



US Army Corps
of Engineers

LONG-TERM EFFECTS OF DREDGING
OPERATIONS PROGRAM

MISCELLANEOUS PAPER D-92-2

RECENT DEVELOPMENTS IN LEACHATE
TESTING AND EVALUATION

by

Tommy E. Myers, James M. Brannon, Cynthia B. Price

Environmental Laboratory

DEPARTMENT OF THE ARMY

Waterways Experiment Station, Corps of Engineers
3909 Halls Ferry Road, Vicksburg, Mississippi 39180-6199



August 1992

Final Report

Approved For Public Release; Distribution Is Unlimited



Prepared for DEPARTMENT OF THE ARMY
U.S. Army Corps of Engineers
Washington, DC 20314-1000

Destroy this report when no longer needed. Do not return
it to the originator.

The findings in this report are not to be construed as an official
Department of the Army position unless so designated
by other authorized documents.

The contents of this report are not to be used for
advertising, publication, or promotional purposes.
Citation of trade names does not constitute an
official endorsement or approval of the use of
such commercial products.

The D-series of reports includes publications of the
Environmental Effects of Dredging Programs:
Dredging Operations Technical Support
Long-Term Effects of Dredging Operations
Interagency Field Verification of Methodologies for
Evaluating Dredged Material Disposal Alternatives
(Field Verification Program)

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE August 1992	3. REPORT TYPE AND DATES COVERED Final report	
4. TITLE AND SUBTITLE Recent Developments in Leachate Testing and Evaluation		5. FUNDING NUMBERS	
6. AUTHOR(S) Tommy E. Myers, James M. Brannon, Cynthia B. Price			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Engineer Waterways Experiment Station Environmental Laboratory 3909 Halls Ferry Road, Vicksburg, MS 39180-6199		8. PERFORMING ORGANIZATION REPORT NUMBER Miscellaneous Paper D-92-2	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Corps of Engineers, Washington, DC 20314-1000		10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Available from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.			
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Laboratory studies of sediment leaching are being conducted at the U.S. Army Engineer Waterways Experiment Station. The purpose of these studies is to develop laboratory tests and data interpretation algorithms for predicting leachate quality in confined disposal facilities (CDFs) for dredged material. Leachate quality predictions are needed for evaluation of potential impacts of leachate seepage on foundation soils and groundwater. Two types of laboratory leach tests are under investigation, batch and column. A sequential batch leach test is being developed to provide a short-term laboratory test that describes the distribution of contaminants between aqueous and solid phases as sediment solids are exposed to increasing amounts of water. Column leach tests are being developed as laboratory-scale physical models of contaminant leaching in a CDF. Significant progress has been made in the development of the sequential batch leach test. Research has shown that sequential batch leach tests conducted at a liquids-to-solids ratio of 4 to 1 (by weight) and a shake			
			(Continued)
14. SUBJECT TERMS Contaminant mobility Dredged material Contaminated sediment Leach tests		15. NUMBER OF PAGES 36	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

13. (Concluded).

time of 24 hr provide the type of information needed for predicting probable long-term contaminant leaching characteristics. Progress in developing a column leach test has been slower, but is promising.

Current studies show that sediment salinity and oxidation status significantly affect contaminant leaching. Sediments from freshwater environments generally behave according to classical desorption theory. Initial concentrations of contaminants in leachate represent worst-case leachate quality, and leachate quality will improve over time as dredged material solids are contacted by additional water infiltrating from the surface.

However, leaching of sediments from estuarine environments with freshwater results in nonideal behavior that significantly complicates prediction of long-term leaching trends. Nonideal behavior is due to release of sediment organic colloids as ionic strength is decreased through salt washout. Data from sequential batch leach tests clearly indicate that elution of several pore volumes through estuarine dredged material is necessary to produce maximum concentrations of contaminants in leachate. In CDFs, the time scale for worst-case leachate quality is on the order of tens of years or more, depending on dredged material hydraulic conductivity and site-specific climatological factors.

Extended dewatering and oxidation of sediments tend to mobilize metals and volatilize or biodegrade organics. Sequential batch leach tests are being conducted on sediments aged for 6 months in thin lifts to investigate the dependency of contaminant mobility on pH changes associated with slow changes in oxidation-reduction potential. The available data indicate that after 6 months exposure to air, pH in some sediments decreases significantly with a companion increase in leachate metal concentrations.

Comparisons of observed column elution histories with predictions based on sequential batch leach test data and mass transport theory indicate qualitative agreement. Quantitative comparisons, however, have been limited because of the column leach apparatus. The major deficiencies are the limited number of pore volumes that can be eluted in a reasonable period of time without increasing pore water velocities to unreasonable values and the potential for sample deterioration during extended elution periods.

These deficiencies have been corrected by redesigning the column leach apparatus. Studies are ongoing with the improved design to evaluate performance. Other areas to be investigated in current or planned studies include detailed batch studies of the effects of organic colloids on leachate quality, development of a column contaminant transport equation that includes salt washout and colloidal organic matter effects on leachate quality, and coupling of leachate quality information from batch and column leach tests with the Hydrologic Evaluation of Landfill Performance water balance model.

Contents

Preface	iv
1—Introduction	1
Background	1
Nature of the Problem	1
2—Desorption Theory for Dredged Material	4
Equilibrium Assumption	4
Equilibrium Controlled Desorption in a CDF	6
3—Sequential Batch Leach Tests	8
Background	8
Recommended Procedure	11
Applications	12
4—Column Leach Tests	18
Background	18
Applications	18
Improved Column Design	24
5—Directions for Future Research	28
References	30

Preface

This report was prepared by Mr. Tommy E. Myers, Water Supply and Waste Treatment Group (WSWTG), Environmental Engineering Division (EED), Environmental Laboratory (EL), and Dr. James M. Brannon and Ms. Cynthia B. Price, Aquatic Processes and Effects Group (APEG), Ecosystem Research and Simulation Division (ERSD), EL. Dr. Judith C. Pennington, Contaminant Mobility and Regulatory Criteria Group, ERSD, EL, and Mr. Daniel E. Averett, WSWTG, EED, EL, were technical reviewers for this report. Ms. Martha Huie, WSWTG, EED, EL, assisted with tabular and graphical data presentation. Funds for this work were provided by the Long-Term Effects of Dredging Operations (LEDO) Program. LEDO is managed within the Office of Environmental Effects of Dredging Programs (EEDP) at the U.S. Army Engineer Waterways Experiment Station (WES). Dr. Robert M. Engler is Manager of EEDP. The Headquarters, U.S. Army Corps of Engineers, Technical Monitors for LEDO were Mr. Dave Mathis, Mr. Joe Wilson, and Dr. William Klesch.

The work was conducted under the direct supervision of Mr. Norman R. Francingues, Jr., Chief, WSWTG, Dr. Thomas L. Hart, Chief, APEG, and Dr. Richard E. Price, Acting Chief, APEG, and under the general supervision of Dr. Raymond L. Montgomery, Chief, EED, Mr. Donald L. Robey, Chief, ERSD, and Dr. John Harrison, Director, EL.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander and Deputy Director was COL Leonard G. Hassell, EN.

This report should be cited as follows:

Myers, Tommy E., Brannon, James M., and Price, Cynthia B. 1992. Recent developments in leachate testing and evaluation. Miscellaneous Paper D-92-2. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.

1 Introduction

Background

When contaminated dredged material is placed in a confined disposal facility (CDF), contaminants may be mobilized and transported to the site boundaries by leachate generation and seepage. Subsurface drainage and seepage through foundation soils and dikes may then reach adjacent surface and groundwaters and act as a source of contamination (Figure 1). Therefore, techniques for predicting leachate quality in CDFs are needed to establish sound engineering and environmental data for the selection, design, and management of CDFs.

Nature of the Problem

Contaminant migration via leachate seepage is a porous-media contaminant transport problem (Figure 2). Leaching is defined as interphase transfer of contaminants from dredged material solids to the pore water

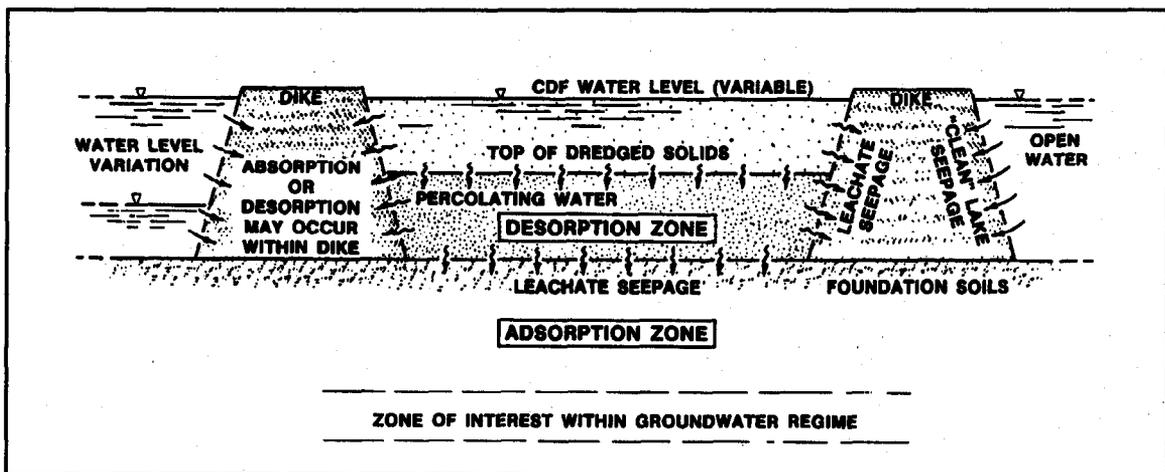


Figure 1. Contaminant migration pathway: leachate seepage

surrounding the solids and the subsequent transport of these contaminants by pore water seepage. Thus, leaching is interphase mass transfer (Equation 2 in Figure 2) coupled with porous-media fluid mechanics (Equation 1 in Figure 2). Interphase mass transfer during dredged material leaching is a complicated interaction of many elementary processes and factors affecting these processes (Figure 3). A complete description of all these processes, their interactions, and factors affecting these processes is not presently possible. Instead, a lumped parameter, the distribution coefficient, is used to describe the distribution of contaminant between aqueous and solid phases.

