499	-3.93
Cd	0.997	0.0001	-4.16
Cr	0.069	0.248	2.75
Cu	0.006	0.747	-1.83
Pb	0.129	0.109	-2.60
Ni	0.965	0.0001	-8.56
Zn	0.976	0.0001	-4.43

Table A8

Steady-State PCB Sediment Concentrations* in Anaerobic New Bedford Sediment

Leached with Distilled Water

Parameter**	Sequential Leach Number 1	2	3	4	5	6	7
C7	0.56	0.56	0.54	0.52	0.48	0.45	0.45
C8	165.59	165.27	163.75	162.60	161.38	160.43	159.87
C28	152.92	152.46	150.49	148.98	147.36	145.98	145.40
C44	84.10	84.00	83.61	83.29	82.88	82.57	82.37
C49	27.99	27.95	27.78	27.61	27.32	27.09	26.54
C52	176.61	176.31	175.16	174.36	173.27	172.43	172.35
C70	59.18	59.12	58.85	58.62	58.34	58.11	57.97
C77	146.66	146.66	146.66	146.37	145.48	144.80	144.66
C82	24.30	24.30	24.24	24.22	24.15	24.01	23.90
C87	8.20	8.19	8.16	8.12	8.06	8.00	7.99
C97	22.89	22.85	22.70	22.56	22.37	22.21	22.12
C101	70.34	70.22	69.74	69.34	68.85	68.47	68.26
C105			Not Detected				
C118	29.58	29.54	29.18	28.97	28.69	28.47	28.08
C136	17.10	17.08	17.03	16.97	16.89	16.82	16.73
C138	25.06	25.03	24.91	24.80	24.68	24.58	24.53
C143	24.70	24.70	24.68	24.67	24.64	24.61	24.55
C153	56.68	56.60	56.28	55.99	55.62	55.35	55.20
C155	50.00	50.00	50.00	49.99	49.98	49.97	49.87
C167	19.20	19.20	19.17	19.15	19.14	19.13	19.11
C180	7.94	7.94	7.81	7.79	7.66	7.75	7.74
A1242	886.19	883.51	872.17	863.24	851.64	842.57	837.92
A1254	661.45	659.87	653.73	651.36	645.49	643.49	642.88
Total PCB	2,165.69	2,159.56	2,141.96	2,128.43	2,112.03	2,099.36	2,092.16

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* Expressed in micrograms per gram.

** See Table 7 of main text for PCB congener identification key.

Table A9

Steady-State PCB Leachate Concentrations* in Anaerobic New Bedford Sediment

Leached with Distilled Water

Parameter	Sequential Leach Number						
	1	2	3	4	5	6	7
C7	<0.001**	<0.001	0.005 (0.0003)	0.006 (0.003)	0.008 (0.003)	0.008 (0.002)	0.0003 (0.0003)
C8	0.029 (0.002)	0.079 (0.002)	0.380 (0.015)	0.287 (0.034)	0.307 (0.050)	0.237 (0.047)	0.140 (0.006)
C28	0.021 (0.0005)	0.113 (0.003)	0.493 (0.017)	0.377 (0.048)	0.407 (0.071)	0.343 (0.098)	0.145 (0.032)
C44	0.008 (0.0006)	0.024 (0.003)	0.098 (0.002)	0.080 (0.013)	0.103 (0.018)	0.079 (0.016)	0.049 (0.004)
C49	0.003 (0.0007)	0.010 (0.00)	0.041 (0.002)	0.045 (0.015)	0.072 (0.012)	0.055 (0.010)	0.139 (0.022)
C52	0.024 (0.002)	0.075 (0.0003)	0.287 (0.013)	0.200 (0.025)	0.273 (0.043)	0.210 (0.040)	0.018 (0.002)
C70	0.005 (0.00)	0.015 (0.00)	0.067 (0.003)	0.058 (0.010)	0.071 (0.012)	0.057 (0.010)	0.036 (0.003)
C77	0.009 (0.009)	<0.001	<0.001	0.073 (0.073)	0.223 (0.038)	0.170 (0.030)	0.035 (0.008)
C82	0.0003 (0.0003)	<0.001	0.014 (0.0003)	0.007 (0.004)	0.016 (0.008)	0.036 (0.019)	0.028 (0.004)
C87	<0.001	0.002 (0.00)	0.009 (0.0001)	0.009 (0.003)	0.016 (0.003)	0.014 (0.0009)	0.003 (0.0004)
C97	0.003 (0.00)	0.009 (0.0009)	0.039 (0.0009)	0.034 (0.008)	0.049 (0.008)	0.040 (0.006)	0.022 (0.0009)
C101	0.007 (0.002)	0.031 (0.0003)	0.120 (0.006)	0.010 (0.016)	0.122 (0.019)	0.097 (0.017)	0.052 (0.005)
C105	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
C118	0.004 (0.0003)	0.010 (0.004)	0.091 (0.034)	0.052 (0.012)	0.071 (0.011)	0.053 (0.010)	0.098 (0.012)
C136	0.001 (0.00)	0.003 (0.00)	0.015 (0.0003)	0.014 (0.003)	0.021 (0.004)	0.017 (0.002)	0.023 (0.0007)
C138	0.003 (0.0003)	0.007 (0.0007)	0.030 (0.0007)	0.027 (0.003)	0.032 (0.006)	0.023 (0.005)	0.013 (0.0003)
C143	<0.001	0.001 (0.00)	0.004 (0.00)	0.002 (0.001)	0.007 (0.004)	0.007 (0.001)	0.017 (0.001)
C153	0.005 (0.001)	0.019 (0.00)	0.081 (0.002)	0.071 (0.013)	0.093 (0.016)	0.068 (0.010)	0.039 (0.003)
C155	<0.001	<0.001	<0.001	0.001 (0.001)	0.004 (0.0009)	0.004 (0.001)	0.024 (0.0007)
C167	<0.001	<0.001	0.009 (0.007)	0.003 (0.001)	0.005 (0.001)	0.003 (0.0003)	0.004 (0.001)
C180	<0.001	0.001 (0.00)	0.032 (0.014)	0.004 (0.0009)	0.006 (0.001)	0.004 (0.0003)	0.003 (0.00)
A1242	0.203 (0.007)	0.670 (0.017)	2.83 (0.120)	2.23 (0.348)	2.90 (0.473)	2.27 (0.418)	1.16 (0.091)
A1254	0.137 (0.027)	0.397 (0.020)	1.53 (0.088)	1.06 (0.148)	1.26 (0.241)	0.887 (0.157)	0.52 (0.010)
Total PCB	0.327 (0.003)	1.53 (0.033)	4.40 (0.10)	3.38 (0.619)	4.10 (0.551)	3.17 (0.517)	1.80 (0.208)

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* Expressed in milligrams per litre (standard error in parentheses).

