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Long-Term Effects of Dredging Operations Program

Leachate Testing and Evaluation for Estuarine Sediments

by *Tommy E. Myers, James M. Brannon, Barbara A. Tardy, WES
Dan M. Townsend, Louisiana State University*

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LONG-TERM EFFECTS
OF DREDGING OPERATIONS PROGRAM

Prepared for Headquarters, U.S. Army Corps of Engineers

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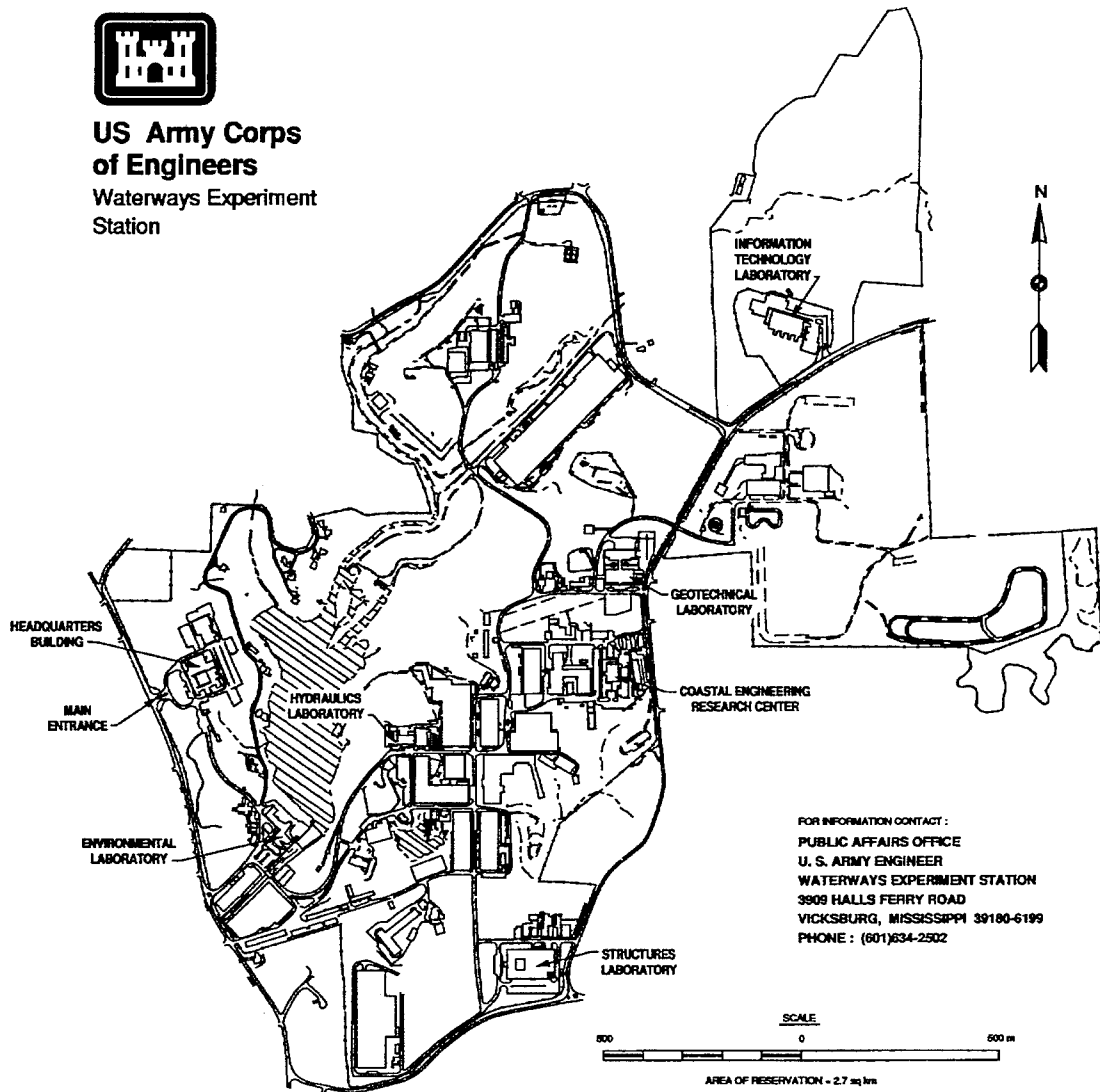
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Environmental Effects of Dredging Programs



Long-Term Effects of Dredging Operations Report Summary

Leachate Testing and Evaluation for Estuarine Sediments (TR D-96-1)

ISSUE: Confined disposal facilities are often used for disposal of contaminated dredged material. To fully evaluate the confined disposal facility alternative, potential leachate impacts should be considered. Research has shown that contaminant leaching from freshwater and estuarine sediments differs substantially. Laboratory procedures for leachate testing and evaluation for freshwater sediments are available. Procedures for estuarine sediments have not been previously available.

RESEARCH: Under the influence of decreasing ionic strength, contaminant release from estuarine sediments and dredged material is affected by destabilization of the sediment colloidal system. These effects are better predicted by column leach testing than by the sequential batch leach test previously recommended for freshwater sediments.

SUMMARY: This report describes procedures for conducting column leach tests and provides guidance on interpretation of results for estuarine sediments. Mathematical formulation of sorption descriptors that account for salt washout effects is also described.

AVAILABILITY OF REPORT: The report is available on Interlibrary Loan Service from the U.S. Army Engineer Waterways Experiment Station (WES) Library, 3909 Halls Ferry Road, Vicksburg, MS 39180-6199; telephone (601) 634-2355.

To purchase a copy, call the National Technical Information Service (NTIS) at (703) 487-4780. For help in identifying a title for sale, call (703) 487-4780. NTIS report numbers may also be requested from the WES librarians.

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Preface

The work reported herein was conducted for the Headquarters, U.S. Army Corps of Engineers (HQUSACE). 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 HQUSACE Technical Monitor for LEDO was Mr. Joe Wilson.

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1 Introduction

Background

Contaminated dredged material is often placed in confined disposal facilities (CDFs) designed and operated to control environmental impacts of the disposed material. A CDF is a diked enclosure having walls that retain dredged material solids. CDFs can be upland, nearshore (partially surrounded by water), and in-water (totally surrounded by water) (Figure 1). When contaminated dredged material is placed in a CDF, contaminants may be mobilized to form leachate that is transported to the site boundaries by seepage. Subsurface drainage and seepage through dikes may reach adjacent surface and groundwaters and act as a source of contamination. Since the contaminants in dredged material are primarily present as sorbed to sediment particles, leaching by water is a mechanism by which contaminant migration potentially occurs.