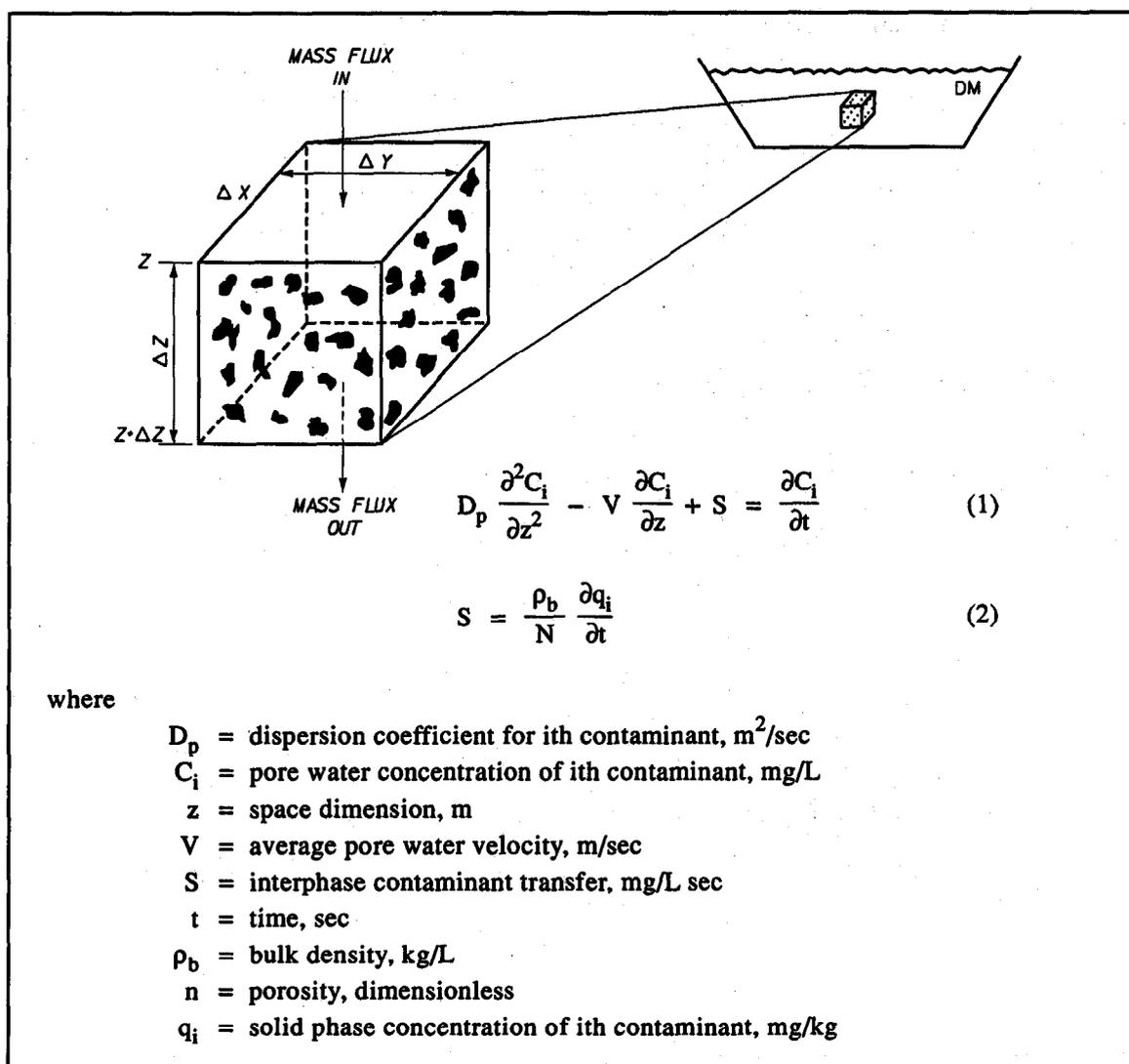


Figure 2. Mathematical model of dredged material leaching (from Hill, Myers, and Brannon 1988)

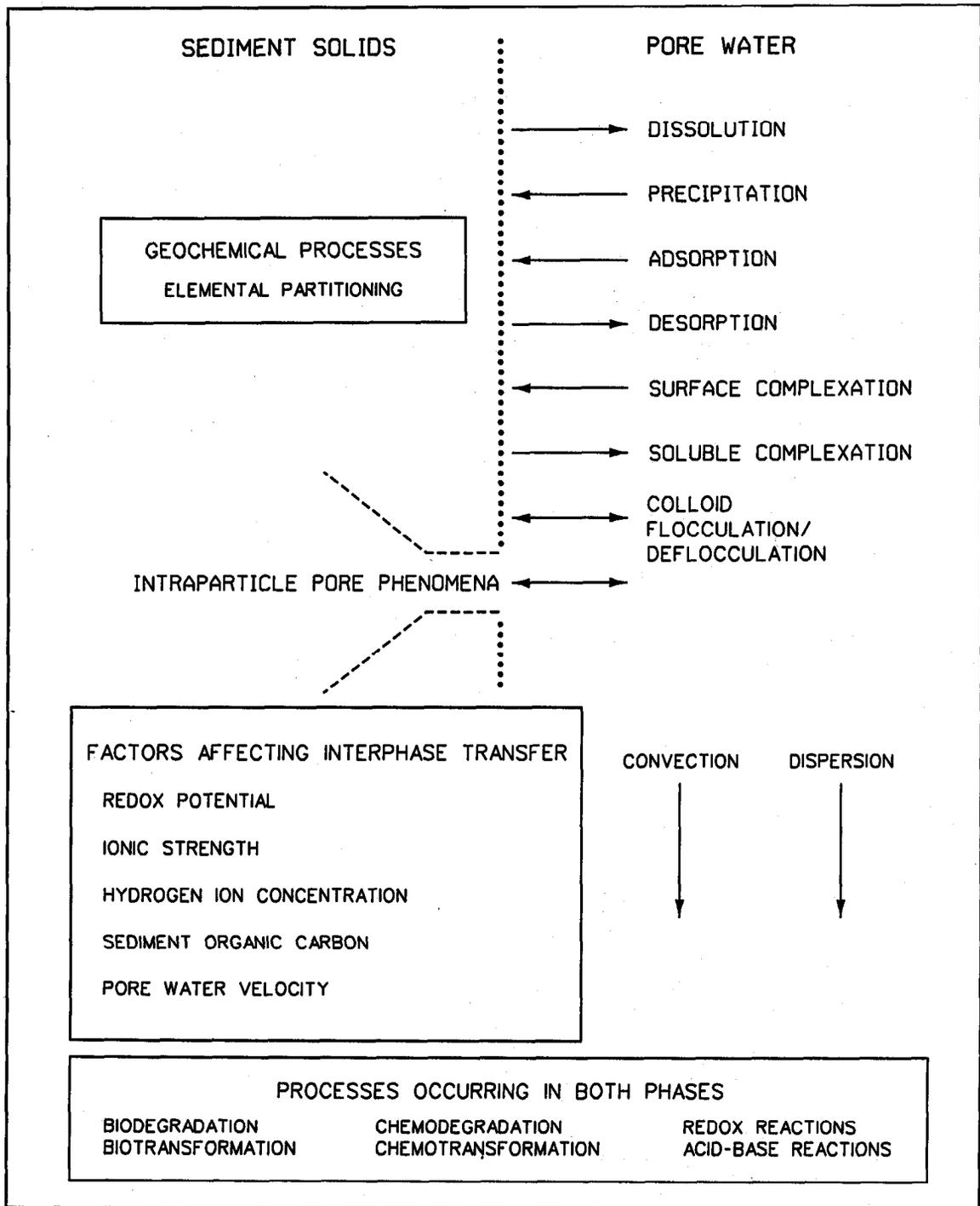


Figure 3. Interphase transfer processes and factors affecting interphase transfer processes

2 Desorption Theory for Dredged Material

Much of the technical approach and rationale for the laboratory testing described in this report has been presented elsewhere in more detail (Hill, Myers, and Brannon 1988; Myers and Brannon 1988a). The following sections present the basic concepts, simplifying assumptions, and recent developments used to conduct leach tests and to interpret the data generated.

Equilibrium Assumption

In order for contaminants to cross the interface between dredged material solids and water, a difference in chemical potentials must exist. Chemicals flow from a region of high chemical potential to a region of low chemical potential just as electric current flows from a region of high electrical potential to one of lower electrical potential, or as mass flows from a position of high gravitational potential to one of low gravitational potential. When chemical potentials are equal, the net transfer of contaminant across the solid-water interface is zero, and the mass of contaminant in each phase is constant, but not necessarily equal. The processes shown in Figure 3 control the rate at which equilibrium is reached and the equilibrium distribution of contaminant between solid and aqueous phases. Once equilibrium is reached, the ratio of contaminant mass in the solid phase to the contaminant mass in the aqueous phases does not change.

In practice, a true equilibrium between dredged material solids and pore water never exists because some of the processes shown in Figure 3 have very slow reaction rates. However, steady-state can be reached between dredged material solids and water if an operational definition of equilibrium is used. In this report, equilibrium is operationally defined for the batch leach tests as the condition at which changes in leachate contaminant concentrations with time cannot be measured; that is, differences are not statistically significant.

By assuming equilibrium between solid and aqueous phases, the need for determining controlling processes and the rate coefficients for these processes is eliminated. Without the equilibrium assumption, laboratory testing and mathematical modeling would require determination of controlling processes and investigation of the kinetics for these processes. As is apparent from Figure 3, predictive laboratory tests and mathematical models based on chemical and mass transfer kinetics would be too complicated for routine application to dredged material leaching. Thus, application of the equilibrium assumption is imperative for the development of predictive techniques suitable for routine use.

Once equilibrium has been reached, only the relative distribution of contaminant between solid and aqueous phases is needed to predict leachate quality. This distribution is conveniently represented by the equilibrium distribution coefficient defined as follows:

$$K_d = \frac{\frac{M_{cs}}{M_s}}{\frac{M_{cw}}{M_w}} \quad (3)$$

where

K_d = equilibrium distribution coefficient, dimensionless

M_{cs} = mass of contaminant in the solid phase, kg

M_s = mass of solids, kg

M_{cw} = mass of contaminant in the aqueous phase, kg

M_w = mass of water, kg

The mass fractions in Equation 3 can be replaced with phase contaminant concentrations without any loss of generality so that Equation 3 becomes

$$K_d = \frac{q}{C} \quad (4)$$

where

K_d = equilibrium distribution coefficient, L/kg

q = contaminant concentration in the solid phase at equilibrium, mg/kg

C = contaminant concentration in the aqueous phase at equilibrium, mg/L

Equations 3 and 4 describe the equilibrium distribution of a single contaminant in a dredged material; that is, equilibrium distribution coefficients are contaminant and dredged material specific. As will be discussed in Chapter 3, K_d is affected by various factors (pH, ionic strength, redox potential, sediment organic carbon). Varying these factors during leaching can shift the equilibrium position of the system and change K_d .

Equilibrium-Controlled Desorption in a CDF

The assumption of equilibrium-controlled desorption in a CDF is based on two arguments: (a) the intuitive argument that the interphase transfer rates affecting leachate quality are fast relative to the volumetric flux of water in the CDF, and (b) the argument that equilibrium-controlled desorption provides conservative predictions of leachate quality. This section discusses these arguments. The term "desorption" as used here and in the remainder of the report refers to the composite effect of the elementary interphase transfer processes shown in Figure 3.

Contaminated dredged material is usually fine grained with hydraulic conductivities in the range of 10^{-5} to 10^{-8} cm/sec. When the hydraulic conductivity is this low, pore water velocities are also low. In filled CDFs, the hydraulic gradient is rarely larger than one, so that pore water velocities approximate hydraulic conductivities; that is, the water moves very slowly at velocities of 10^{-8} to 10^{-5} cm/sec.

When the rate at which water moves is slow relative to the rate at which equilibrium is approached, a local chemical equilibrium exists between the pore water and the sediment solids. The local equilibrium concept is illustrated in Figure 4. The local equilibrium assumption implies that as a parcel of water passes a parcel of dredged material solids, the water and solids come to chemical equilibrium before the parcel of water moves to contact the next parcel of dredged material solids. Leachate quality at the surface of a CDF will differ from leachate quality at the bottom of a CDF, while leachate in both locations will be in equilibrium with the dredged material solids. Some soil column studies have indicated that the local equilibrium assumption is valid for pore water velocities as high as 10^{-5} cm/sec (Valocchi 1985). In reality, equilibrium-controlled desorption requires an infinitely fast desorption rate. However, if the critical interphase transfer rates are sufficiently fast, the equilibrium assumption can yield results indistinguishable from full kinetic modeling (Jennings and Kirkner 1984; Valocchi 1985; Bahr and Rubin 1987).

In addition to being a good approximation, the assumption of equilibrium-controlled desorption is conservative; that is, predictions based on the equilibrium assumption will overestimate leachate contaminant concentrations for dredged material. The equilibrium assumption is conservative because interphase transfer is from the dredged material solids to the pore water, and equilibrium means that all of the desorption that can occur has

occurred. Thus, for clean water entering the dredged material, pore water contaminant concentrations cannot be higher than the equilibrium value.