** Detection limits are higher than those in the main text due to increased dilution prior to quantification.

Table A10

Steady-State PCB Sediment Concentrations* in Anaerobic New Bedford Sediment Leached with Saline Water

Parameter	Sequential Leach Number						
	1	2	3	4	5	6	7
C7	Not Detected						
C8	165.62	165.53	165.48	165.48	165.39	165.33	165.27
C28	152.90	152.79	152.71	152.67	152.63	152.56	152.53
C44	84.11	84.08	84.06	84.05	84.04	84.02	84.01
C49	27.99	27.98	27.98	27.97	27.97	27.96	27.96
C52	176.64	176.58	176.53	176.51	176.49	176.44	176.41
C70	59.19	59.17	59.16	59.15	59.14	59.13	59.13
C77	146.66	146.62	146.60	146.56	146.52	146.49	146.47
C82	24.29	24.29	24.28	24.28	24.28	24.28	24.28
C87	Not Detected						
C97	22.89	22.88	22.88	22.87	22.86	22.86	22.86
C101	70.35	70.32	70.30	70.29	70.29	70.27	70.26
C105	36.69	36.68	36.67	36.67	36.67	36.67	36.67
C118	29.59	29.57	29.57	29.56	29.55	29.55	29.54
C136	17.09	17.09	17.08	17.08	17.08	17.08	17.08
C138	25.07	25.06	25.06	25.05	25.05	25.05	25.04
C143	24.70	24.70	24.70	24.70	24.69	24.69	24.69
C153	56.68	56.67	56.66	56.65	56.64	56.63	56.63
C155	49.99	49.97	49.96	49.95	49.95	49.95	49.94
C167	Not Detected						
C180	Not Detected						
A1242	886.27	885.51	884.95	884.31	883.73	883.28	882.97
A1254	661.67	661.34	661.11	660.87	660.62	660.36	660.20
Total PCB	2165.85	2164.64	2163.76	2162.85	2162.13	2161.35	2160.80

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* Expressed in micrograms per gram.

Table A11

Steady-State PCB Leachate Concentrations* in Anaerobic New Bedford Sediment

Leached with Saline Water

Parameter	Sequential Leach Number						
	1	2	3	4	5	6	7
C7	<0.001*	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
C8	0.020 (0.002)	0.022 (0.003)	0.014 (0.007)	0.013 (0.001)	0.009 (0.002)	0.016 (0.003)	0.015 (0.0007)
C28	0.025 (0.002)	0.026 (0.004)	0.020 (0.002)	0.012 (0.001)	0.009 (0.002)	0.017 (0.0006)	0.008 (0.0004)
C44	0.006 (0.0006)	0.006 (0.001)	0.005 (0.0003)	0.003 (0.0003)	0.003 (0.0003)	0.004 (0.00)	0.002 (0.0003)
C49	0.002 (0.00)	0.002 (0.00)	0.002 (0.0003)	0.001 (0.00)	0.001 (0.00)	0.002 (0.0003)	0.001 (0.00)
C52	0.015 (0.001)	0.016 (0.003)	0.012 (0.001)	0.006 (0.0006)	0.005 (0.001)	0.011 (0.00)	0.007 (0.0003)
C70	0.004 (0.0003)	0.004 (0.0007)	0.003 (0.0003)	0.003 (0.0003)	0.002 (0.0006)	0.002 (0.0003)	0.001 (0.00)
C77	0.010 (0.002)	0.009 (0.001)	0.006 (0.002)	0.011 (0.0009)	0.008 (0.002)	0.007 (0.004)	0.007 (0.0006)
C82	0.002 (0.00)	0.002 (0.0003)	0.001 (0.00)	0.001 (0.0006)	0.0003 (0.0003)	<0.001	<0.001
C87	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
C97	0.002 (0.00)	0.002 (0.0003)	0.002 (0.0003)	0.001 (0.0003)	0.002 (0.0003)	0.001 (0.00)	0.001 (0.00)
C101	0.006 (0.0003)	0.006 (0.001)	0.005 (0.0009)	0.003 (0.00)	0.002 (0.0007)	0.004 (0.0003)	0.002 (0.00)
C105	0.003 (0.00)	0.003 (0.0003)	0.002 (0.00)	<0.001	<0.001	<0.001	<0.001
C118	0.003 (0.00)	0.003 (0.0003)	0.002 (0.00)	0.002 (0.0002)	0.001 (0.0003)	0.002 (0.0002)	0.001 (0.00)
C136	0.002 (0.0003)	0.001 (0.0003)	0.001 (0.00)	<0.001	<0.001	0.001 (0.0003)	<0.001
C138	0.001 (0.00)	0.001 (0.0003)	0.001 (0.00)	0.001 (0.00)	0.0007 (0.0003)	0.001 (0.0006)	0.001 (0.00)
C143	<0.001	<0.001	<0.001	0.001 (0.00)	0.0007 (0.0003)	<0.001	<0.001
C153	0.004 (0.00)	0.004 (0.0003)	0.003 (0.0003)	0.002 (0.00)	0.002 (0.0003)	0.002 (0.00)	0.001 (0.0003)
C155	0.004 (0.0003)	0.003 (0.0003)	0.003 (0.00)	0.002 (0.00)	0.0003 (0.0003)	0.002 (0.00)	0.001 (0.0003)
C167	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
C180	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
A1242	0.183 (0.012)	0.190 (0.030)	0.140 (0.025)	0.160 (0.010)	0.144 (0.038)	0.113 (0.003)	0.077 (0.004)
A1254	0.083 (0.003)	0.078 (0.011)	0.058 (0.005)	0.277 (0.217)	0.063 (0.017)	0.065 (0.012)	0.042 (0.008)
Total PCB	0.287 (0.024)	0.303 (0.043)	0.220 (0.035)	0.227 (0.019)	0.180 (0.040)	0.197 (0.012)	0.137 (0.009)

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* Expressed in milligrams per litre (standard error in parentheses).

** Detection limits are higher than those in the main text due to increased dilution prior to quantification.

Table A12

Summary of New Bedford Sequential Distilled Water Leaching Results for PCBs

Parameter	r^2	P <	Slope
C7	0.262	0.017	-6.18
C8	0.155	0.078	-6.62
C28	0.145	0.087	-6.06
C44	0.258	0.019	-8.87
C49	0.806	0.0001	-9.88
C52	0.072	0.239	-3.95
C70	0.291	0.012	-9.43
C77	0.346	0.005	-6.05
C82	0.619	0.0001	-6.85
C87	0.288	0.012	-7.38
C97	0.335	0.006	-9.84
C101	0.222	0.031	-8.11
C105		Not Detected	
C118	0.461	0.0007	-9.68
C136	0.735	0.0001	-13.68
C138	0.208	0.038	-7.87
C143	0.835	0.0001	-8.22
C153	0.254	0.0198	-8.56
C155	0.955	0.0001	-5.43
C167	0.186	0.051	-4.23
C180	0.094	0.176	-2.56
A1242	0.214	0.034	-7.86
A1254	0.203	0.032	-6.68
Total PCB	0.179	0.056	-7.79