Leachate from dredged material placed in a CDF is produced by three potential sources: gravity drainage of the original pore water, infiltration of groundwater, and percolation of rainwater and snowmelt. Thus, leachate generation and transport in a CDF depend on site-specific hydrology, engineering controls at the disposal site, dredged material hydraulic conductivity, initial water content, and nature of contaminants. Immediately after dredging and disposal, dredged material is saturated (all voids are filled with water). As evaporation and seepage removes water from the voids, the amount of water stored and available for gravity drainage decreases. Regulatory compliance with the Clean Water Act requires consideration of the potential for ground and surface water contamination. To predict time-varying leachate flow, all these factors must be considered. Leachate quality must also be predicted in order to evaluate potential impacts. Because contaminant mobility in dredged materials is variable and highly site specific, laboratory testing is required to predict leachate quality.

A sequential batch leach test (SBLT) has been recommended for leachate testing of freshwater sediments (Brannon, Myers, and Tardy 1994). However, major differences in leaching characteristics of freshwater and estuarine sediment make it difficult to predict leachate quality for estuarine sediments using the SBLT.

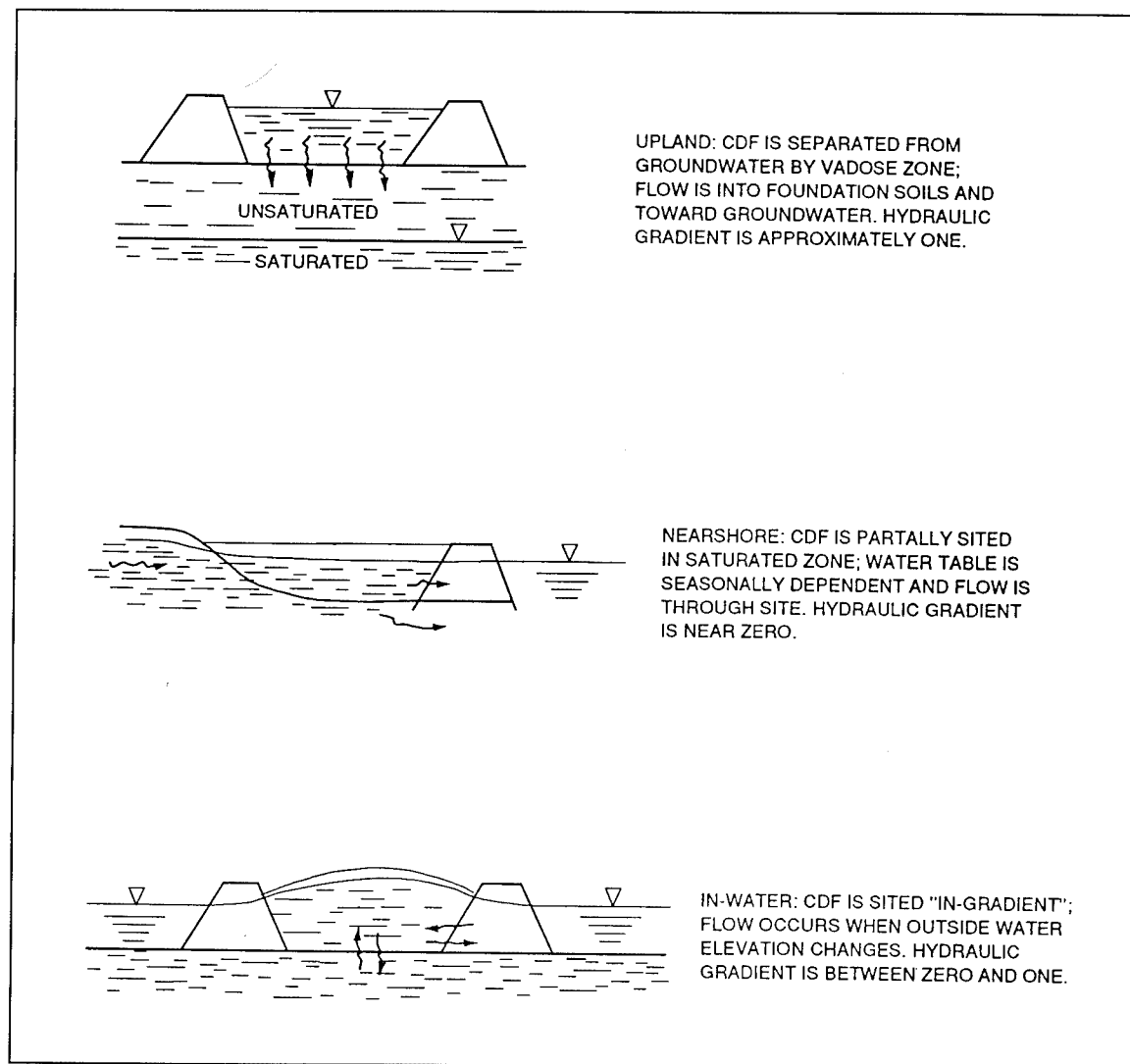


Figure 1. Contaminant migration pathway: leachate seepage

Scope

This report describes laboratory column leaching procedures for simulating leaching of estuarine dredged material disposed in CDFs. Guidance for using column data to predict leachate quality is also provided. Models for simulating leachate flow and leachate impacts on groundwater are not discussed here. Tools for estimating leachate flow and guidance for evaluating groundwater impacts are under development as part of the Automated Dredging and Disposal Alternatives Management System (ADDAMS).

2 Theoretical Basis for Leachate Quality Evaluations

This chapter briefly summarizes the theoretical framework used to develop the recommended test procedures. Explanations of leachate theory can be found elsewhere (Hill, Myers, and Brannon 1988; Myers, Brannon, and Price 1992; Brannon, Myers, and Tardy 1994).

Nature of the Problem

Contaminant migration via leachate seepage is a porous-medium contaminant transport problem (Figure 2). Leaching is defined as interphase transfer of contaminants from dredged material solids to the pore water 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, factors, and interactions is not presently possible. Instead, a lumped parameter, the distribution coefficient, is used to describe the distribution of contaminant between aqueous and solid phases.