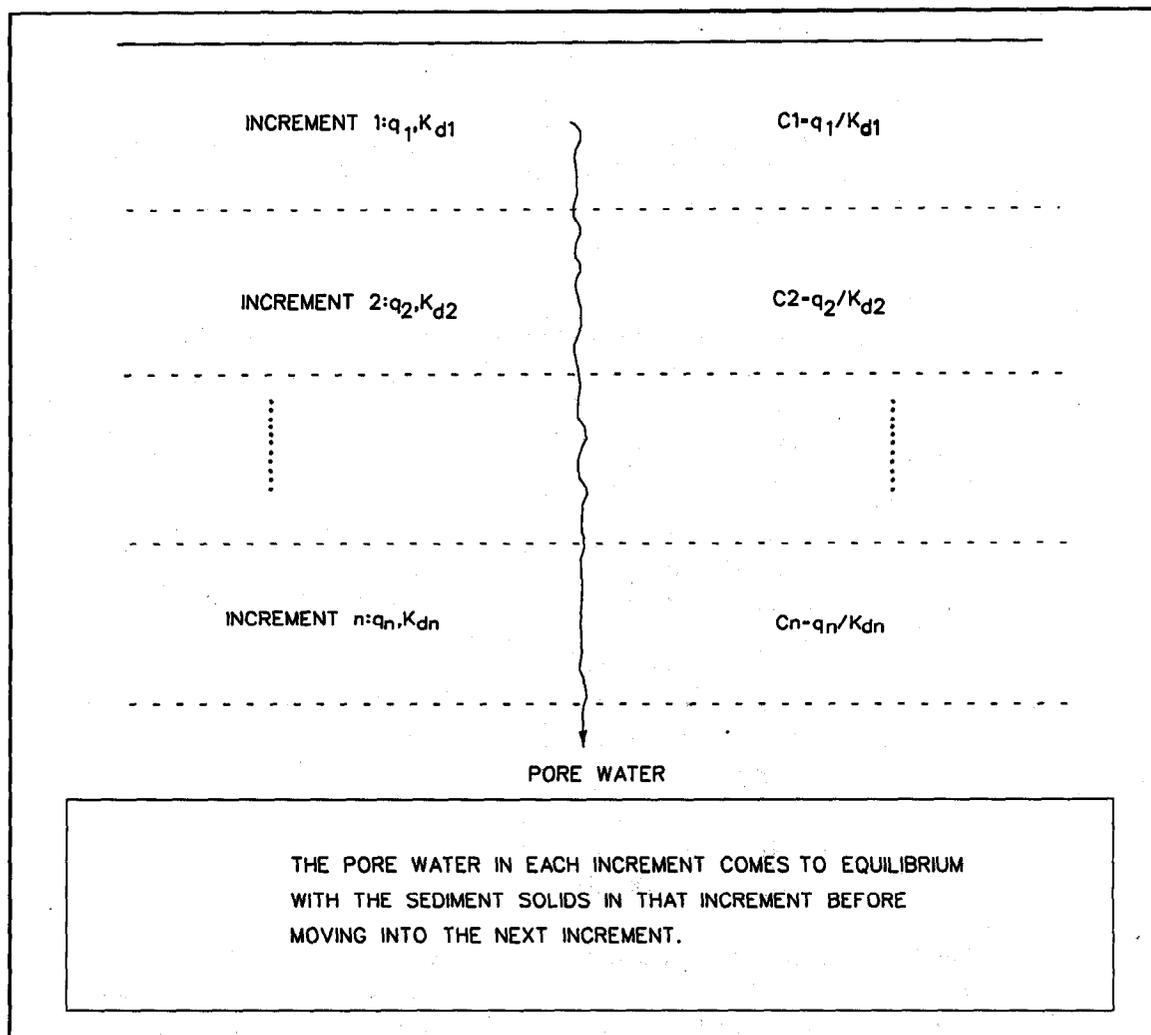


Figure 4. Illustration of the local equilibrium assumption for leaching in a CDF

3 Sequential Batch Leach Tests

Background

Batch leaching is a procedure for determining how contaminant mass is distributed between solid q and aqueous phases C at equilibrium. Sequential batch leaching is a procedure for determining how the equilibrium distribution of contaminant between solid phase and aqueous phase changes during elution with water. Details are described in the following section. A relationship between q and C is needed to evaluate the source term S in the mathematical model shown in Figure 2. The source term is obtained by using the chain rule as follows:

$$S = -\frac{\rho_b}{n} \frac{\partial q}{\partial t} = -\frac{\rho_b}{n} \frac{\partial q}{\partial C} \frac{\partial C}{\partial t} \quad (5)$$

The term $\partial q/\partial C$ represents the functional dependence of leachate quality on contaminant levels in the dredged material solids. Sequential batch leach tests provide the information needed to evaluate $\partial q/\partial C$.

By sequentially leaching an aliquot of sediment solids, a table of solid phase contaminant concentrations q and aqueous phase contaminant concentrations C can be developed and plotted (successive batches have differing q and C concentrations). A plot of q versus C yields a desorption isotherm, the slope of which is the distribution coefficient. Several types of desorption isotherms have been observed in sequential batch leach tests for sediments (Environmental Laboratory 1987; Myers and Brannon 1988b; Palermo et al. 1989). The two most important types are discussed below.

Constant K_d

Sequential batch leaching of freshwater sediments usually yields a desorption isotherm such as shown in Figure 5. This is referred to as a "classical desorption isotherm." Its key feature is a single distribution

coefficient that is constant throughout the sequential leaching procedure. A commonly observed feature of desorption isotherms for metals in freshwater sediments is that they do not go through the origin, but intercept the ordinate at some other point. The intercept indicates the amount of metal in geochemical phases that is resistant to aqueous leaching.

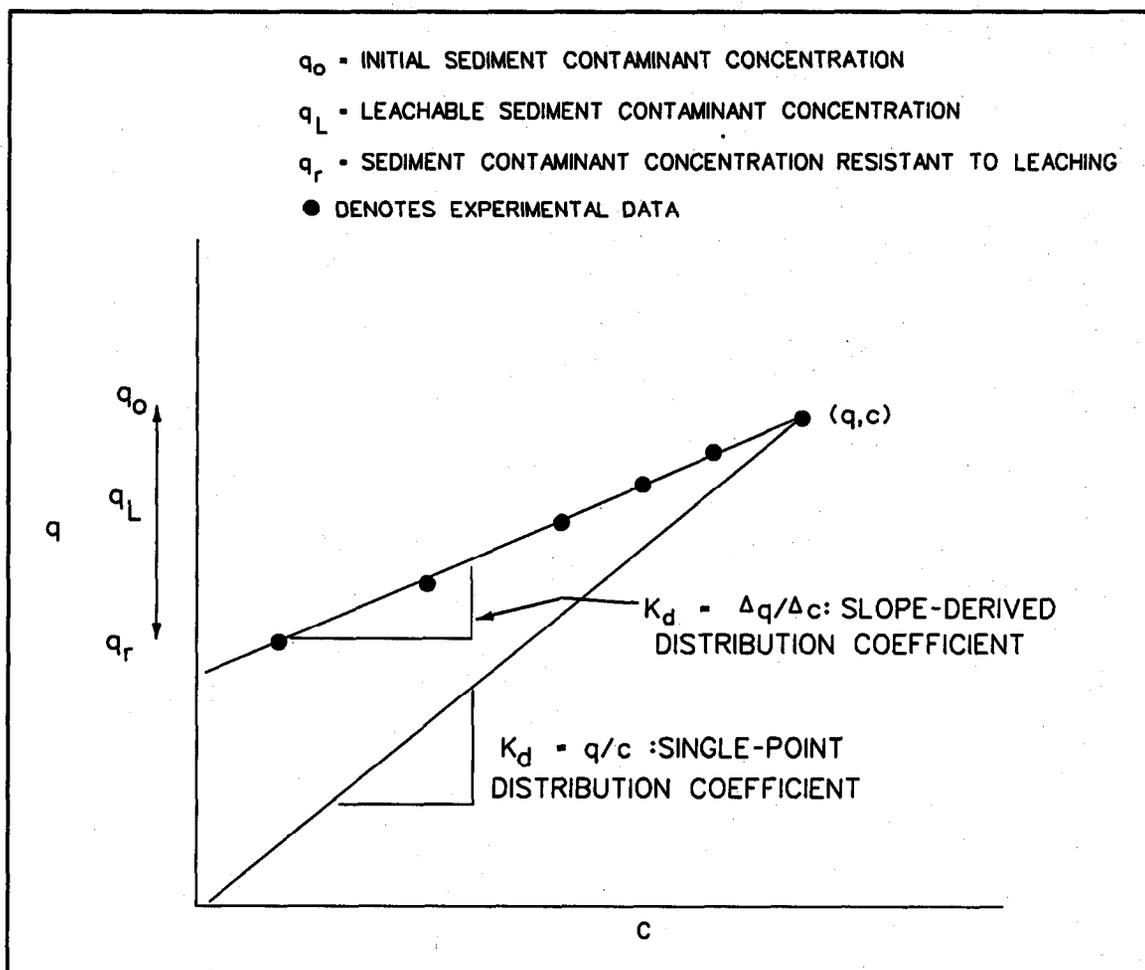


Figure 5. Desorption isotherms for slope-derived and single-point distribution coefficients

The general form of the q versus C relationship for classical desorption isotherms is as follows:

$$q = K_d C + q_r \quad (6)$$

where q_r = solid phase concentration resistant to leaching, mg/kg. Differentiating Equation 6 with respect to time yields

$$\frac{\partial q}{\partial C} = K_d \quad (7)$$

The source term S in Equation 1 is obtained by substituting K_d for $\partial q/\partial C$ in Equation 5.

Nonconstant K_d

During sequential batch leaching of estuarine sediments with distilled-deionized water, the distribution of contaminant between aqueous and solid phases is nonconstant (Brannon et al. 1989; Brannon, Myers, and Price 1990; Brannon et al. 1991). Nonconstant contaminant partitioning yields an isotherm for which the distribution coefficient changes as the solid phase concentration q decreases during sequential leaching until a turning point is reached (Figure 6). At the turning point, the distribution coefficient becomes constant, and desorption begins to follow the classical isotherm. The nonconstant portion of the desorption isotherm is related to elution of salt.

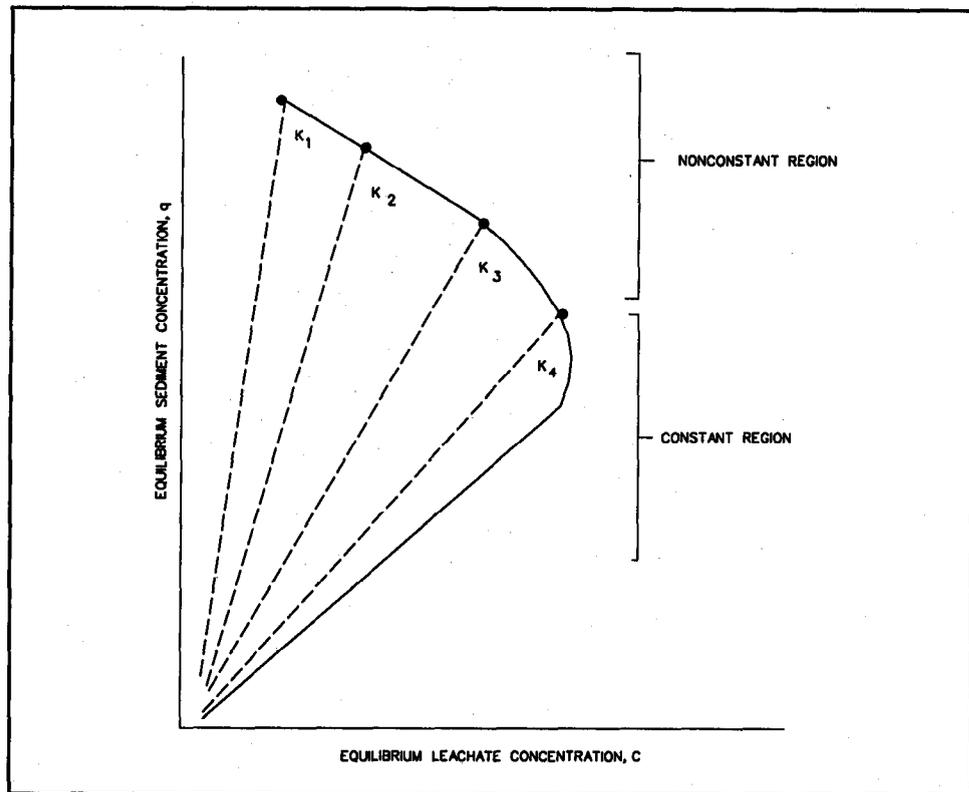


Figure 6. Desorption isotherm illustrating nonconstant and constant partitioning

As salt is eluted, the ionic strength of the aqueous phase is reduced. According to the Gouy-Chapman model of charge distribution in double layers, decreasing the ionic strength increases repulsive forces (Stumm and Morgan 1981) so that flocculated colloidal matter becomes dispersed. Deflocculation of sediment organic carbon increases the concentration of dissolved organic carbon (DOC) in the aqueous phase, mobilizing metals

and organic contaminants bound to the colloidal matter (Brannon et al. 1991). For these reasons, the type of desorption isotherm shown in Figure 6 is referred to as a DOC-facilitated desorption isotherm. Since the relationship of q versus C is not a one-to-one correspondence for DOC-facilitated desorption isotherms, q as a function of C cannot be developed from the isotherm. Research is continuing on how to model $\partial q/\partial C$ with K_d as a variable.