Table A13

Concentrations of PCBs After 24 hr of Shaking

	Treatment		
Compound	Distilled Water	Saline Water	5% Na Metaphosphate
C7	<0.001	<0.001	0.00012 (0.0003)
C8	0.029 (0.002)	0.020 (0.002)	0.095 (0.016)
C28	0.021 (0.0005)	0.025 (0.002)	0.11 (0.03)
C44	0.008 (0.0006)	0.004 (0.0006)	0.03 (0.007)
C49	0.003 (0.0007)	0.002 (0.00)	0.10 (0.02)
C52	0.024 (0.002)	0.015 (0.001)	0.013 (0.003)
C70	0.005 (0.00)	0.004 (0.0003)	0.02 (0.009)
C77	0.009 (0.009)	0.010 (0.002)	0.0034 (0.0008)
C82	0.0003 (0.0003)	0.002 (0.00)	0.02 (0.005)
C87	<0.001	<0.001	0.0013 (0.0001)
C97	0.003 (0.00)	0.002 (0.00)	0.013 (0.003)
C101	0.007 (0.002)	0.006 (0.0003)	0.033 (0.007)
C105	<0.001	0.003 (0.00)	<0.001
C118	0.004 (0.0003)	0.003 (0.00)	0.135 (0.003)
C136	0.001 (0.00)	0.002 (0.0003)	0.010 (0.007)
C138	0.003 (0.0003)	0.001 (0.00)	0.006 (0.001)
C143	<0.001	<0.00001	0.011 (0.003)
C153	0.005 (0.001)	0.004 (0.00)	0.024 (0.007)
C155	<0.001	0.004 (0.0003)	0.02 (0.004)
C167	<0.001	<0.001	0.0015 (0.0003)
C180	<0.001	<0.001	0.0016 (0.0003)
A1242	0.203 (0.007)	0.183 (0.012)	0.80 (0.14)
A1254	0.137 (0.02)	0.083 (0.003)	0.39 (0.13)
Total PCB	0.327 (0.003)	0.287 (0.024)	1.18 (0.22)

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* Expressed in milligrams per litre (standard error in parentheses).

Table A14

Summary of New Bedford Sequential Saline Water Leaching Results for PCBs

Parameter	r^2	P <	Slope
C7	Not Detected		
C8	0.059	0.285	4.74
C28	0.497	0.0004*	11.88
C44	0.521	0.0002*	14.39
C49	0.320	0.0075*	12.40
C52	0.330	0.0065*	9.94
C70	0.445	0.001*	12.59
C77	0.002	0.962	-0.25
C82	0.382	0.0028*	4.78
C87	Not Detected		
C97	0.399	0.0021*	12.96
C101	0.359	0.0041*	9.60
C105	0.563	0.0001*	3.96
C118	0.635	0.0001*	15.28
C136	0.149	0.084	2.53
C138	0.023	0.513	-3.00
C143	0.133	0.104	-2.85
C153	0.716	0.0001*	13.54
C155	0.453	0.0008*	9.34
C167	Not Detected		
C180	Not Detected		
A1242	0.372	0.003*	14.56
A1254	0.209	0.067	12.67
Total PCB	0.455	0.0008*	16.89

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* Statistically significant relationship.

Table A15

Summary of New Bedford Sequential Distilled Water Leaching Results for PCBs with Day 1 and Day 2 Data Omitted

Parameter	r^2	P <	Slope
C7	0.059	0.385	-2.79
C8	0.412	0.010*	10.09
C28	0.253	0.056	7.00
C44	0.095	0.264	5.82
C49	0.685	0.0001*	-9.15
C52	0.235	0.067	5.29
C70	0.084	0.294	5.90
C77	0.217	0.080	-4.57
C82	0.478	0.004*	-5.70
C87	0.017	0.641	-1.76
C97	0.005	0.807	1.35
C101	0.176	0.120	7.50
C105	Not Detected		
C118	0.108	0.231	-4.96
C136	0.499	0.003*	-15.89
C138	0.176	0.119	7.31
C143	0.767	0.0001*	-7.65
C153	0.086	0.289	5.37
C155	0.948	0.0001*	-5.37
C167	0.052	0.416	-1.97
C180	0.011	0.705	-0.66
A1242	0.151	0.151	6.71
A1254	0.120	0.182	4.41
Total PCB	0.223	0.075	8.34

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* Statistically significant relationship.