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

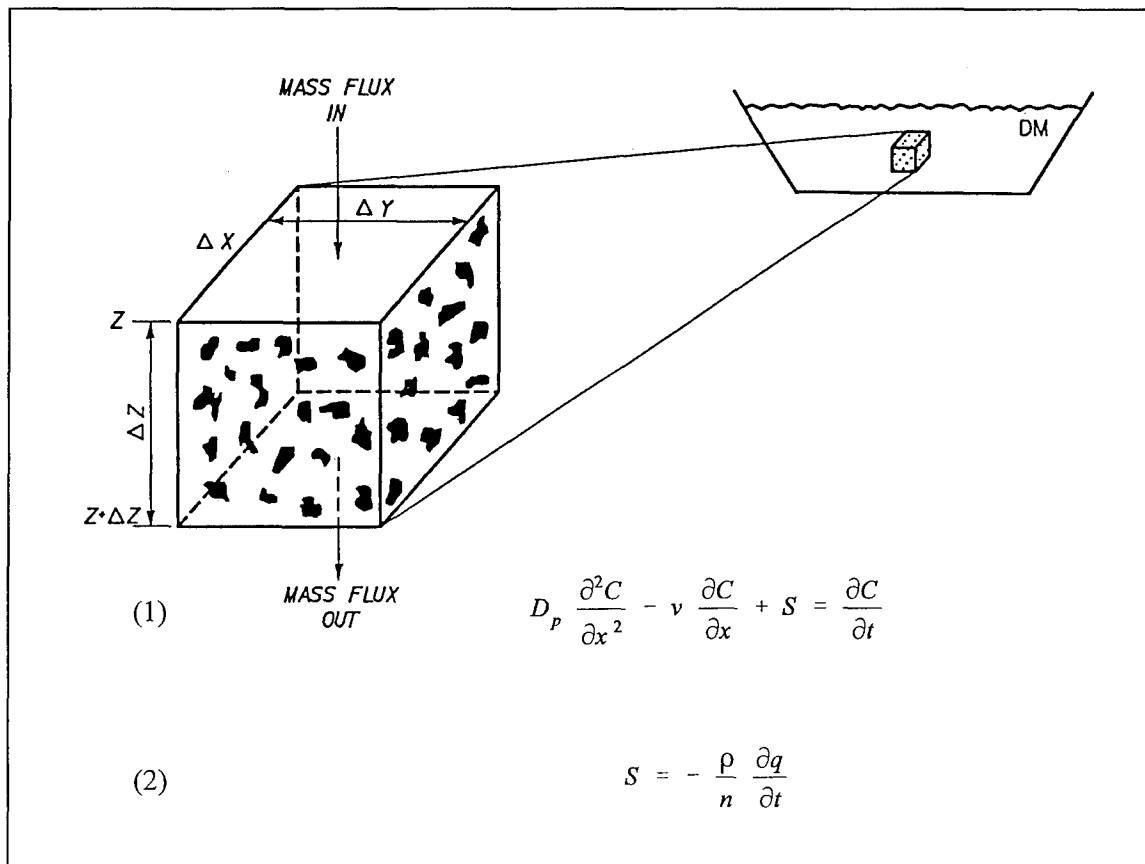


Figure 2. Mathematical model of dredged material leaching (from Hill, Myers, and Brannon 1988)

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, a pseudo steady state can be reached between dredged material solids and water if the water is moving past the solids slow enough, as discussed in a following section.

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

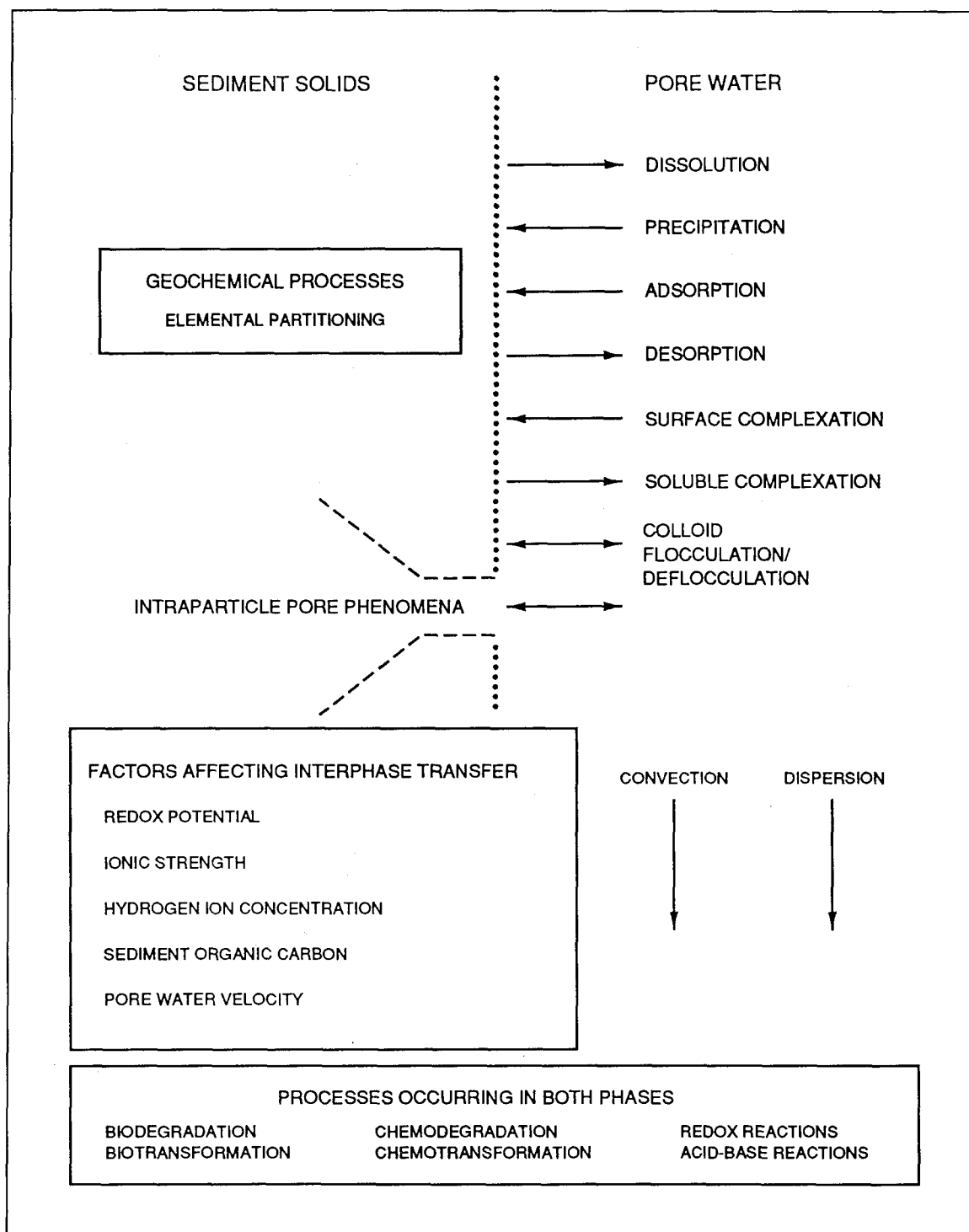


Figure 3. Interphase transfer processes and factors affecting interphase transfer processes

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 solid phase, kg

M_s = mass of solids, kg

M_{cw} = mass of contaminant in 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 solid phase at equilibrium, mg/kg

C = contaminant concentration in 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 a later section, K_d is affected by various factors (sediment oxidation status, pH, and ionic strength). 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 CDFs 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 materials are usually fine grained and have hydraulic conductivities in the range of 10^{-8} to 10^{-5} cm/sec. When the hydraulic conductivity is this low, pore water velocities are also low for the gradients normally encountered in CDFs. Consolidation with excess pore pressure can yield greater localized gradients at the bottom. For gradients near 1, 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. 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.