Recommended Procedure

Research on sequential batch leach tests for dredged material and sediments has included investigations of liquid-solid ratio and kinetics. Liquid-solid ratio batch testing has been conducted to find the optimum sediment-water ratio for use in sequential batch testing. Results indicate that a 4 to 1 ratio of water-to-solids by weight is optimal and that 24 hr shaking time is sufficient to achieve steady-state conditions (Environmental Laboratory 1987; Myers and Brannon 1988a; Myers and Brannon 1988b; Palermo et al. 1989; Brannon, Myers, and Price 1990).

Research has also included batch testing of anaerobic and aerobic sediment. Leaching of aerobic, aged sediment has been used to simulate leaching of the surface crust in a CDF, and anaerobic leaching has been used to simulate leaching in the saturated-anaerobic zone of a CDF. 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 dewateres by evaporation and seepage. The oxidized crust may eventually be several feet thick, but, in general, never represents a significant portion of the vertical dredged material profile for fine-grained material. The procedure described below, therefore, describes the technique for anaerobic leaching. The technique for aerobic leaching is described elsewhere (Environmental Laboratory 1987; Myers and Brannon 1988b; Palermo et al. 1989).

The recommended procedure for anaerobic sequential batch leaching of sediments and dredged material is as follows:

- a. Step 1.** Load sediment into appropriate centrifuge tubes fitted with leakproof, airtight tops: 500 ml polycarbonate for metals and 450 ml stainless steel for organic contaminants. Add sufficient deoxygenated distilled-deionized water to each tube to bring final water-to-sediment ratio to 4:1. All operations should be conducted in a glove box under a nitrogen atmosphere.
- b. Step 2.** Place centrifuge tubes for metals horizontally on a reciprocating shaker and shake at 160 cycles per minute for 24 hr. Place centrifuge tubes for organic contaminants in a rotary tumbler

such as described by Garrett et al. (1984) and turn at 40 revolutions per minute for 24 hr.

- c. **Step 3.** Centrifuge for 30 min at 6,500 g's for organics and 9,000 g's for metals.
- d. **Step 4.** Filter leachate through 0.45- μ m membrane filters for metals. Filter leachate through a Whatman GD/F glass-fiber prefilter followed by a Gelman AE glass-fiber filter of 1.0- μ m nominal pore size for organics.
- e. **Step 5.** Set aside a small amount of leachate for analysis of pH and electrical conductivity. Acidify leachate for organic analysis with 1 ml of concentrated HCl per liter of leachate and with 1 ml of concentrated Ultrex nitric acid per liter of leachate for metals analysis. Store samples in the dark. Acetone-rinsed glass bottles should be used for storage of organic samples, and acid-washed polycarbonate bottles should be used for metals. Bottles for organics should be filled to the top.
- f. **Step 6.** Return to Step 2 after replacing leachate removed in Step 4 with fresh deoxygenated distilled-deionized water. Repeat the entire procedure to obtain a minimum of four complete cycles for freshwater sediments and seven complete cycles for estuarine sediments.

The procedure described above is still developmental and subject to revision.

Applications

The sequential batch test described above has been applied to estuarine and freshwater sediments (Environmental Laboratory 1987; Myers and Brannon 1988b; Brannon et al. 1989; Palermo et al. 1989; Brannon, Myers, and Price 1990). Selected results are discussed below.

Freshwater sediments

Cadmium and zinc desorption isotherms prepared from anaerobic sequential batch leach tests conducted on sediment from Indiana Harbor, IN (Environmental Laboratory 1987), are shown in Figure 7. These are well defined and follow the theory for constant K_d . For the desorption isotherms shown in Figure 6, K_d is the slope of the isotherm.

Anaerobic sequential batch leaching for polychlorinated biphenyls (PCBs) in Indiana Harbor sediment produced clustered desorption isotherms that did not show a well-defined trend (Environmental Laboratory 1987) (Figure 8). The insert in the upper right-hand corner of Figure 8

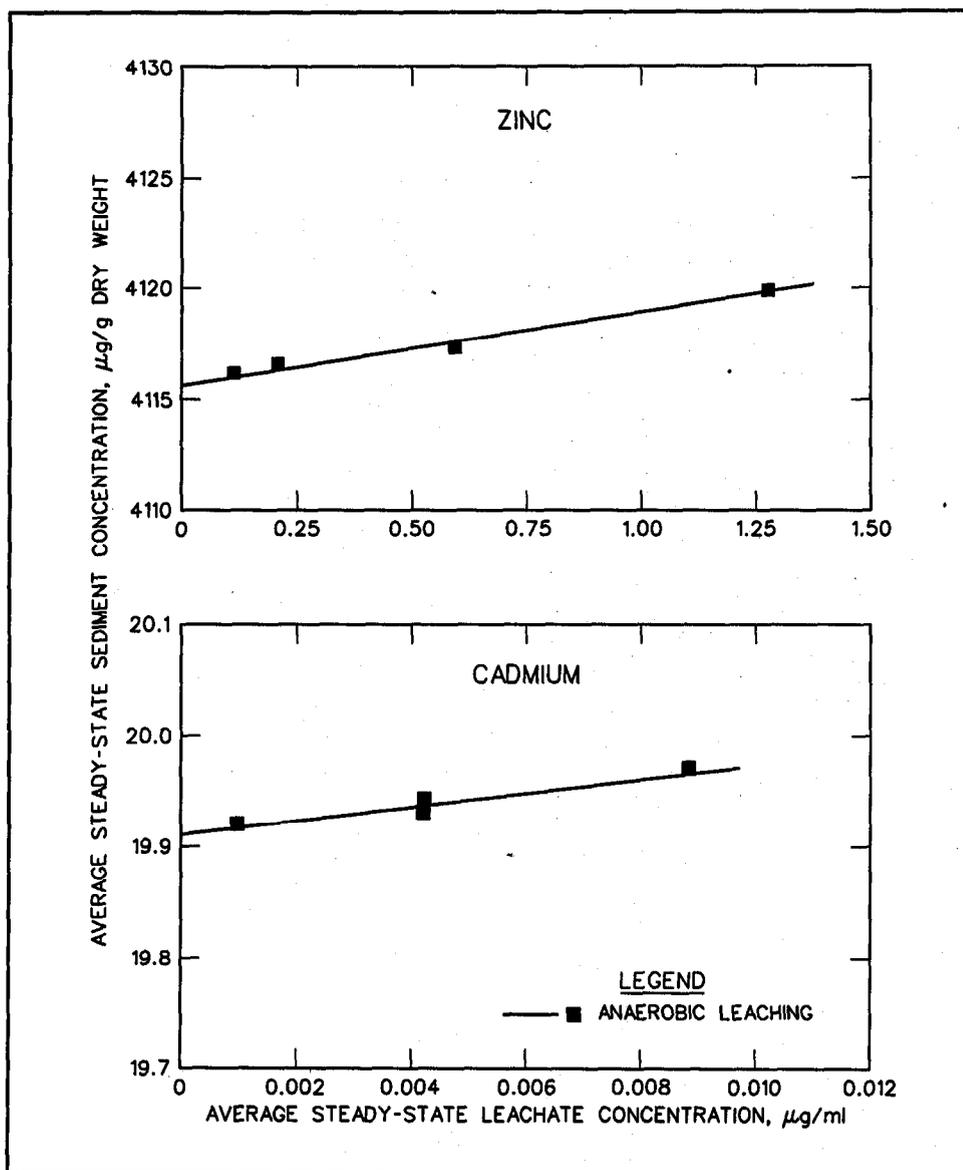


Figure 7. Desorption isotherms for zinc and cadmium in Indiana Harbor sediment

shows that when plotted with the graph origin at the point 0,0 the data reduce to a dot. For clustered desorption isotherms, K_d is the single-point distribution coefficient shown in Figure 5 with the centroid of the cluster as the point q,C . Although the desorption isotherm is clustered, the distribution coefficient is interpreted as a constant. Preliminary confirmation of this interpretation has been obtained in column leach tests discussed in Chapter 4 of this report.

Results of other sequential batch leach tests on freshwater sediments have shown the classical desorption isotherms presented in Figures 7 and 8 (Brannon et al. 1989; Brannon, Myers, and Price 1990; Myers 1991). In general, distribution coefficients for metals are small, usually less than

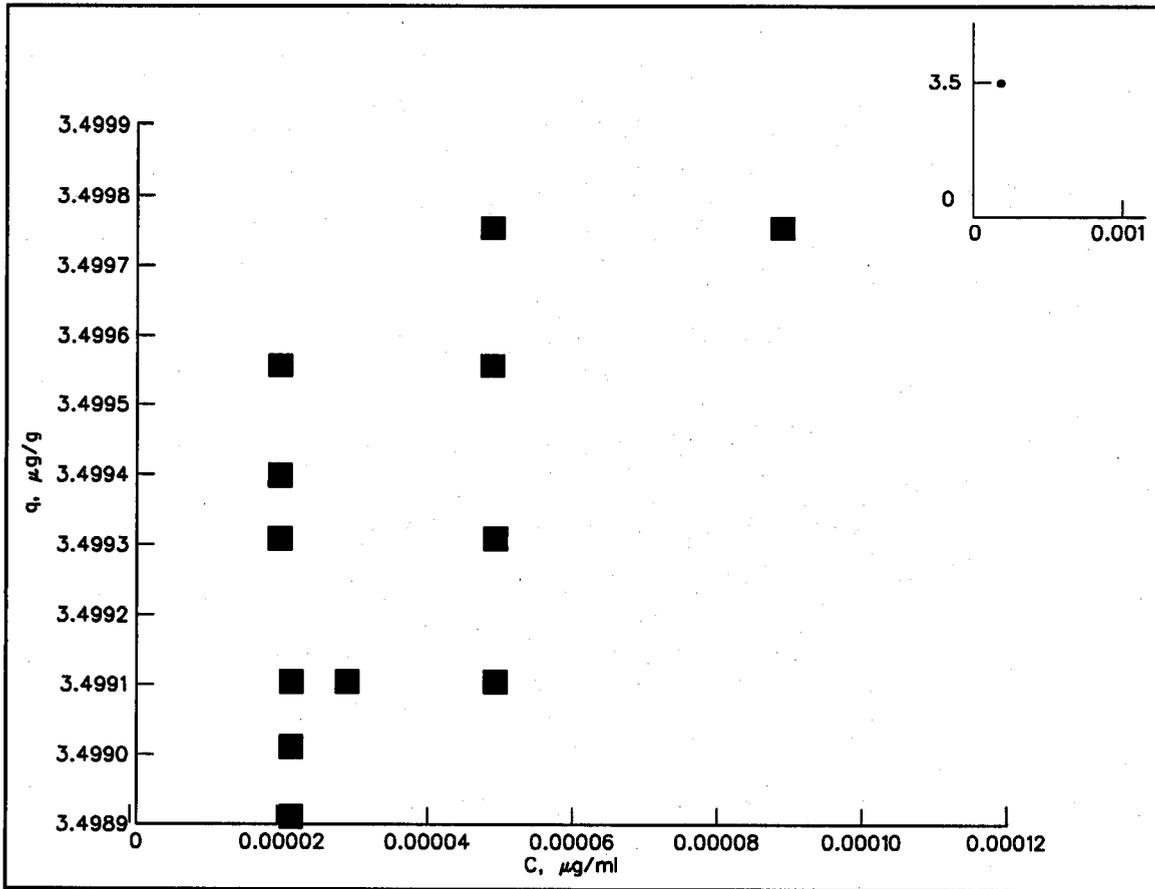


Figure 8. Desorption isotherm for 2,2',4,4'-tetrachlorobiphenyl for anaerobic leaching of Indiana Harbor sediment

10 L/kg, and the fraction of metal resistant to aqueous leaching is large, usually greater than 99 percent of the bulk metal concentration. The distribution coefficient for PCBs in freshwater sediments is constant and usually greater than 1,000 L/kg, and the fraction resistant to leaching is usually assumed to be zero.