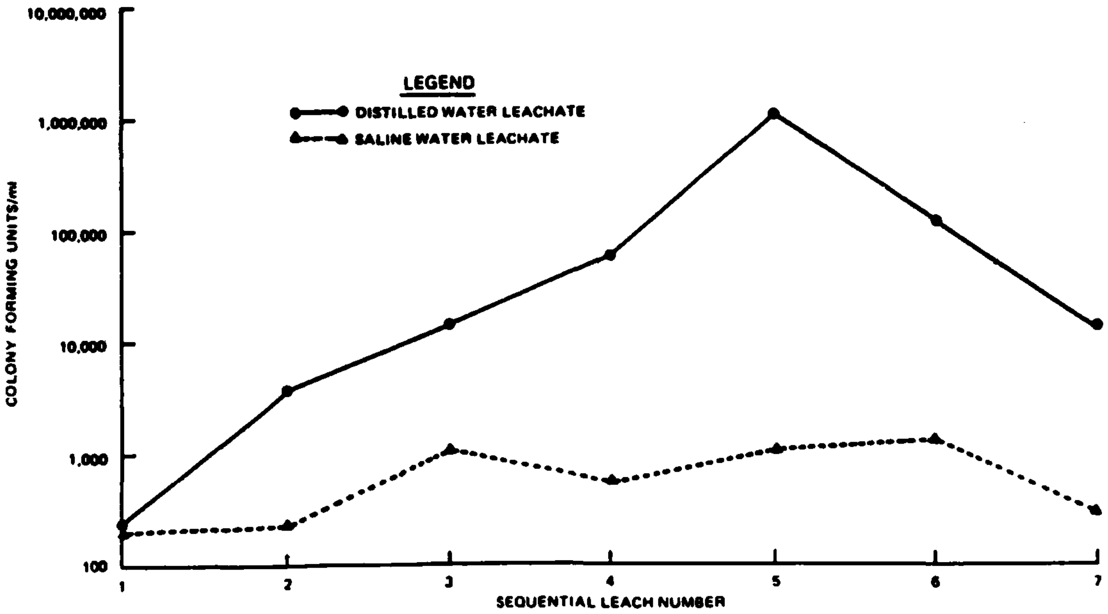

Figure A1. Microbe counts for New Bedford Harbor sequential batch leachate

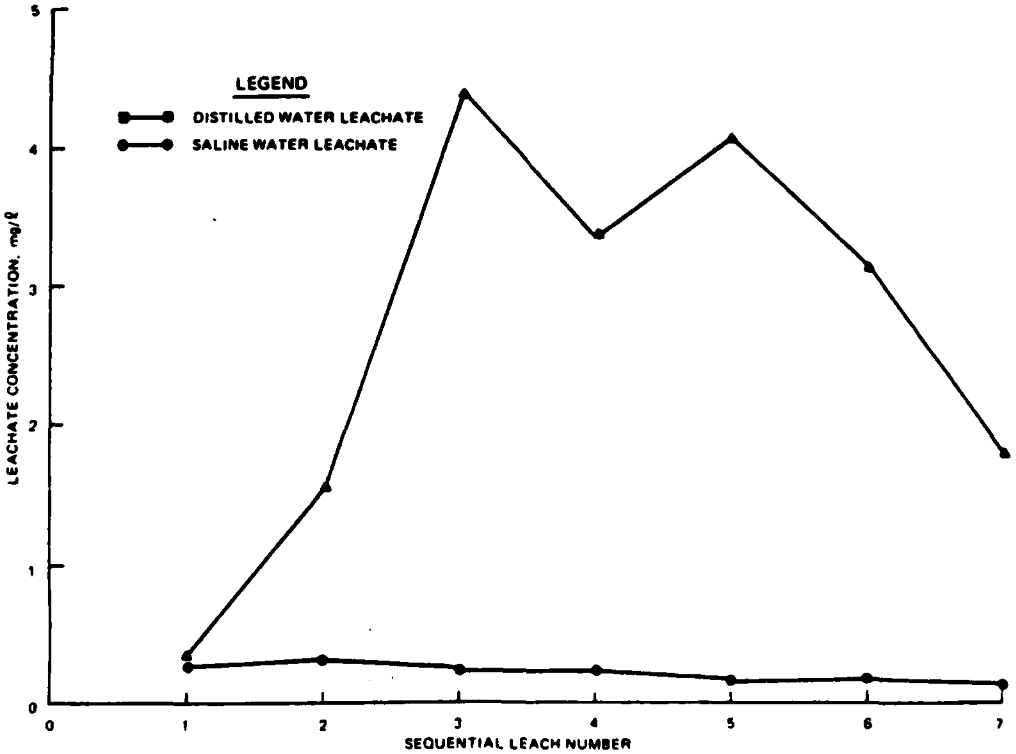

Figure A2. Total PCB concentrations in New Bedford Harbor sequential batch leachate

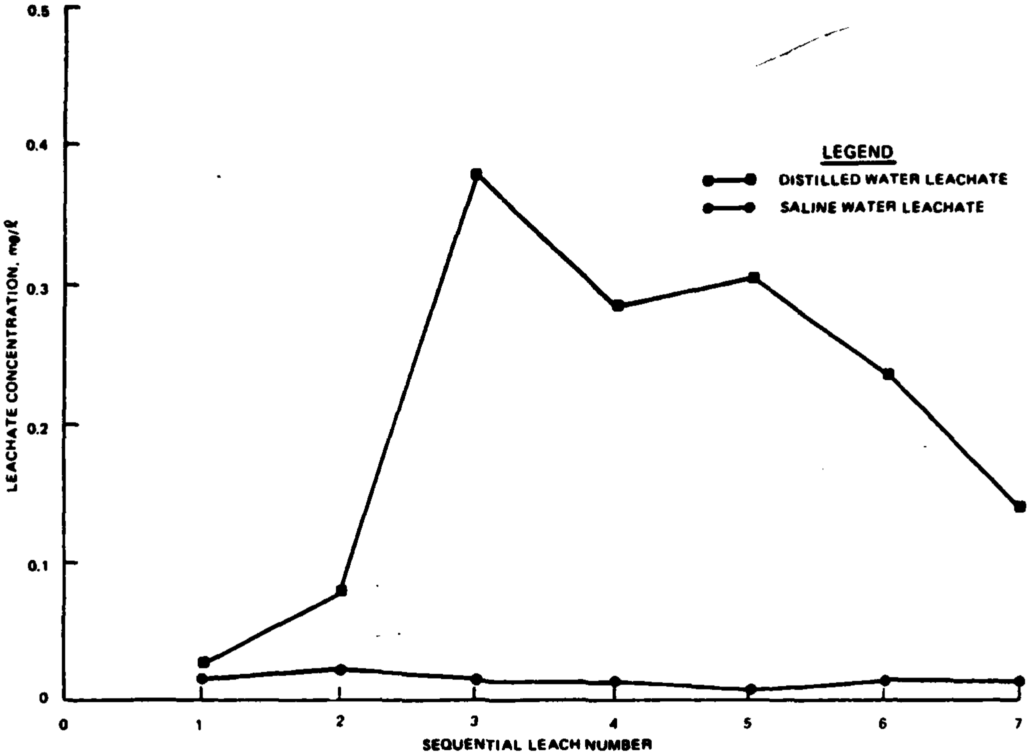

Figure A3. Congener C8 concentrations in New Bedford Harbor sequential batch leachate

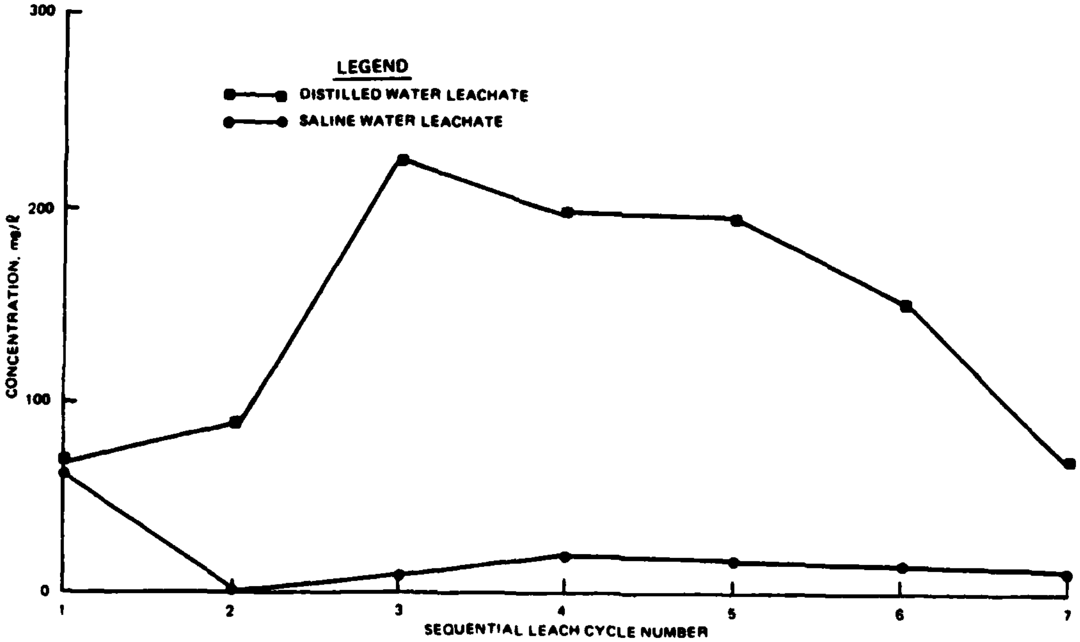

Figure A4. Dissolved organic carbon concentrations in New Bedford Harbor sequential batch leachate