Oxidation Status of Sediment

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 may

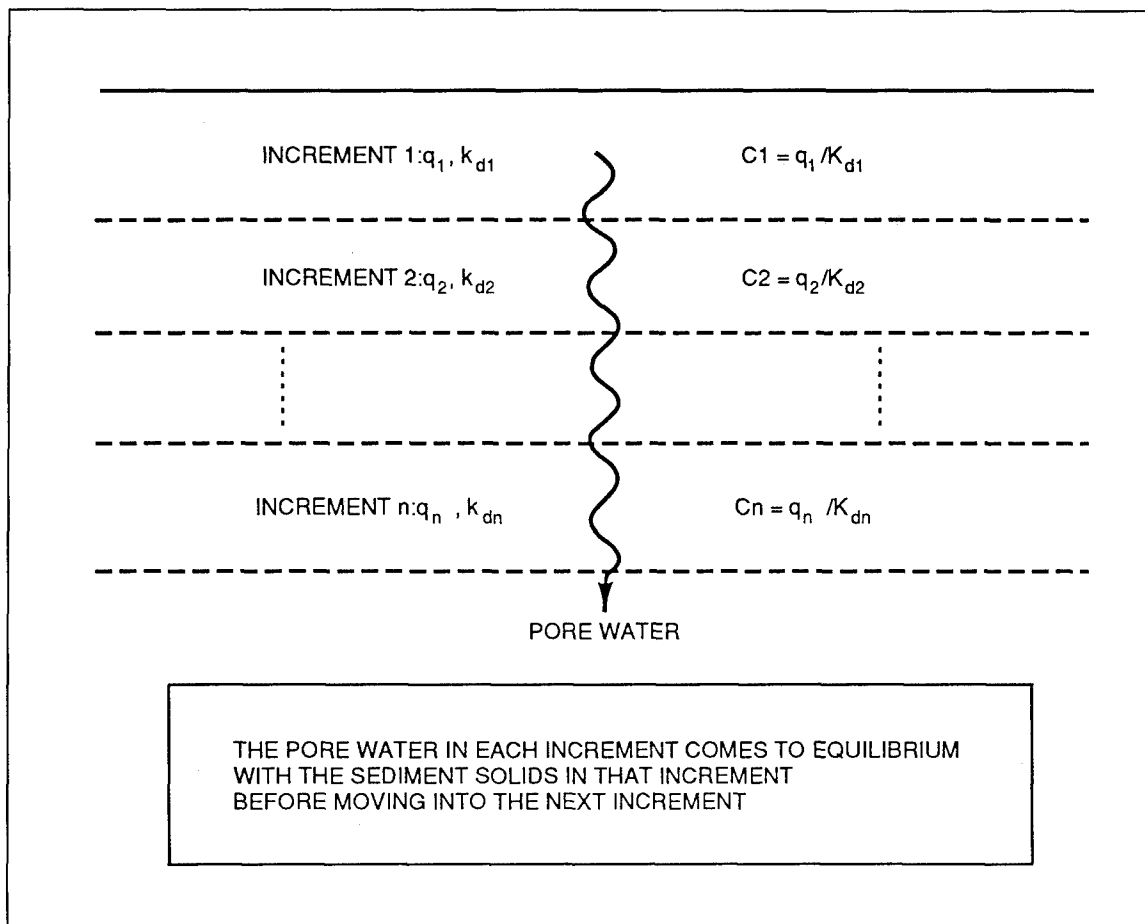


Figure 4. Illustration of local equilibrium assumption for leaching in a CDF

develop if the CDF dewateres by evaporation and seepage. Such an oxidized crust may eventually be several feet thick, but seldom represents a significant portion of the vertical profile for the typically fine-grained material in CDFs. The procedure described in this report simulates anaerobic leaching in the saturated zone of CDFs. An aerobic leaching procedure may be necessary if the full lift thickness is dewatered prior to placement of the next lift. Sequential batch leaching of aerobic, aged sediment can be used to simulate leaching of the surface crust in a CDF (Brannon, Myers, and Tardy 1994).

Ionic Strength

Sequential batch leaching of freshwater sediments usually yields desorption isotherms such as shown in Figure 5 (Brannon, Myers, and Tardy 1994). 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