Estuarine sediment

Arsenic and nickel concentrations in anaerobic sequential batch leachate from Everett Bay, WA, sediments as a function of sequential leach cycle number are shown in Figure 9. Arsenic and nickel concentrations were low initially, peaked at either the third or fourth leach cycle, then declined. The arsenic and nickel desorption isotherms prepared from the data in Figure 9 are shown in Figure 10. Initially, the isotherm slopes for these elements were negative; that is, leachate metal concentrations increased as the bulk sediment metal concentrations decreased. After the third or fourth leaching cycle, the isotherms form changed to a classical form.

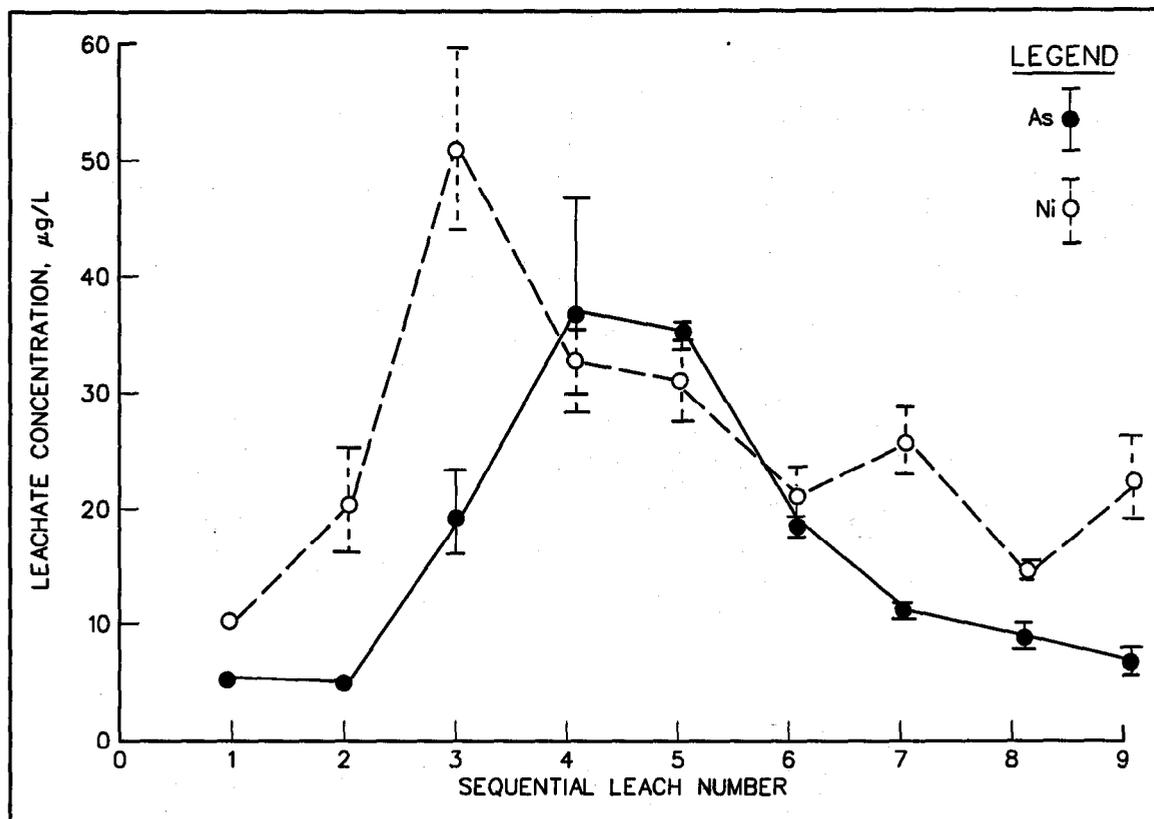


Figure 9. Arsenic and nickel concentrations in anaerobic sequential batch leachate for Everett Harbor sediment

In some studies of estuarine sediments, slopes of metal desorption isotherms have been negative through the entire leaching sequence (Figure 11). A turning point was never reached, although a turning point must exist; otherwise, the desorption isotherm will intersect the abscissa. This is a physical impossibility because it implies that a clean sediment can leach contaminant.

The type of metal desorption isotherm shown in Figure 10 is not limited to west coast sediments. Similarly, the type of metal desorption isotherm shown in Figure 11 is not limited to east coast sediments. Both types of isotherms have been observed in the same sediment. In the limited testing conducted thus far, these types of desorption isotherms have been found only for estuarine sediments.

Figure 12 shows a PCB desorption isotherm prepared from anaerobic sequential batch leach tests conducted on sediment from the New Bedford Harbor Superfund site, New Bedford, MA (Myers and Brannon 1988b). This desorption isotherm indicates nonconstant K_d during sequential leaching. Nonconstant PCB partitioning during sequential leaching has recently been related to salt washout and subsequent deflocculation of colloidal sediment organic carbon containing PCBs (Brannon et al. 1991). As previously discussed, deflocculation of colloidal sediment organic

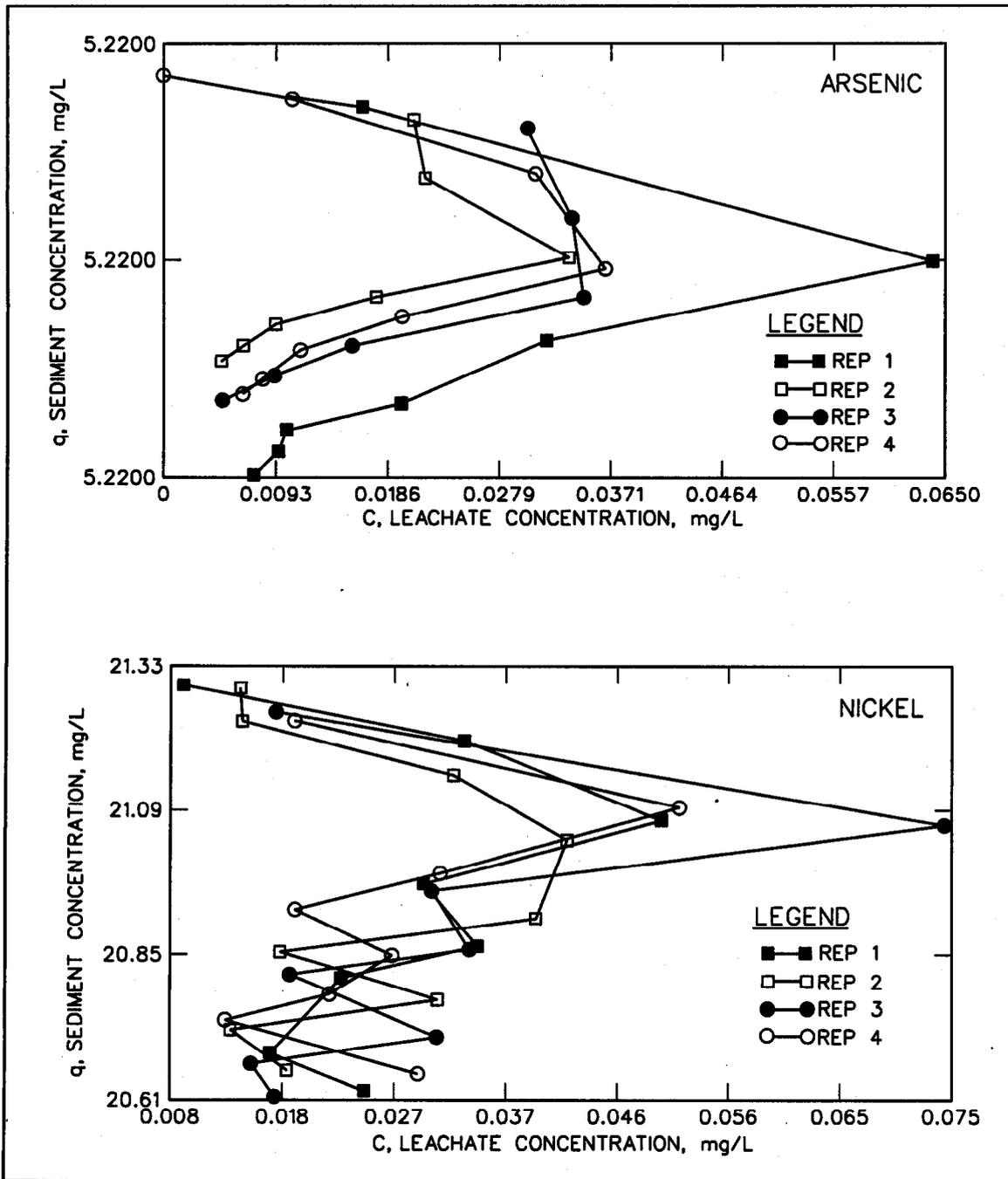


Figure 10. Arsenic and nickel desorption isotherms, anaerobic Everett Harbor sediment

carbon refers to release of organic carbon associated with sediment. The overall result is an elution curve that has a distinct peak in leachate PCB concentrations that occurs after the first four leaching cycles. This same effect has been observed in other studies (Brannon et al. 1989) and probably also explains some of the nonclassical-metals desorption isotherms observed for estuarine sediments.

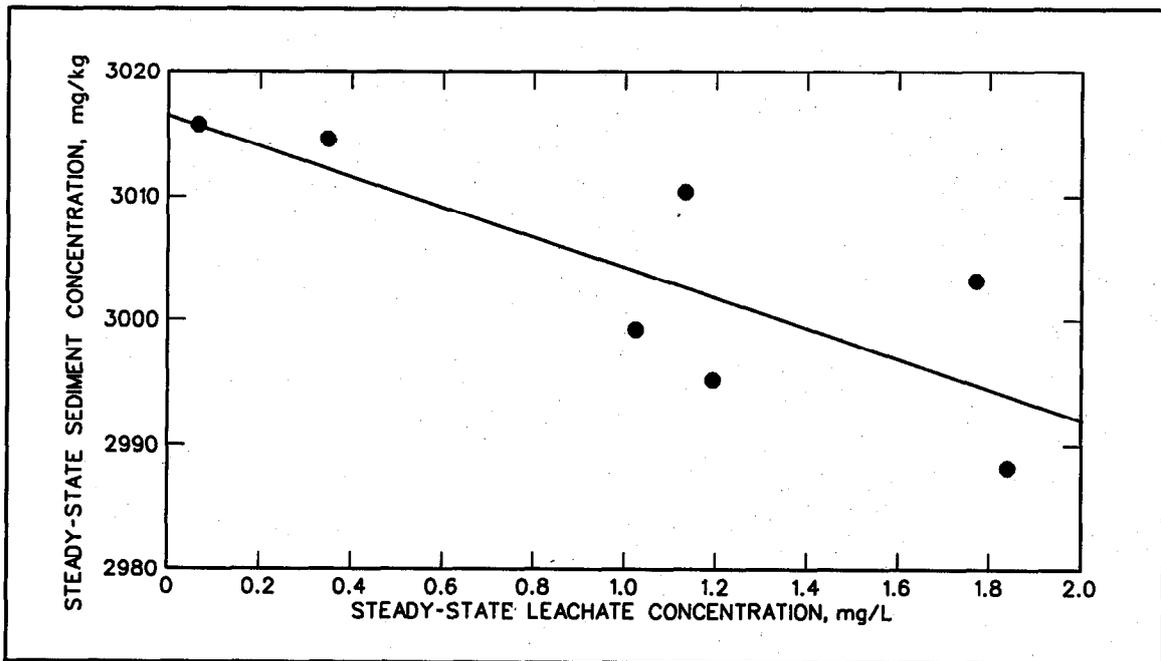


Figure 11. Desorption plot for zinc from anaerobic sequential batch testing of New Bedford Harbor sediment