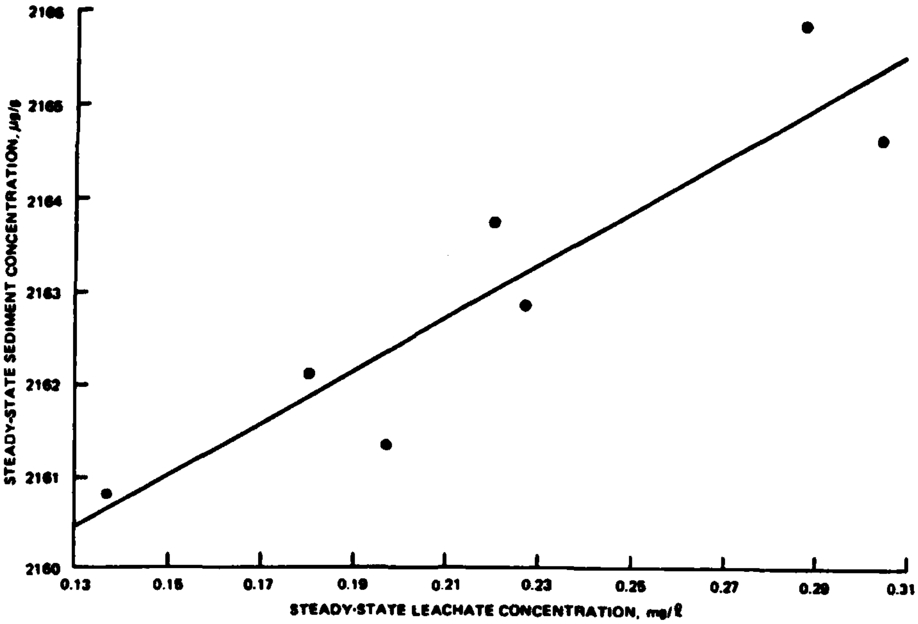

Figure A5. Total PCB desorption isotherm for New Bedford Harbor sediment saline water sequential batch leach test

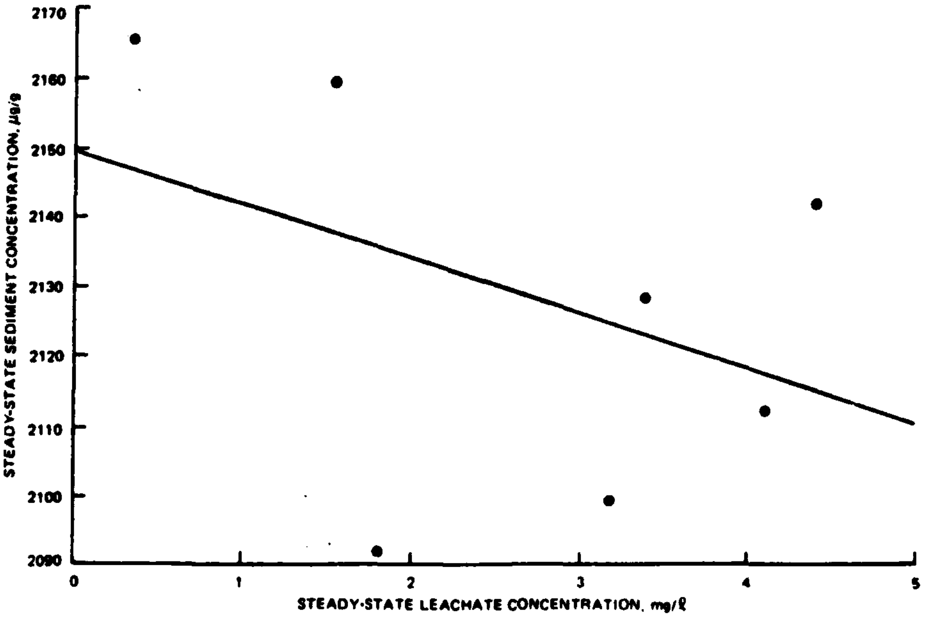

Figure A6. Total PCB desorption isotherm for New Bedford Harbor sediment distilled water sequential batch leach test

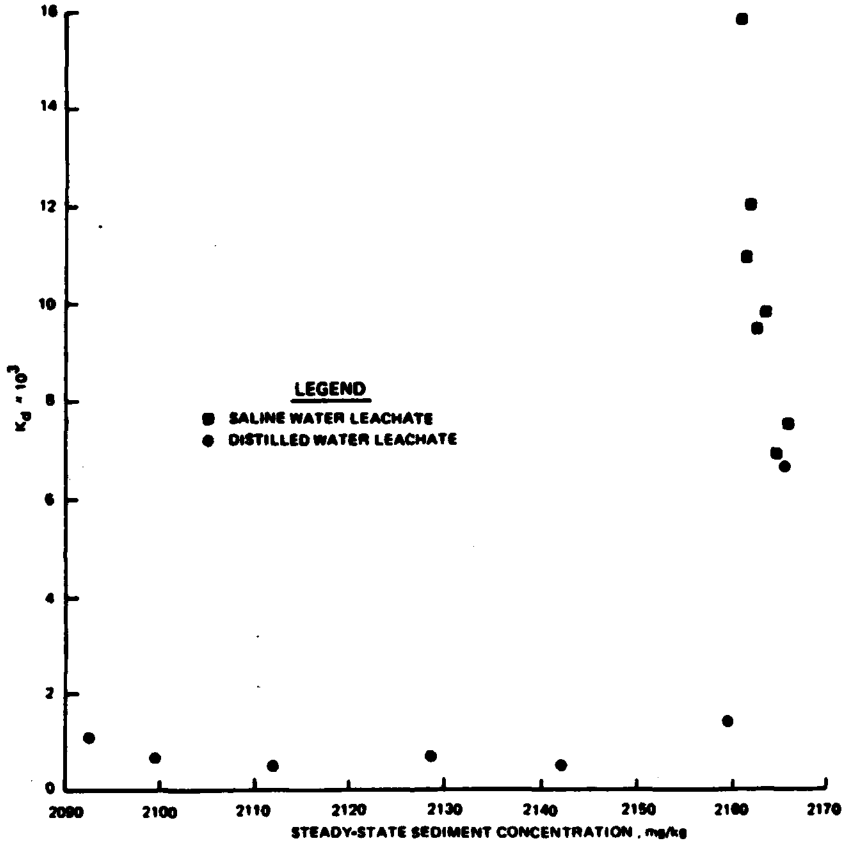

Figure A7. Single-point distribution coefficients (K_d) for total PCB during saline and distilled water sequential batch leaching tests as a function of steady-state sediment concentration

APPENDIX B: VOID VOLUME CALCULATIONS

Change in Void Volume During Testing

1. The pressure required to maintain constant flow in a permeameter is inversely proportional to hydraulic conductivity, which in turn is dependent on void ratio. Void volume changes during testing were approximated by relating the pressure required to maintain constant flow to changes in hydraulic conductivity and void ratio.

2. The change in hydraulic conductivity with respect to change in void ratio was mathematically modeled as follows:

$$\frac{dk}{de} = C_1 k \tag{B1}$$

where

k = hydraulic conductivity, cm/sec

e = void ratio, dimensionless

C_1 = empirical constant, dimensionless

Integrating yields

$$\ln k = C_1 e + C_2 \tag{B2}$$

where C_2 is a constant of integration (dimensionless). Equation B2 is of the form indicated by Cargill's (1983)* plots of void ratio versus hydraulic conductivity during consolidation of dredged material in confined disposal facilities. The constants C_1 and C_2 were determined from the initial and final conditions as follows:

$$C_1 = \frac{\ln (k_f/k_o)}{(e_f - e_o)} \tag{B3}$$

$$C_2 = \left(\ln k_o\right) - \left(C_1 e_o\right) \tag{B4}$$

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* See References at the end of the main text.

where

k_f = final hydraulic conductivity, cm/sec

k_o = initial hydraulic conductivity, cm/sec

e_f = final void ratio, dimensionless

e_o = initial void ratio, dimensionless

3. Initial and final hydraulic conductivities were determined from permeameter operating records as follows:

$$k_o = \frac{Q_o L_o}{AH_o} \tag{B5}$$

$$k_f = \frac{Q_f L_f}{AH_f} \tag{B6}$$

where

Q_o = initial flow, cm^3/sec

L_o = initial sediment column length, cm

A = area, cm^2 (75.43 cm^2)

H_o = initial head, cm

Q_f = final flow, cm^3/sec

L_f = final sediment column length, cm

H_f = final head, cm

Initial and final flows, heads, and hydraulic conductivities are given in Tables B1 and B2, respectively. The constants C_1 and C_2 for each type of permeameter test are listed in Table B3.