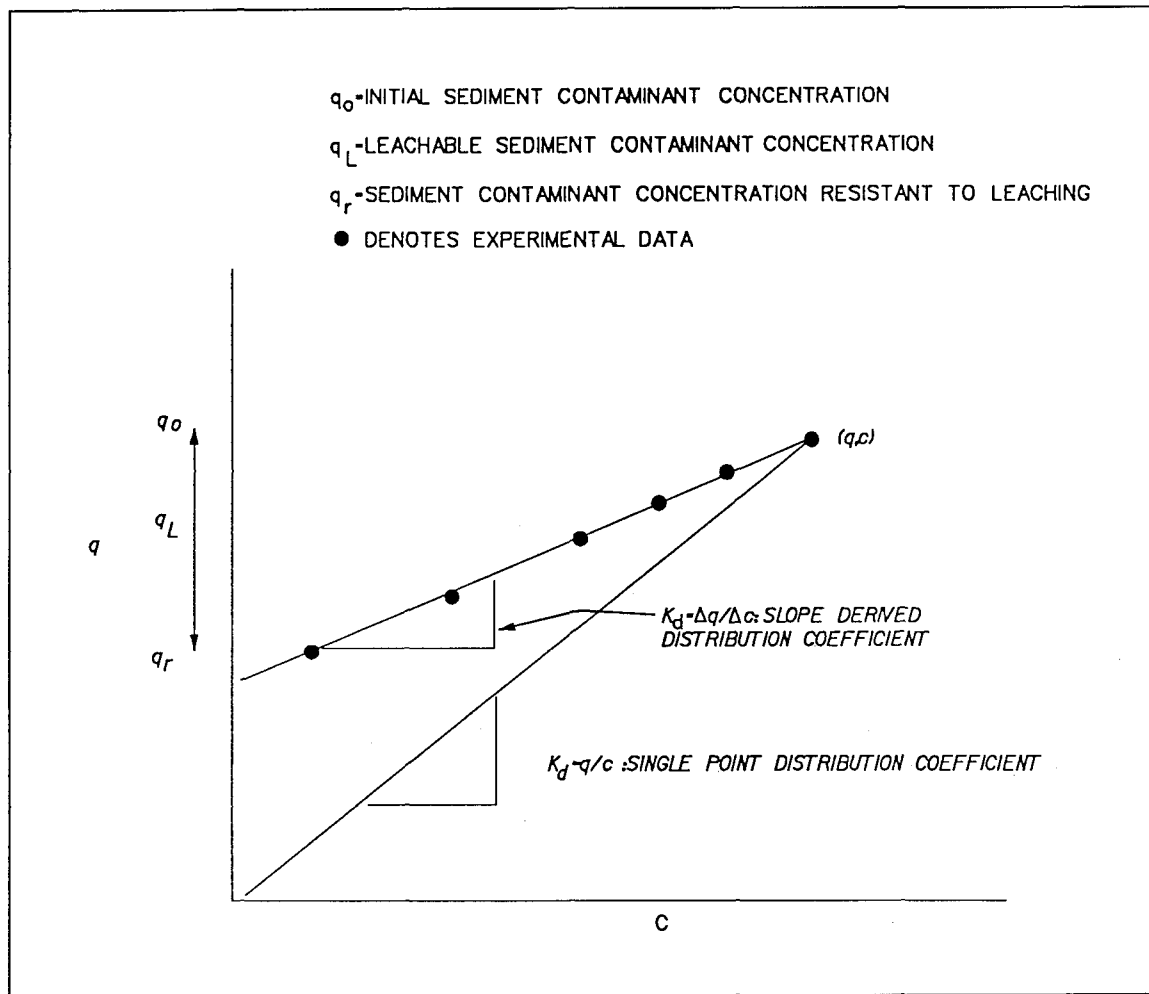


Figure 5. Desorption isotherms for slope-derived and single-point distribution coefficients

intercept the ordinate at some other point. The intercept indicates the amount of metal in geochemical phases that is resistant to aqueous leaching.

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

$$q = K_d C + q_r \quad (5)$$

where q_r = solid phase concentration resistant to leaching, mg/kg.

Differentiating Equation 5 with respect to time yields

$$\frac{\partial q}{\partial C} = K_d \quad (6)$$

The constancy of K_d during leaching of freshwater sediments and dredged materials is critical to the predication of leachate quality in CDFs from sequential batch leach test data (Brannon, Myers, and Tardy 1994).

Nonconstant distribution of contaminants between dredged material solids and water is commonly observed during leaching of estuarine sediments (Brannon et al. 1989; Brannon, Myers, and Price 1990; Brannon et al. 1991). Nonconstant contaminant partitioning yields batch isotherms 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 distribution coefficient portion of the desorption isotherm is related to elution of salt.

As salt is eluted from estuarine sediments, 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) and causes the double-layer thickness between colloids to increase. Flocculated colloidal matter becomes increasingly deflocculated and more easily entrained in flow. The overall effect is an increase in dissolved organic carbon (DOC) concentrations 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.

Colloid release from sediment particles under the influence of decreasing ionic strength is affected by the shear velocity at particle surfaces. The shear velocities developed by agitation during batch testing are infinitely large relative to the low shear velocities developed as water percolates through dredged material in a CDF. Colloidal mass release in a batch test, therefore, is not representative of colloidal mass release in a CDF under the influence of decreasing ionic strength. In addition, batch testing requires a liquid-solids separation step that alters the size distribution of colloids that are included in the dissolved phase. Thus, in a batch test, neither the mass nor size distribution of colloidal release to pore waters in a CDF are properly represented. For these reasons, it is difficult to couple results from sequential batch leaching with porous media fluid mechanics (advection and dispersion) and from this coupling predict leachate quality.