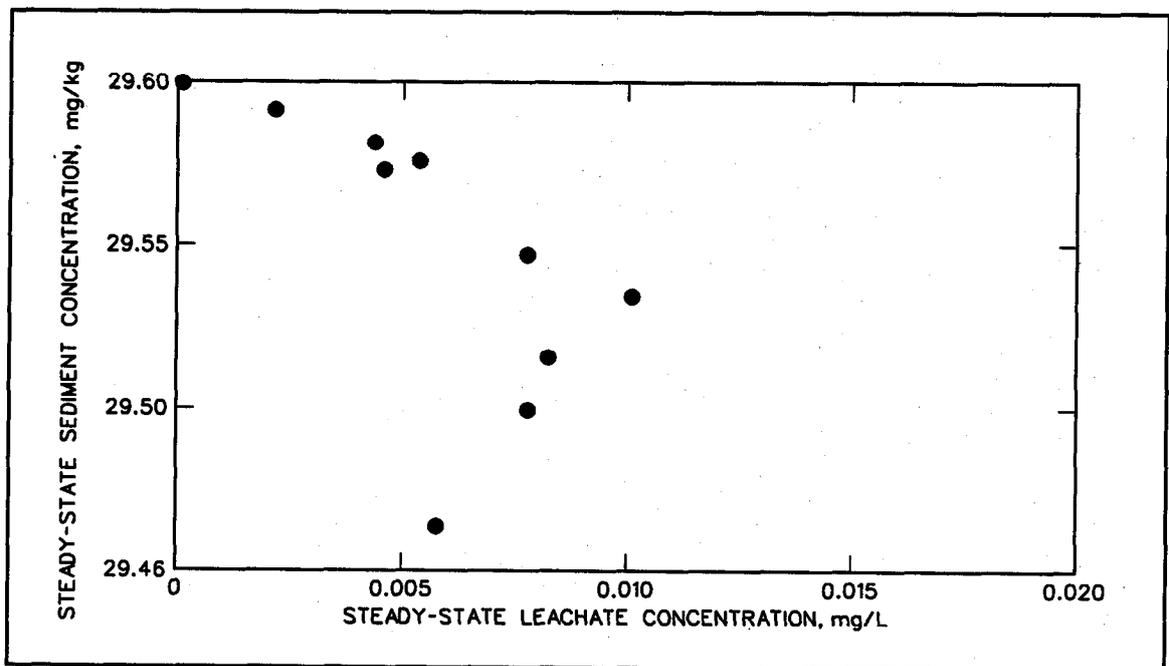


Figure 12. Desorption isotherm for PCB congener 118 from sequential batch leaching of New Bedford Harbor sediment

4 Column Leach Tests

Background

Sequential batch leach tests, useful for determining desorption kinetics, equilibrium distribution coefficients, and long-term leaching characteristics, cannot simulate advective-dispersive and other mass transfer effects occurring in CDFs. Column leach tests are being used as laboratory-scale physical models of contaminant elution from dredged material that include advective-dispersive and other mass transfer effects. The primary purpose of column leaching is to demonstrate that the local equilibrium assumption (LEA) discussed in Chapter 2 and data from batch tests can be used to predict contaminant leaching in a CDF.

Prediction of long-term contaminant leaching requires proper mathematical formulation of the source term in Equations 1 and 2. An integrated approach is being used to examine the applicability of source terms formulated on the basis of sequential batch leach data to contaminant transport in porous media (Figure 13). In the integrated approach, parameters from sequential batch leach tests, soils tests, and column operating records are used in a contaminant transport equation to predict column elution histories. Predictions are then compared with observed elution behavior. If predicted and observed column elution histories agree, the conclusion may be reached that the processes governing transfer of contaminants from dredged material solids to water have been adequately described. If not, other source term formulations may be needed. Once interphase transfer has been adequately described, contaminant migration by leaching can be evaluated for the flow conditions that apply in the field.

Applications

To date, column leaching studies have been conducted on sediments from Indiana Harbor, IN (Environmental Laboratory 1987), New Bedford Harbor, MA (Myers and Brannon 1988a), and Everett Harbor, WA (Palermo et al. 1989). Each study employed continuous-flow leaching (saturated conditions) in divided-flow, stainless-steel columns designed to minimize

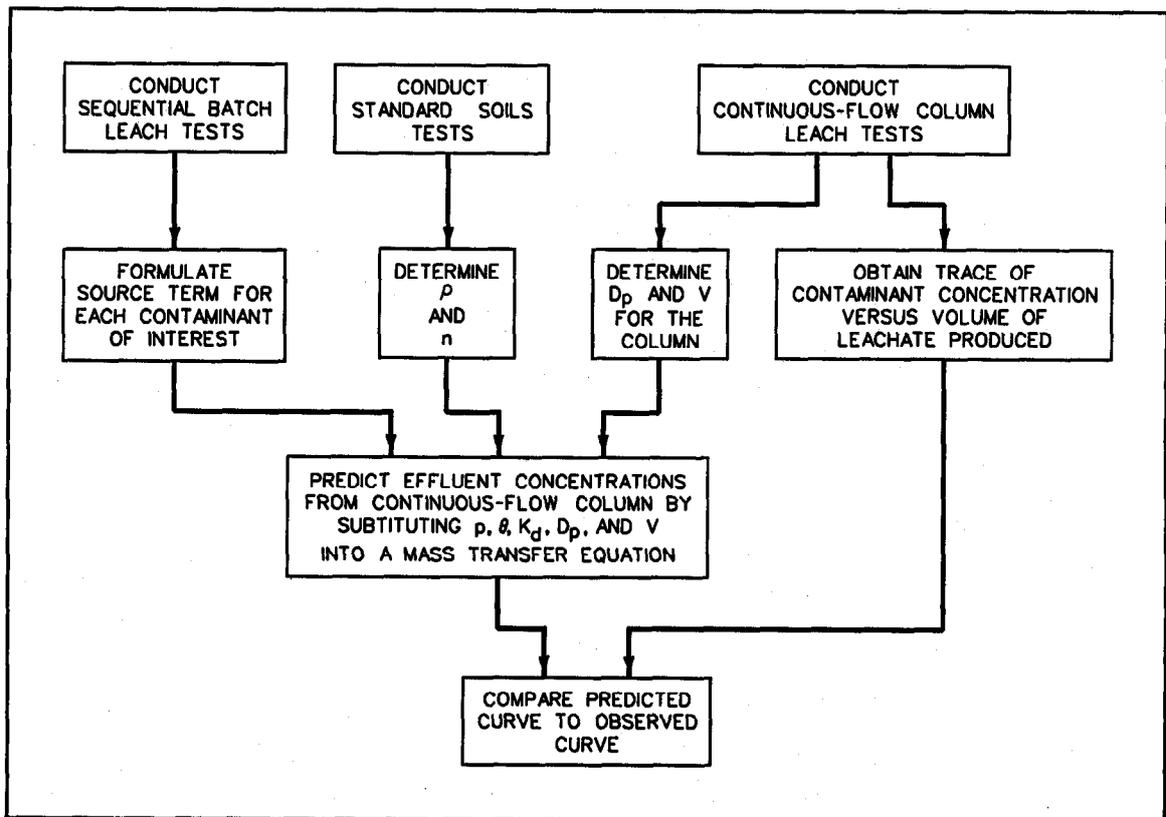


Figure 13. Integrated approach for examining the source term

wall effects (Figure 14). The double-ring design divided flow, separating the water flowing through the center of the column from that flowing down the walls. Column inside diameter was 15.2 cm, and the diameter of the flow-through area for leachate collection and analysis was 9.8 cm. Separate columns were set up for obtaining leachate for metal and organic contaminant analysis because of differences in the volume of leachate required for metals (0.1 L) and organic analyses (1 L). Sediment height was approximately 18 cm for metal analysis and 36 cm for organic analysis. Flow was regulated by adjusting the pressure in the head space gas during testing. Average pore water velocities were in the range of 1 E-06 to 1 E-05 cm/sec. Initial operating pressures were 0.0 psig (0.0 kPa gage). Final operating pressures ranged from 15 to 30 psig (103 to 207 kPa gage), depending on the sediment column height (type of contaminant). Sediments were leached with distilled-deionized water. Leachate from the center tap on the column was collected in graduated 1000-ml glass cylinders. The collection vessels were isolated from the atmosphere by a constant nitrogen gas purge and a water trap. Samples were filtered under nitrogen through glass fiber filters (1.0- μ m nominal pore size) prior to analysis.

Column leaching studies were also conducted on sediment that had been aged by exposure to air at ambient temperatures for 6 months (Environmental Laboratory 1987; Palermo et al. 1989; Myers and Brannon 1988a). The experimental conditions were the same as for untreated sediment except

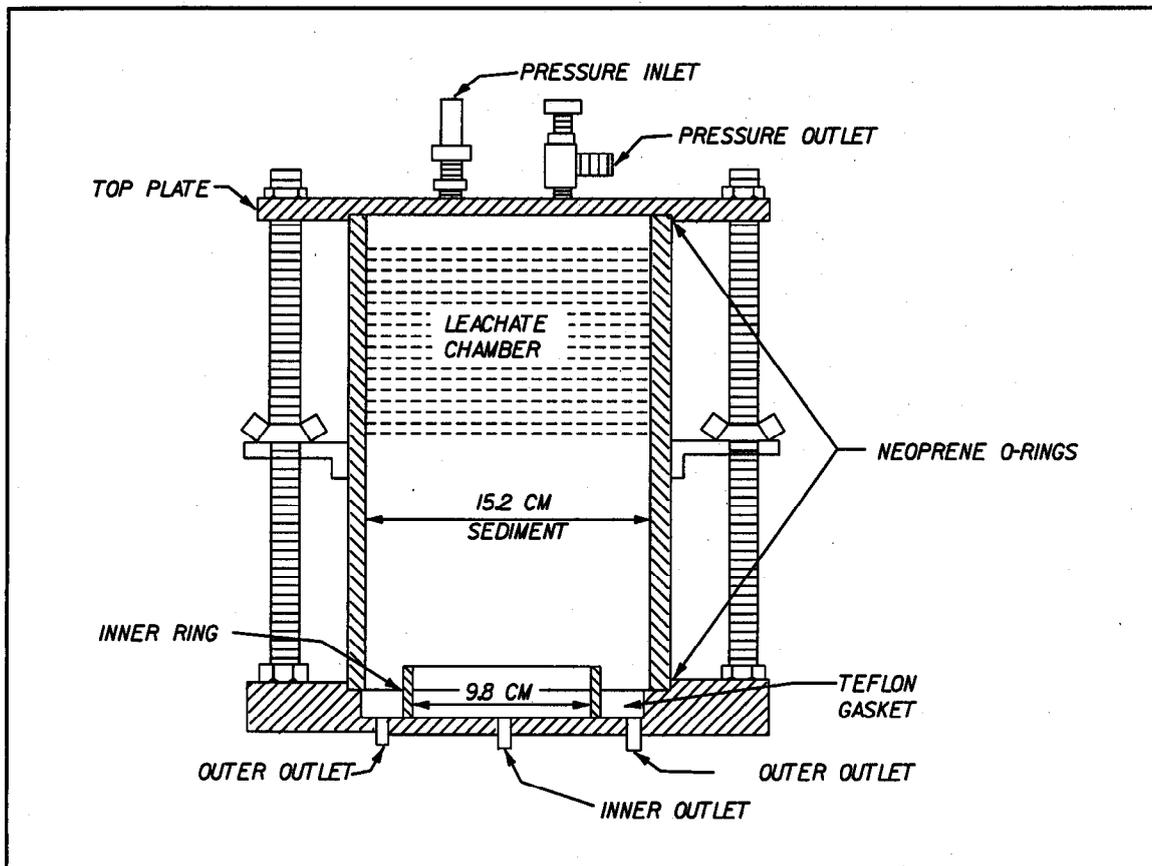


Figure 14. Divided-flow leaching column

that air was used as the head space gas, and samples were filtered in an air environment.