4. The initial void ratio e_o was calculated as follows:

$$e_o = wG_s \tag{B7}$$

where

w = water content, the ratio of the weight of water to the weight of dry sediment solids, dimensionless

G_s = specific gravity of the sediment solids, dimensionless

The specific gravity of the solids in the composite sample from New Bedford Harbor sediment is 2.35 (see Report 3 of EFS series). Initial water content

(Table B1) was determined on sediment samples collected during permeameter loading by standard soil testing procedures (US Army Corps of Engineers 1970). Initial water contents and initial void ratios are given in Table B1.

5. At the end of testing, the sediment column length was measured. Since the sediment column was saturated at all times and the loss of sediment solids was negligible, the change in void ratio was equated to the change in column length. Final void ratios were calculated as follows:

$$e_f = e_o\left(\frac{L_f}{L_o}\right) \qquad \text{(B8)}$$

Final sediment column lengths and void ratios are given in Table B2.

Solution Technique

6. Equation B2 can be converted to a single variable expression in terms of sediment column length L by making the following substitutions:

$$k = \left(\frac{QL}{AH}\right) \qquad \text{(B9)}$$

$$e = e_o\left(\frac{L}{L_o}\right) \qquad \text{(B10)}$$

where

Q = flow associated with H , cm^3/sec

L = length of sediment column, cm

H = applied head, cm

Making the substitutions indicated above, Equation B2 becomes

$$\ln\left(\frac{QL}{AH}\right) = C_1\left(\frac{e_oL}{L_o}\right) + C2$$

or after rearranging,

$$\ln\left(\frac{QL}{AH}\right) - C_1\left(\frac{e_oL}{L_o}\right) - C2 = 0 \qquad \text{(B11)}$$

Using values obtained from column operating records for , H , average flows presented in Table 28 of the main text for Q , and the values listed in Table 3 (main text) for C_1 and C_2 , Equation B11 was solved for L by the Newton-Raphson method for finding roots of an equation (Burden and Faires 1985).

7. Once the sediment column lengths were calculated, Equations B10 and B12 were used to calculate void ratio and void volume, respectively. Heads H and associated void volumes for each sample collected are presented in Tables B4-B7 according to permeameter type.

$$V_v = \left(\frac{e}{e + 1}\right) V_t \qquad \text{(B12)}$$

where

V_v = void volume, cm^3

V_t = total volume of sediment column, cm^3

$= \frac{LD^2}{4}$

D = diameter of sediment column, cm

Table B1

Initial Conditions in Anaerobic and Aerobic Permeameters

Parameter	Anaerobic Metals	Anaerobic Organics	Aerobic Metals	Aerobic Organics
L, cm	17.8	35.6	17.8	35.6
Q, cm^3/day	16.7	17.0	13.0	8.9
H, cm	28.0	25.4	28.0	25.4
k, cm/sec	1.6 E-06	3.7 E-06	1.3 E-06	1.9 E-06
w	1.879	1.879	1.474	1.474
e	4.42	4.42	3.46	3.46

Table B2

Final Conditions in Anaerobic and Aerobic Permeameters

Parameter	Anaerobic Metals	Anaerobic Organics	Aerobic Metals	Aerobic Organics
L, cm	10.2	20.3	15.8	24.1
Q, cm^3/day	21.0	14.0	31.0	25.0
H, cm	2103	2103	1051	2033
k, cm/sec	1.6 E-08	2.1 E-08	7.1 E-08	4.5 E-08
e	2.53	2.52	3.06	2.43

Table B3

Model Constants for Equation B6

Constant	Anaerobic Metals	Anaerobic Organics	Aerobic Metals	Aerobic Organics
C_1	2.4366	2.7219	15.75725	3.6339
C_2	-24.1153	-24.5373	-66.3755	-25.74705

Table B4

Heads and Void Volumes During Permeameter Leach Testing for Anaerobic Metals

Head, cm	Void Volume, cm^3
140.2	872.8
350.5	749.7
1,332.0	568.6
1,402.1	561.5
2,033.0	510.6

Table B5

Heads and Void Volumes During Permeameter Leach Testing for Anaerobic Organics

Head, cm	Void Volume, cm^3
699.9	1,414.9
909.9	1,352.3
1,119.8	1,302.8
1,819.7	1,186.6
1,959.7	1,168.9
2,029.7	1,160.5
2,099.7	1,152.3

Table B6

Heads and Void Volumes During Permeameter Leach Testing for Aerobic Metals

Head, cm	Void Volume, cm^3
140.2	977.9
350.5	929.8
420.6	920.2
701.0	893.4
911.4	879.6
1,051.6	872.1

Table B7

Heads and Void Volumes During Permeameter Leach Testing for Aerobic Organics

Head, cm	Void Volume, cm^3
420.6	1,682.0
490.7	1,648.0
630.9	1,592.6
701.0	1,569.4
841.2	1,529.2
1,051.6	1,480.0
1,261.9	1,439.8
1,962.9	1,342.5
2,103.1	1,327.3

APPENDIX C: DISPERSION MEASUREMENT

Introduction

1. During the transit of water from the top of the sediment column in a permeameter to the bottom, the water can take many different routes, requiring different lengths of time to pass through the sediment column. Parcels of water introduced at the top at the same time will arrive at the permeameter exit at different times. Thus, leachate exiting a permeameter is a mixture of leachates generated by parcels of water taking different routes through the sediment column. Mixing that is a result of the water taking different flow paths is referred to as mechanical dispersion (Freeze and Cherry 1979).*

2. Molecular diffusion is another process that affects leachate quality exiting a permeameter. Together, molecular diffusion and mechanical dispersion are referred to as hydrodynamic dispersion. In many flow through porous media problems, mechanical dispersion dominates. However, when the pore water velocity is sufficiently slow, diffusion is an important process.

3. Hydrodynamic dispersion is typically determined by introducing a tracer and measuring the tracer concentration at some convenient point downstream of the point of introduction. The shape of the tracer concentration versus time curve is indicative of the significance of hydrodynamic dispersion.