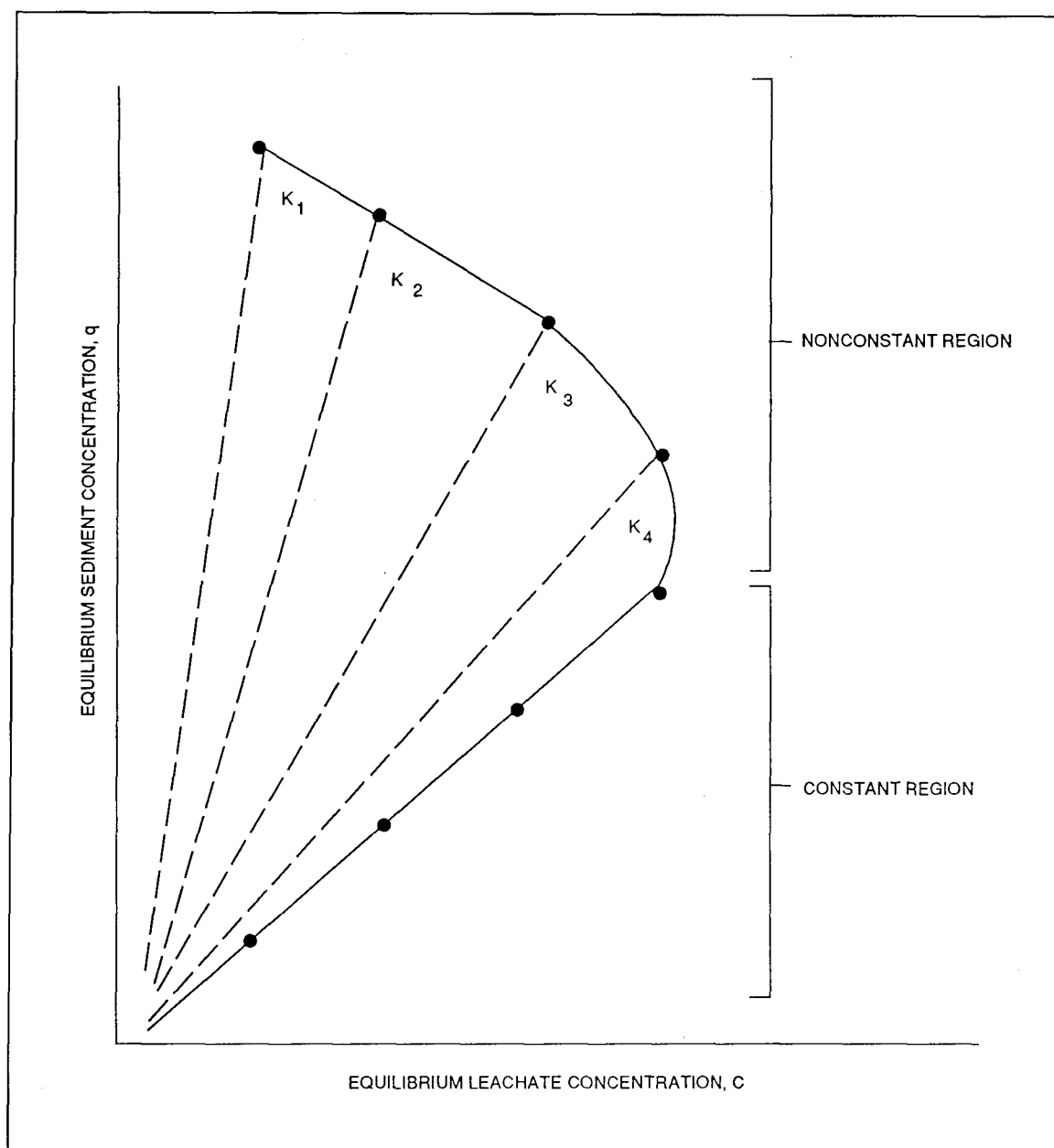


Figure 6. Desorption isotherm illustrating nonconstant and constant partitioning

3 Recommended Column Leach Tests

Column leach tests serve as laboratory-scale physical models of contaminant elution from dredged material that include advection-dispersion, colloid release, and other mass transfer effects.

Leaching Column

A divided flow permeameter was used in many of the early leaching studies with dredged materials (Environmental Laboratory 1987; Myers and Brannon 1988a; Palermo et al. 1989). Problems with the apparatus, primarily the extended time needed to elute the number of pore volumes necessary for leachate evaluation and the potential for sample deterioration during collection (Myers and Brannon 1988b), prompted redesign of the column apparatus. The improved column design (Figure 7) (Myers, Gambrell, and Tittlebaum 1991) is being used in current column leaching studies and is recommended for use where column studies are required. A brief description of the thin-layer column is given in the following paragraphs.

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 10^{-5} cm/sec 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 25.4 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

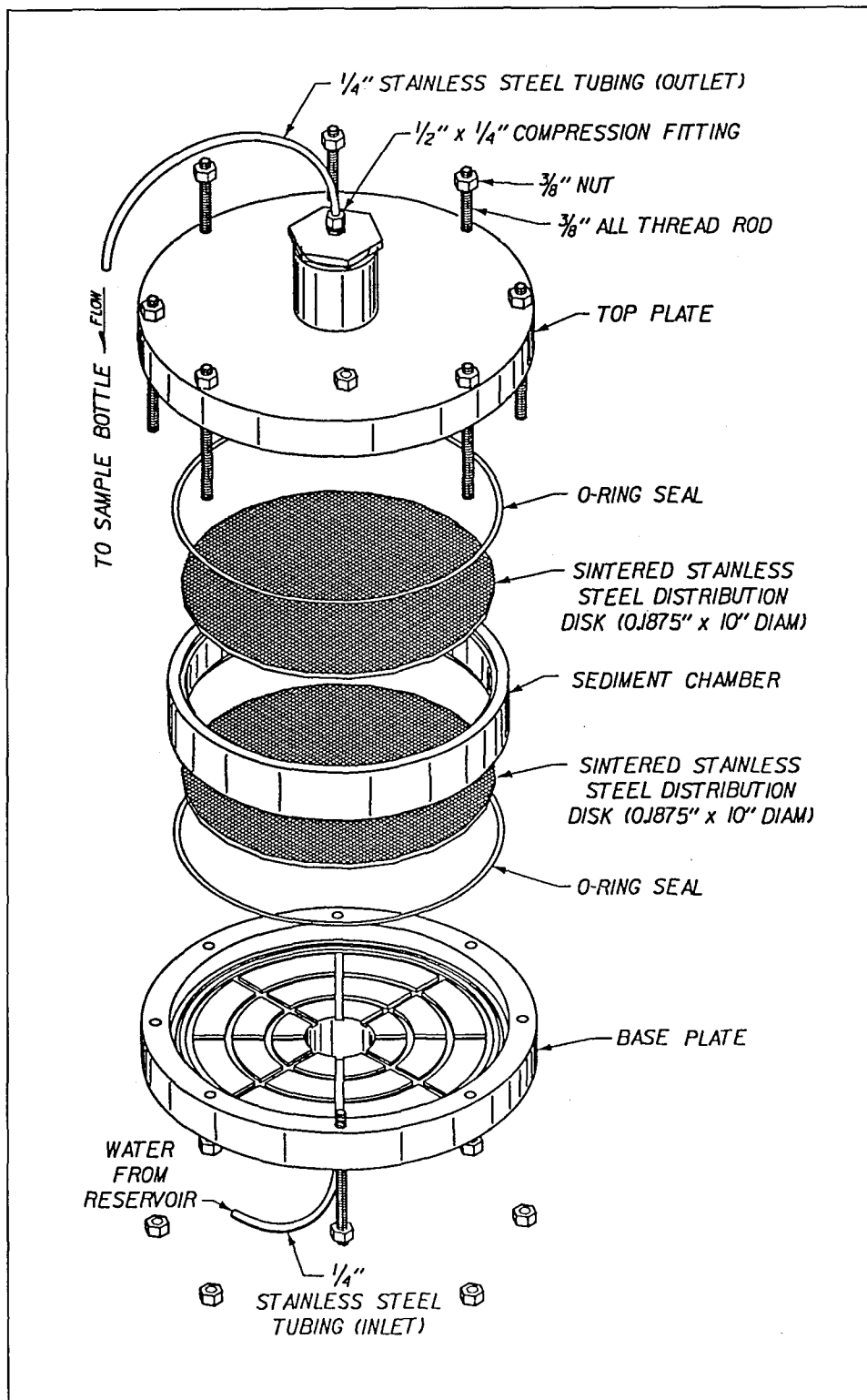


Figure 7. Thin-layer column

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.

The new column design also incorporates improvements in flow delivery and control. Upflow mode of operation using a constant-volume pump provides better flow control than was possible using downflow 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 fluctuated widely from the average flow calculated for an entire study period. Flow provided by a constant-volume pump eliminates or significantly reduces 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 the concentric and radial grooves in the improved column design also improve 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 is restricted to grooves in the end-plates, and flow is one dimensional throughout the sediment profile.