Some problems were encountered in using the divided-flow column leaching apparatus (Figure 14). The major problems were the number of pore volumes that could be eluted and the potential for sample deterioration during collection. These problems are discussed in the following sections on applications to freshwater and estuarine sediments and column redesign.

Freshwater sediment

Anaerobic column leach tests conducted on Indiana Harbor sediment indicated that a source term based on contaminant-specific constant K_d adequately described observed elution curves for metals and PCBs (Environmental Laboratory 1987). Figure 15 shows predicted and observed column elution curves for PCBs from Indiana Harbor sediment. The column leach tests also showed that the sequential batch leach test overestimated metals and PCB concentrations in column leachates and was, therefore, a conservative estimator of leachate quality for Indiana Harbor dredged material.

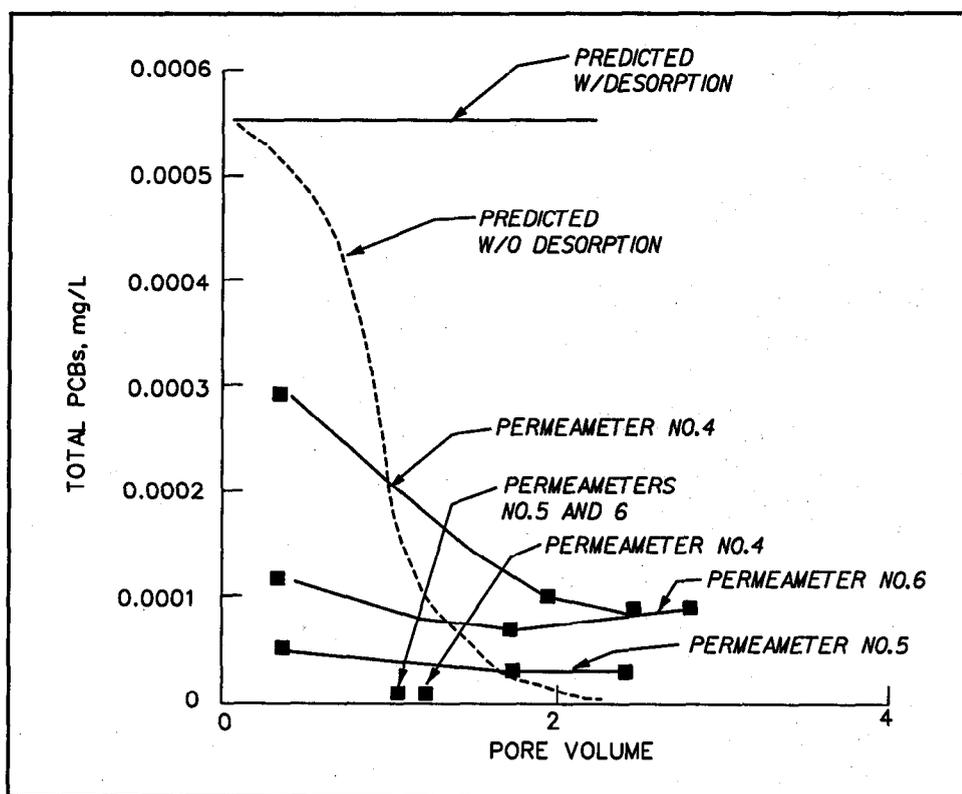


Figure 15. Total PCB concentrations in anaerobic column leachate for Indiana Harbor sediment

The prediction shown in Figure 15 was developed using a semi-infinite analytical solution to Equation 1 with constant K_d . Sequential batch leach tests on other freshwater sediments indicate that source term formulations based on constant K_d will probably describe contaminant leaching for freshwater sediments (Brannon et al. 1989; Myers 1991). However, Indiana Harbor sediment is the only freshwater sediment that has been investigated in column leaching studies. Furthermore, only four pore volumes were eluted. Operational limitations of the columns prevented collection of more data. Elution of the volume of sample needed for PCB analysis required several months, and elution of additional pore volumes would have extended the period of data collection to beyond the scope of the study. An improved column design that overcomes these limitations is discussed in a later section. Additional column leaching studies on freshwater sediments with elution of more than four pore volumes are needed before the type of source term formulations applied to anaerobic Indiana Harbor sediment can be recommended for routine application.

Aerobic column leaching studies were also conducted on aged Indiana Harbor sediment. These studies were largely unsuccessful because the residual oxygen demand in the sediment converted "aerobic" columns to anaerobic columns shortly after they were flooded (Environmental Laboratory 1987). Since aerobic batch and column leach tests were not conducted under equivalent redox conditions, source term formulations

nonconstant partitioning, and source term formations for this type of partitioning are not available.

Aerobic column leaching studies were also conducted on aged Everett Harbor sediment. Residual sediment oxygen demand, as previously discussed for Indiana Harbor sediment, made application of the integrated approach inappropriate (Palermo et al. 1989).

New Bedford Harbor. Leach tests conducted on anaerobic New Bedford Harbor sediment showed that desorption theory based on contaminant-specific constant K_d did not adequately describe leaching of metals or PCBs in either batch or column leach tests (Myers and Brannon 1988b). Desorption isotherms showed the nonconstant partitioning previously observed for Everett Harbor sediment. Since sequential batch leach data indicated that maximum leachate contaminant concentrations would not occur until after several pore volumes were eluted, the time period for data collection from column leach tests was extended for New Bedford Harbor sediment relative to the data collection periods used for Indiana Harbor and Everett Harbor sediments.

Column leachate PCB data for anaerobic New Bedford Harbor sediment showed complicated elution curves in which concentrations first tended to decrease and then increase to peak values after about three pore volumes had been eluted. These trends are illustrated for Aroclor 1242 in Figure 17. The decrease in Aroclor 1242 concentrations from initial values corresponded to the period in which electrical conductivity rapidly decreased, and the increase to peak concentrations corresponded to the period following

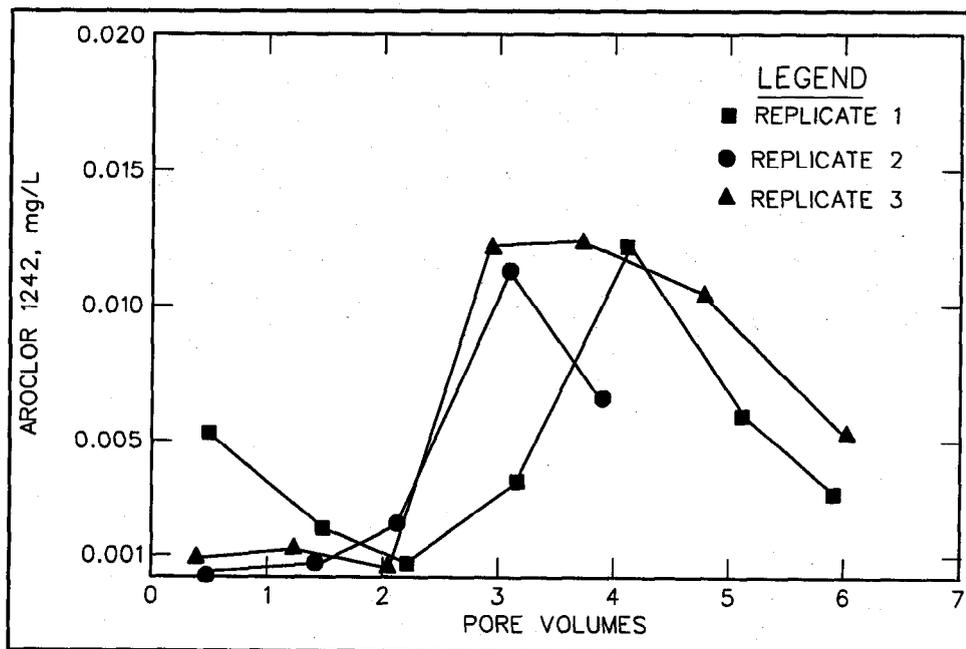


Figure 17. Aroclor 1242 concentration in column leachate from anaerobic New Bedford Harbor sediment

development of lower, relatively constant electrical conductivity in column leachate. More than a year was required to elute the six pore volumes shown in Figure 17.

Although predicted and observed curves are not shown in Figure 17, the shape of the observed PCB elution curve is in agreement with the shape predicted from sequential batch leach tests (Myers and Brannon 1988b). The PCB concentrations in column leachate, however, were significantly lower than in the batch leachates. Several explanations for concentration differences include loss of contaminants by sorption to collection vessels during extended periods of leachate collection, particle disaggregation effects related to differences in hydraulic regimes in batch and column leach tests, and the inability to elute more pore volumes may have precluded discovery of true peak concentrations at higher pore volumes. An improved column design that overcomes some of these problems is discussed in the next section. Additional column leaching studies on estuarine sediments with elution of more than six pore volumes is needed to verify the correlation of contaminant elution curves with changes in electrical conductivity observed in the New Bedford Harbor study.

Aerobic column leaching studies were also conducted on aged New Bedford Harbor sediment. Residual sediment oxygen demand, as previously discussed for Indiana and Everett Harbor sediments, made application of the integrated approach inappropriate.

Improved Column Design

Participants of a workshop organized to review U.S. Army Engineer Waterways Experiment Station studies on sediment leaching recommended redesign of the column leach apparatus to include thin-layer columns with improved leachate collection systems (Myers and Brannon 1988a). As previously discussed, the major problems with the column leach apparatus (Figure 14) are the time required to conduct a column leach test and the potential for sample deterioration during leachate collection. An improved column leaching apparatus has been designed (Myers, Gambrell, and Tittlebaum 1991) and is being used in current column leaching studies (Figure 18).

Flow

To increase the number of pore volumes eluted in a given period of time, column length was reduced. Pore water velocity (flow) could have been increased, but pore water velocity affects the processes controlling contaminant release (Rubin 1983; Valocchi 1985; Bahr and Rubin 1987; Brusseau and Rao 1989). Therefore, adjustments must be made cautiously and judiciously. Average pore water velocity in the improved column design is about the same as in the old design, that is, about $1 \text{ E-}05 \text{ cm/sec}$