Methods

4. A separate permeameter was loaded with anaerobic sediment and operated for estimating hydrodynamic dispersion. The permeameter was loaded using the same procedures previously described for anaerobic permeameter leach tests for metals. The sediment was leached with a solution containing 1,000 mg/ℓ bromide over a period of 98 days. Prior to introducing the bromide solution, the permeameter was leached with distilled-deionized water for 30 days to allow the operation of the permeameter to stabilize. Leachate samples were collected from the center tube at the bottom of the permeameter

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* See References at the end of the main text.

during the test period and analyzed for bromide. A total of 61 leachate samples of approximately 100-ml size were collected and analyzed.

5. Samples were digested prior to bromide analysis according to the digestion method developed by Chain and DeWalle (1975) for analyzing chloride in sanitary landfill leachate. The digestion step was needed because sediment leachate contains substances that interfere with chemical analytical procedures for bromide. Following digestion, the samples were analyzed by silver nitrate titration using a bromide-specific ion probe and a recording titrator.

Data Analysis

Data reduction

6. The methods described in Levenspiel (1972) were used to reduce the bromide data. Bromide concentrations in leachate collected at the permeameter exit and sample times are shown in Figure C1. The breakthrough curve shown in Figure C1 is referred to as an F curve (Levenspiel 1972). The F curve is related to the exit age distribution curve, the C curve, as follows (Levenspiel 1972):

$$\frac{dF}{dt} = C \qquad \text{(C1)}$$

Figure C2 is the C curve developed by numerical differentiation of the F curve. Forward, central, and backward three-point formulas (Burden and Faires 1978) with selected step sizes were used to numerically differentiate the F curve. The type of three-point formula and the step size used at each point are listed in Table C1.

7. The variance of the C curve was calculated using Equation C2.

$$\sigma^2 = \frac{\sum (t_i)^2 C_i \Delta t}{\sum C_i t_i} - (\bar{t})^2 \qquad \text{(C2)}$$

$$\bar{t} = \frac{\sum t_i C_i \Delta t}{\sum C_i t} \qquad \text{(C3)}$$

The variance is a descriptive quality of the spread or dispersion that is occurring. The greater the variance, the greater the hydrodynamic dispersion that is influencing leachate quality. The quantity $\bar{t}$ is the mean residence time of a parcel of water in the sediment column. The variance obtained by the above calculation procedure was 366.4 day^2, and the mean residence time was 40.9 days.

8. For matching experimental curves to the mathematical concepts used in tracer work, it is particularly useful to normalize the variance as follows:

$$\sigma_\theta^2 = \frac{\sigma^2}{(\bar{t})^2} \tag{C4}$$

For closed vessels, the normalized variance is related to dispersivity D as follows (Levenspiel 1972):

$$\sigma_\theta^2 = 2D - 2D^2 \left[1 - \exp\left(\frac{-1}{D}\right) \right] \tag{C5}$$

Equation C5 was solved using the Newton-Raphson method (Burden and Faires 1978) to yield $D = 0.125$.

Interpretation and application

9. Significance of the dispersivity value. An intermediate amount of dispersion is indicated by a dispersivity value of 0.025, and a large amount of dispersion is indicated by a dispersivity value greater than or equal to 0.2 (Levenspiel 1972). The tailing shown in the C curve (Figure C2) is responsible for the dispersivity value being as high as it is. The F and C curves suggest that bromide is diffusing into regions of immobile water (water adsorbed to sediment solids and water trapped in deadend pores). Until the bromide concentration in the immobile water reaches the input bromide concentration of 1,000 mg/ℓ, the bromide concentration exiting the permeameter will not reach the input value. This effect is clearly indicated in the F curve (Figure C1).

10. During leaching experiments, contaminants will diffuse from the immobile water regions to the mobile water regions. Until the immobile region

reservoir of contaminants is depleted, there will always be a trace of contaminant in the leachate exiting the permeameters.

11. Dispersion coefficient. The dispersion coefficient D_p is used to model dispersion in the contaminant transport equation (Equation 3 of the main text). Dispersivity and the dispersion coefficient are related as follows:

$$D = \frac{D_p}{vL} \tag{C6}$$

where

D = dispersivity, dimensionless
D_p = dispersion coefficient, cm^2/sec
v = average pore water velocity, cm/sec
L = sediment column length, cm

The dispersivity value obtained from the bromide test was used to calculate dispersion coefficients for the anaerobic permeameters setup for metals and organic leaching. The appropriate average pore water velocities and sediment column lengths for these permeameters were used to calculate dispersion coefficients for each.

Table C1

Bromide Data and Calculations

F Curve*	C Curve**	Formula for Derivative†	$C_i\Delta t$	$t_iC_i\Delta t$	$(t_i^2)C_i\Delta t$
0	0	3 Pt-f, h=2	0	0	0
0	0	3 Pt-f, h=2	0	0	0
0	0	3 Pt-c, h=2	0	0	0
0	0	3 Pt-c, h=2	0	0	0
0	0	3 Pt-c, h=2	0	0	0
0	0	3 Pt-c, h=2	0	0	0
0	0.75	3 Pt-c, h=2	0.75	5.25	36.75
0	1.525	3 Pt-c, h=2	1.525	12.2	97.6
3	2.275	3 Pt-c, h=2	2.275	20.475	184.275
6.1	3.8	3 Pt-c, h=2	3.8	38	380
9.1	3.05	3 Pt-c, h=2	3.05	33.55	369.05
15.2	2.25	3 Pt-c, h=2	2.25	27	324
15.2	1.267	3 Pt-c, h=6	1.266666	16.46666	214.0666
15.1	1.220	3 Pt-c, h=5	1.22	17.08	239.12
12.8	1.267	3 Pt-c, h=6	1.266666	19	285
12.8	0.375	3 Pt-c, h=4	0.75	12.75	216.75
15.2	5.490	3 Pt-c, h=5	10.98	208.62	3,963.78
18.2	17.738	3 Pt-c, h=4	35.475	744.975	15,644.47
26	24.850	3 Pt-c, h=4	49.7	1,143.1	26,291.3
70	32.633	3 Pt-c, h=3	32.63333	783.2	18,796.8
154.7	47.000	3 Pt-c, h=2	47	1,175	29,375
211	44.025	3 Pt-c, h=2	44.025	1,144.65	29,760.9
214	35.217	3 Pt-c, h=3	35.21666	950.85	25,672.95
246.1	37.838	3 Pt-c, h=4	37.8375	1,059.45	29,664.6
253.2	35.900	3 Pt-c, h=5	35.9	1,041.1	30,191.9
281.3	31.650	3 Pt-c, h=2	31.65	949.5	28,485
281.3	31.650	3 Pt-c, h=2	31.65	981.15	30,415.65
372.7	25.750	3 Pt-c, h=6	25.75	824	26,368
379.8	27.390	3 Pt-c, h=5	27.39	903.87	29,827.71
429	29.838	3 Pt-c, h=4	29.8375	1,014.475	34,492.15
463.6	29.450	3 Pt-c, h=4	29.45	1,030.75	36,076.25
520	26.100	3 Pt-c, h=4	78.3	2,975.4	113,065.2
516.9	20.558	3 Pt-c, h=6	20.55833	801.775	31,269.22
614	16.290	3 Pt-c, h=5	16.29	651.6	26,064
637.8	18.267	3 Pt-c, h=3	36.53333	1,534.4	64,444.8
626.5	16.400	3 Pt-c, h=3	49.2	2,214	99,630
705.9	15.886	3 Pt-c, h=7	15.88571	730.7428	33,614.17
716.6	15.150	3 Pt-c, h=1	15.15	712.05	33,466.35

(Continued)

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* Bromide concentration, mg/ℓ.