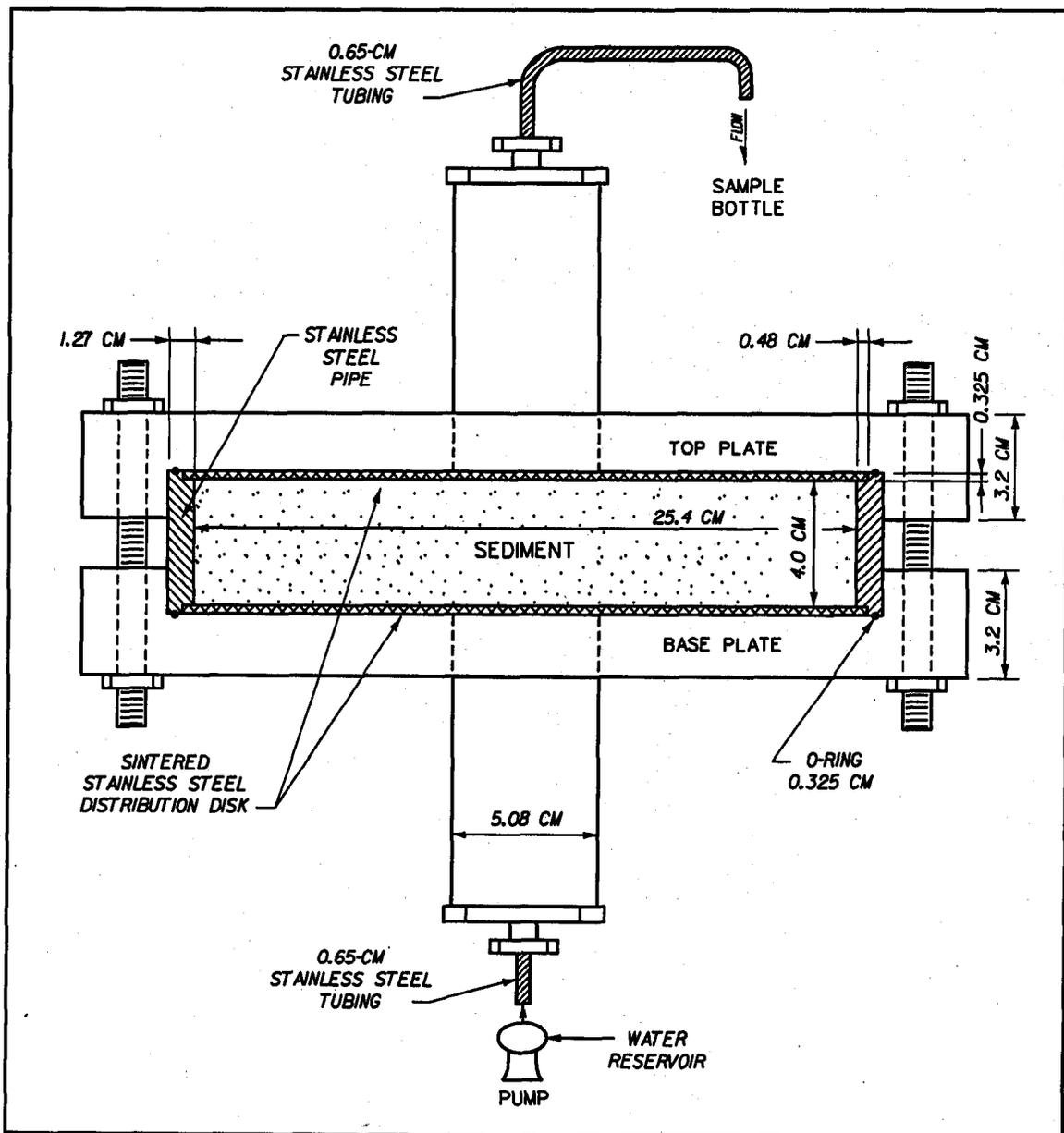


Figure 18. Improved column leaching apparatus for sediment

or less. By reducing the distance water has to travel, more pore volumes can be eluted in a given period of time for the same pore water velocities used in previous studies.

In order to provide the sample volume needed for chemical analysis at fractional pore volumes, the flow-through area was increased. The diameter selected for the improved column design is 25 cm. This diameter provides sufficient sample volume for chemical analysis of fractional pore volumes (Myers, Gambrell, and Tittlebaum 1991). As a consequence of reducing length and increasing diameter, the improved column leaching apparatus is a thin-layer column resembling a pancake. Side-wall effects were also

considered in selecting the diameter for the improved column design (Myers, Gambrell, and Tittlebaum 1991). Review of work by Montgomery (1978) on column settling tests for dredged material and the theoretical work of Sommerton and Wood (1988) showed that side-wall effects should be minimal for the improved column design; however, experiments are needed to substantiate that these effects are negligible.

The new column design also incorporates improvements in flow delivery and control. Up-flow mode of operation using a constant-volume pump provides better flow control than was possible using down-flow and pressure in the old design. In the old design, flow was controlled by manual adjustment of operating pressure. Because pressure adjustment could not be made continuously, flow typically fluctuated from the average flow calculated for an entire study period. Flow provided by a constant-volume pump will eliminate or significantly reduce variations in flow. This is an important advantage because the model equation (Equation 2) assumes flow is constant. Thus, the improved column design should more closely approximate model assumptions than the old design.

The distribution disks and concentric and radial grooves in the improved column design also should provide better experimental approximation of model assumptions. Equation 2 is a one-dimensional equation; that is, flow is in only one direction. With the old design, no collection gallery for the leachate exit was provided. Throughout most of the sediment profile, flow was probably one-dimensional, but near the column exit two-dimensional flow in the sediment was necessary. In the improved column design, two-dimensional flow will be restricted to grooves in the end-plates, and flow should be one-dimensional throughout the sediment profile.

Sample collection and preservation

In the column leaching tests conducted on Indiana Harbor, Everett Harbor, and New Bedford Harbor sediments, column leachate was collected and held in vessels for several weeks. Graduated cylinders were used so that the volume of leachate could be measured. Samples were transferred from the collection vessels to a filtration apparatus and filtered before placement into sample bottles. After filtration, samples for metals analysis were preserved with nitric acid. Samples for organic analysis were stored at 4 °C in amber glass bottles. These procedures have raised concerns about deterioration during extended holding periods in sample collection vessels and other aspects of sample collection and preservation (Myers, Gambrell, and Tittlebaum 1991).

Myers, Gambrell, and Tittlebaum (1991) recommended using an adaptation of the apparatus used to study the chemistry of soil and sediment suspension under controlled redox potential and pH conditions (Patrick, Williams, and Moraghan 1973) for collection and preservation of column leachates for metals analysis and use of a trapping solvent in a Neilson-Kryger steam distillation apparatus for collection and preservation of

organics. The recommended procedures are being investigated in current column leaching studies. In current column leaching studies using the improved column design, samples collected for metals analysis are preserved as collected by daily adjustment of pH to less than 2 using concentrated nitric acid. This procedure accommodates the recommendations of Myers, Gambrell, and Tittlebaum (1991) for preservation of metals. Samples for organic analysis are collected in glass jugs, and the entire contents of the glass jugs are extracted as part of the chemical analytical procedure. This procedure is intended to ensure that all of the analyte in the leachate sample is included in the analysis. In addition, experiments are being conducted using hexane as a trapping solvent in a Neilson-Kryger steam distillation apparatus for comparison with the jug extraction technique.

Continued research and development of preservation techniques for column leachates that take several days or weeks to collect is a priority need for full implementation of the integrated approach. Leachate from anaerobic sediment is highly perishable due to flocculation of iron in the presence of air. Acidification to pH less than 2 for metals should hold the iron in solution, but other factors, such as precipitation of base-extractable dissolved organic carbon, also need to be investigated.

5 Directions for Future Research

In the leaching studies conducted to date, each sediment has provided unique leachate quality data. Some general trends, however, are beginning to emerge related to redox conditions and sediment initial salinity. Sediment aged to simulate development of an aerobic crust tends to release metals, whereas anaerobic sediments tend to retain metals. The pH changes associated with oxidation of sediments are believed to be the underlying cause of increases in the mobility of metals. Furthermore, estuarine and freshwater sediments behave differently. Desorption isotherms for contaminants in freshwater sediments tend to follow classical sorption theory, whereas isotherms for estuarine sediments are unlike any previously reported. Sediment organic matter and the tendency to release sediment organic matter under changing ionic strength are believed to be the underlying factors causing differences between freshwater and estuarine sediment leaching studies.

Since redox potential has been shown to strongly influence leachate quality, continued work on pH changes and associated metals' releases with aging and crust development is necessary. Sediment geochemical factors influencing pH changes during development of an oxidized crust will continue to be investigated in sequential batch leach tests.

Since sediment organic matter and the tendency to release sediment organic matter has been shown to strongly affect contaminant desorption, detailed studies of the role of ionic strength, and other factors affecting release of sediment colloidal organic matter and the partitioning of organic contaminants between water, sediment, and colloidal phases, are needed. The roles of sediment organic matter and dissolved organic carbon in the release of contaminants from sediments will continue to be investigated in sequential batch and column leaching studies.

Use of laboratory data to predict contaminant losses associated with leaching at existing and planned CDFs will be investigated. This will require coupling contaminant desorption information from laboratory studies with a water balance model for CDFs. Coupling in this context represents a new effort which should, however, build up existing expertise for modeling water budgets. An existing water budget model, Hydrologic Evaluation of

Landfill Performance (HELP) model, can be coupled with data obtained from batch and column leach tests to estimate contaminant leaching from CDFs with time. Work is planned for modifying the HELP model computer code so that contaminant elution can be predicted for the hydrologic conditions at CDFs.

References

- Bahr, J. M., and Rubin, J. 1987. Direct comparison of kinetic and local equilibrium formulations for solute transport affected by surface reactions. *Water Resources Research*. 23(3):438-452.
- Brannon, J. M., Pennington, J. C., Myers, T. E., and Price, C. B. 1989. Factors affecting leachate quality. Environmental Effects of Dredging Notes, EEDP-02-11. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.
- Brannon, J. M., Myers, T. M., and Price, C. B. 1990. Factors affecting the behavior of metals in leachate. Environmental Effects of Dredging Notes, EEDP-02-13. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.
- Brannon, J. M., Myers, T. E., Gunnison, D., and Price, C. B. 1991. Nonconstant polychlorinated biphenyl partitioning in New Bedford Harbor sediment during sequential batch leaching. *Environmental Science and Technology*. 25(6):1082-1087.
- Brusseau, M. L., and Rao, P. S. C. 1989. Sorption nonideality during organic contaminant transport in porous media. *Critical Reviews in Environmental Control*. 19(1):33-99.
- Environmental Laboratory. 1987. Disposal alternatives for PCB-contaminated sediments from Indiana Harbor, Indiana, Volume II. Miscellaneous Paper EL-87-9. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.
- Garrett, B. C., Jackson, D. R., Schwartz, W. E., and Warner, J. S. 1984. Solid waste leaching procedure. SW-924. Washington, DC: U.S. Environmental Protection Agency.
- Hill, D. O., Myers, T. E., and Brannon, J. M. 1988. Development and application of techniques for predicting leachate quality in confined disposal facilities: Background and theory. Miscellaneous Paper D-88-1. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.

- Jennings, A. A., and Kirkner, J. J. 1984. Instantaneous equilibrium approximation analysis. *Journal of Hydraulic Engineering*. 110(12):1700-1717.
- Montgomery, R. L. 1978. Methodology for design of fine-grained dredged material containment areas for solids retention. Technical Report D-78-56. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.
- Myers, T. E., and Brannon, J. M. 1988a. New Bedford Harbor Superfund Project, Acushnet River Estuary engineering feasibility study of dredging and dredged material disposal alternatives; Report 5, Evaluation of leachate quality. Technical Report E-88-15. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.
- _____. 1988b. Synthesis of leaching research and workshop results. Environmental Effects of Dredging Technical Notes, EEDP-02-7. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.
- Myers, T. E. 1991. Polychlorinated biphenyl levels in the saginaw confined disposal facility during disposal operations, fall 1987. Miscellaneous Paper EL-91-4. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.
- Myers, T. E., Gambrell, R. P., and Tittlebaum, M. E. 1991. Design of an improved column leaching apparatus for sediments and dredged material. Miscellaneous Paper D-91-3. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.
- Palermo, M. R., Shafer, R. A., Brannon, J. M., Myers, T. E., Truitt, C. L., Zappi, M. E., Skogerboe, J. G., Sturgis, T. C., Wade, R., Gunnison, D., Griffin, D. M., Jr., Tatum, H., Portzer, S., and Adamec, S. A. 1989. Evaluation of dredged material disposal alternatives for U.S. Navy Homeport at Everett, Washington. Technical Report EL-89-1. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.
- Patrick, W. H., Jr., Williams, B. G., and Moraghan, J. T. 1973. A simple system for controlling redox potential and pH in soil suspensions. *Soil Science Society America Proceedings* 37:331-332.
- Rubin, J. 1983. Transport of reacting solutes in porous media: Relation between mathematical nature of problem formulation and chemical nature of problem. *Water Resources Research*. 19(3):1231-1252.
- Sommerton, C. W., and Wood, P. 1988. Effect of walls in modeling flow through porous media. *Journal of Hydraulic Engineering*. American Society of Civil Engineers. 114(12):1431-1448.
- Stumm, W., and Morgan, J. J. 1981. *Aquatic Chemistry*. New York: John Wiley and Sons.

Valocchi, A. J. 1985. Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soils. *Water Resources Research*. 21(6):808-820.