** Derivative of F curve with respect to time.

† Three-point formula used to calculate derivative, where f = forward-difference, c = central-difference, and b = backward-difference formulas; h = step size.

Table C1 (Concluded)

F Curve	C Curve	Formula for Derivative	$C_i \Delta t$	$t_i C_i \Delta t$	$(t_i^2) C_i \Delta t$
736.2	9.075	3 Pt-c, h=8	9.075	435.6	20,908.8
720.5	8.671	3 Pt-c, h=7	8.671428	424.9	20,820.1
739.3	9.469	3 Pt-c, h=8	37.875	2,007.375	106,390.8
716.1	6.031	3 Pt-c, h=8	6.03125	325.6875	17,587.12
770.4	4.792	3 Pt-c, h=6	4.791666	263.5416	14,494.79
759.2	6.757	3 Pt-c, h=7	6.757142	378.4	21,190.4
778	6.790	3 Pt-c, h=5	33.95	2,070.95	126,327.9
802.4	7.782	3 Pt-c, h=17	7.782352	482.5058	29,915.36
815.1	6.900	3 Pt-c, h=2	6.9	434.7	27,386.1
831.1	6.175	3 Pt-c, h=2	6.175	395.2	25,292.8
805.6	5.331	3 Pt-c, h=16	5.33125	346.5312	22,524.53
827.1	5.838	3 Pt-c, h=13	5.838461	385.3384	25,432.33
891.1	4.088	3 Pt-c, h=13	53.15	4,198.85	331,709.1
891.1	4.077	3 Pt-c, h=15	8.153333	660.42	53,494.02
907.2	3.722	3 Pt-c, h=16	3.721875	305.1937	25,025.88
929.8	4.950	3 Pt-c, h=2	9.9	831.6	69,854.4
927	3.275	3 Pt-c, h=4	6.55	563.3	48,443.8
946.2	3.250	3 Pt-c, h=6	6.5	572	50,336
933.4	2.400	3 Pt-c, h=4	4.8	432	38,880
933.4	1.600	3 Pt-c, h=6	3.2	294.4	27,084.8
946.2	1.600	3 Pt-c, h=4	3.2	300.8	28,275.2
949.4	3.700	3 Pt-b, h=6	7.4	710.4	68,198.4
946.2	2.667	3 Pt-b, h=6	5.333333	522.6666	51,221.33
			1,005.652	41,118.78	2,049,720.

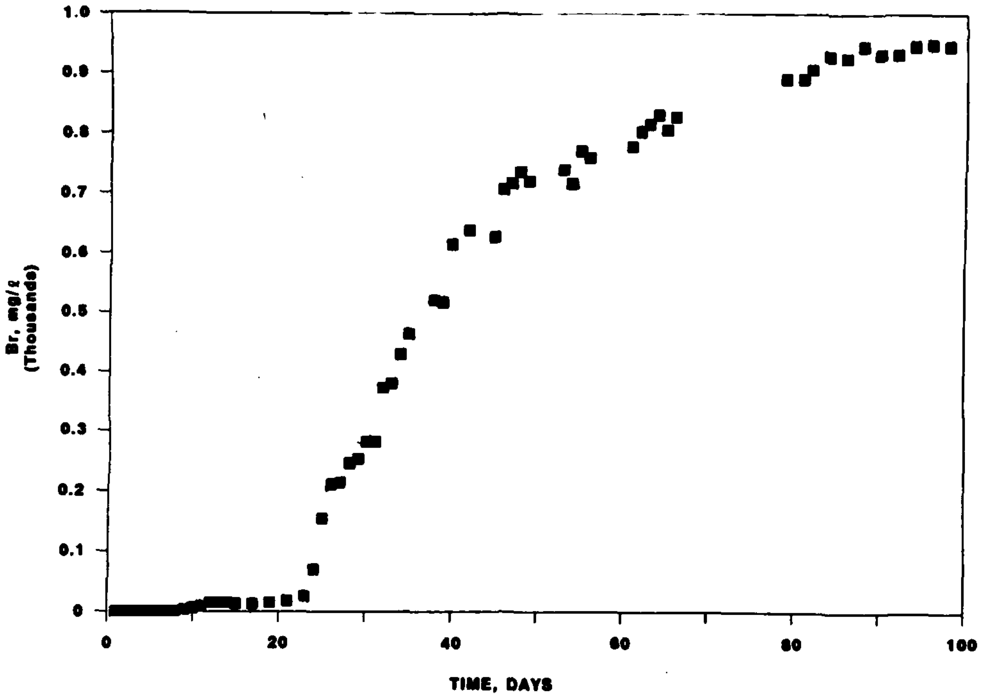

Figure C1. Plot of F curve for bromide experiment

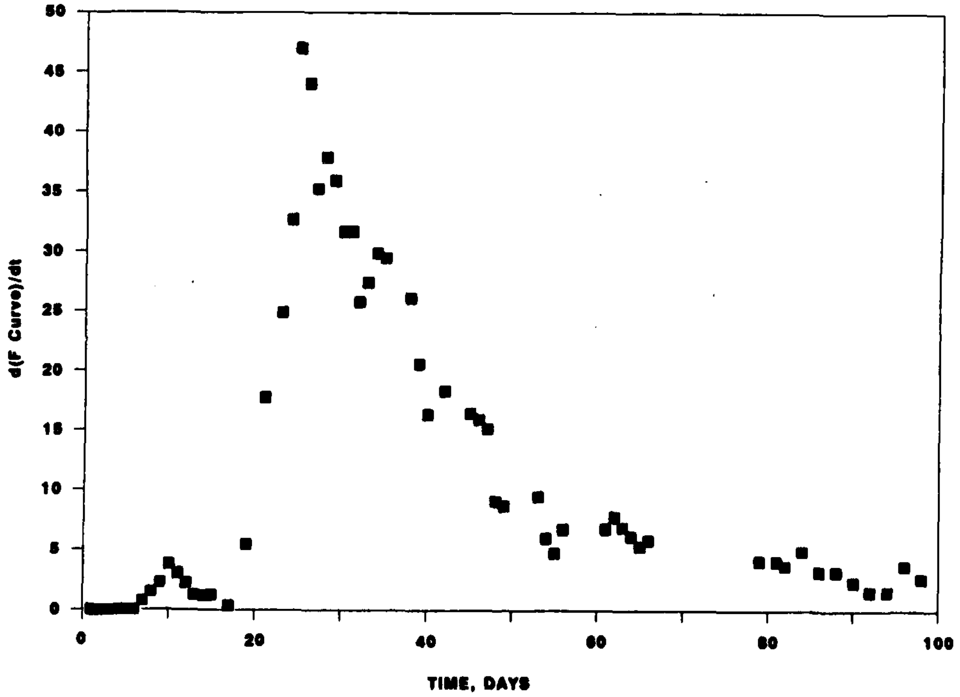

Figure C2. Plot of C curve for bromide experiment