Procedures

Column loading

Loading should be conducted to minimize introduction of voids and exposure to air. Sediments collected for leach testing are typically fluid and can be poured or spooned into columns. Sediments should not be dewatered and packed into columns. The supernate usually covering sediment collected and stored for a month or more prior to testing should not be decanted. The supernate is pore water released by consolidation. This type of sediment should be mixed (anaerobically) to return it to its original water content. Sediments collected by coring may have overlying site water in the core tube. This water should be siphoned or decanted before mixing. Details of the procedures used to load sediment leaching columns at the U.S. Army Engineer Waterways Experiment Station (WES) are described in Appendix A. Since there are probably several ways to load a sediment leaching column and obtain valid results, Appendix A describes one way, not the only way.

Leachant

In most navigation dredging projects, the CDF is exposed to the atmosphere (no cap). Precipitation as rain and snow are long-term sources of low ionic-strength water at these sites. Adjustment of leachant pH and acidity to stimulate acid rain are not necessary for several reasons. One, sediment has tremendous buffering capacity. Two, low pH conditions often naturally exist in the surface crust of estuarine dredged materials. The low pH water leaving the crust and entering the anaerobic zone is quickly neutralized in the anaerobic zone. Groundwater that moves from upland areas is also low in ionic strength compared with estuarine dredged material. For these reasons, deaired, distilled-deionized water is recommended for simulating leaching in the anaerobic zone of a CDF containing estuarine dredged material.

In some projects, such as sediment remediation projects, the CDF may be designed to minimize inflow of low ionic-strength waters. If low ionic-strength waters will not be a major source of water for generating leachate in estuarine dredged material, a leachant that characterizes the primary source of water is appropriate. If this source of water has an ionic strength similar to the pore water of the sediment, the appropriate leach test to conduct is the SBLT (Appendix G) using a leachant formulated to represent the water that is anticipated to leach the disposed dredged material.

Flow

Column testing should be conducted in upflow mode using constant volume pumps set to deliver average pore water velocities of 1×10^{-5} cm/sec or less. Higher average pore water velocities should be avoided, as these velocities are not representative of conditions in CDFs containing fine-grain dredged material. Maximum acceptable flow is given by

$$Q = \frac{\left[10^{-5} \frac{\text{cm}}{\text{sec}} \right] \left[\frac{\pi(25.4\text{cm})^2}{4} \right]}{n} \quad (7)$$

where Q is flow in cm^3/sec , and n is effective porosity. Since the sediment is saturated with water, water content and specific gravity can be used to calculate total porosity. Effective porosity can be determined from tracer studies discussed later. In sediment column leaching studies, the effective porosity is usually 70 to 100 percent of the total porosity. Normally, the target flow is only approximately achieved. Flows lower than the maximum extend the leaching time, but do not compromise the results. Higher flows should be avoided unless justified by existing or anticipated site conditions. Elution of thirty (30) pore volumes is recommended in order to clearly define contaminant concentration peaks. Sediment pore volume is the volume of the leaching chamber times effective porosity. Sample volumes should be measured as

samples are collected and used to keep track of the number of pore volumes eluted.

Sample collection and handling

Column leachate samples should not be filtered. Sample collection and handling procedures should be coordinated with the analyzing laboratory. The procedures described in Appendixes B, C, and D for sample collection and handling were developed specifically for sample analysis by the Environmental Chemistry Branch at WES. Depending on the analytical techniques used, sample handling procedures different from those in Appendixes B, C, and D may be needed. Separate columns for metals and organics are recommended, as the sample volumes, types of sample containers, and preservation and handling techniques are usually different.

Elution of electrical conductivity (EC) and total organic carbon (TOC) should be measured for each estuarine sediment leaching column. These are important parameters that govern contaminant elution from estuarine sediment. Specific procedures for TOC analysis are described in Appendix H.

Tracer tests

Tracer tests are used to determine effective porosity and obtain dispersion coefficients that account for hydrodynamic mixing in columns. These coefficients are needed if an advection-dispersion equation is used to model column contaminant elution curves. Tracer tests are not currently required since the model equation used to interpret data is a complete-mix model that does not include dispersion. Tracer tests have been conducted routinely at WES as part of estuarine sediment leaching studies and may be recommended in the future.

If tracer tests are conducted simultaneously with contaminant elution, bromide is the tracer of choice for estuarine sediments. Chloride can be used if tracer tests are conducted after contaminant elution (30 pore volumes). There are various ways to conduct tracer tests. Tracer can be introduced to the column either as an instantaneous slug or as a steady input concentration. The steady input concentration approach is, as a practical matter, easier to accomplish. Levenspiel (1972) describes tracer testing and interpretation of results in detail. Analytical procedures for chloride and bromide are described in Appendixes E and F, respectively. These procedures apply to analysis with specific ion electrodes. As there are several manufacturers of specific ion electrodes, manufacturer's directions should be followed.

4 Interpretation of Results

Information Provided by Column Leach Tests

Column leach tests are laboratory-based physical models of contaminant leaching in a CDF, designed to show leachate concentration (C) as a function of pore volumes eluted (T). Unlike freshwater sediment leaching, where maximum leachate contaminant concentrations occur at the beginning of leaching, estuarine sediment leaching yields maximum leachate contaminant concentrations after a number of pore volumes have been leached. This phenomenon is due to the release of colloids as ionic strength decreases. Since batch tests are unreliable predictors of colloid release, column tests are recommended. Column tests provide estimates of peak leachate contaminant concentration as well as estimates of the number of pore volumes needed to reach this peak.

Figure 8 shows the type of elution curves to expect when leaching estuarine sediment with deaired, distilled-deionized water. TOC and contaminant concentrations start out low in most cases and increase to a maximum value and then decrease. Electrical conductivity starts high and rapidly decreases. Peak concentrations observed during elution can be used to represent contaminant source input to a groundwater model.

The number of pore volumes required to reach the peak on contaminant elution curves can be used to estimate the time to reach maximum contaminant concentrations in a CDF. This time will depend on a number of site-specific factors that govern hydraulic flux. These factors include dredged material hydraulic conductivity, degree of saturation, and hydraulic gradients. A simple, but crude, method for estimating the field time to peak concentrations is as follows:

$$t_p = \frac{T_p L}{v_f} \quad (8)$$

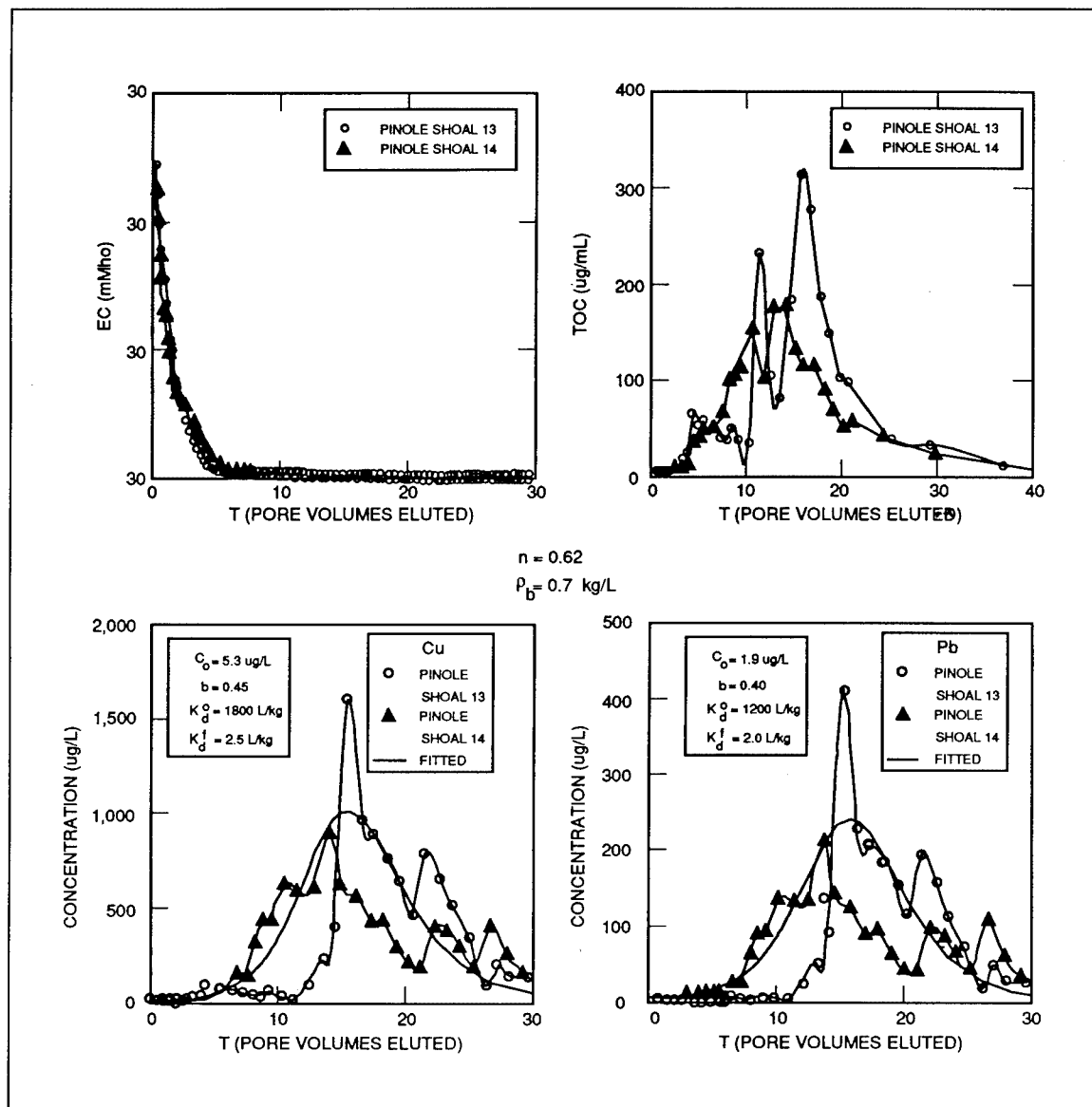


Figure 8. Typical column elution curves for estuarine sediment

where

t_p = time to peak concentrations at bottom of a CDF, years

T_p = pore volumes eluted to reach peak in laboratory leaching column

L = depth of fill in CDF, m

v_f = annual average pore water velocity in CDF, m/year

To use Equation 8, an estimate of the annual average pore water velocity is needed. In some cases, the annual average pore water velocity is

approximated by the hydraulic conductivity of the dredged material. Better estimates can be obtained by modeling water movement in the CDF. The Hydrologic Evaluation of Landfill Performance (HELP) model is applicable for some CDFs (Schroeder et al. 1994). Full groundwater modeling is an alternative, but requires allocation of substantial resources for model calibration.

In addition to modeling water movement, contaminant transport can be modeled. Contaminant transport modeling usually requires more than estimates of peak contaminant concentrations and pore volumes or time to peak concentrations. A mathematical formulation of the source term in Equation 1 is required. Interim formulations for the source term in Equation 1 that are applicable to leaching of estuarine dredged material are discussed in the following section.

Parameter Estimation

Development of transport models for contaminant leaching in CDFs involves modeling advection, dispersion, and desorption from dredged material solids. To develop the portion of the model dealing with desorption, a term in the governing equation that mathematically represents desorption must be formulated. An interim mathematical formulation of contaminant desorption from estuarine dredged material under the influence of decreasing ionic strength is described below.

As previously discussed, distribution coefficients for estuarine sediments are nonconstant due to destabilization of the colloid system by decreasing ionic strength. For nonconstant K_d , equilibrium-controlled sorption is written as

$$q = K_d(T) C \quad (9)$$

where $K_d(T)$ is some function of T , the number of pore volumes eluted. Since the nonconstant characteristic of K_d is related to salt elution (Brannon et al. 1991) and salt elution can be represented as a decaying exponential, $K_d(T)$ is written as

$$K_d(T) = K_d^f + (K_d^o - K_d^f) e^{(-\beta T)} \quad (10)$$

where

K_d^o = initial distribution coefficient, that is, before salt has been washed out, ℓ/kg

K_d^f = freshwater distribution coefficient, that is, after salt has been washed out, ℓ/kg

β = empirical coefficient, dimensionless

Substituting into Equation 9 from Equation 10 for $K_d(T)$ and taking the derivative with respect to T yields

$$\frac{dq}{dT} = - \left[C\beta \left[K_d^o - K_d^f \right] e^{(-\beta T)} \right] + \left[K_d^f + \left(K_d^o - K_d^f \right) e^{(-\beta T)} \right] \frac{dC}{dT} \quad (11)$$

Equations 10 and 11 above can be used to formulate transport models to account for the salt washout effect on contaminant distribution coefficients.

A complete mix model was developed for the thin-layer column to facilitate parameter estimation from column elution curves. This model includes non-constant partitioning but neglects spatially dependent advective and dispersive effects. The complete mix equation is

$$-C + \frac{\rho_b}{n} \frac{dq}{dT} = \frac{dC}{dT} \quad (12)$$

Substituting from Equation 11 for dq/dT yields

$$\frac{dC}{dT} = \left[\frac{\left[\frac{\beta \rho_b (K_d^o - K_d^f)}{n} e^{(-\beta T)} \right] - 1}{1 + \frac{\rho_b}{n} \left[K_d^f + (K_d^o - K_d^f) e^{(-\beta T)} \right]} \right] C \quad (13)$$

For the initial condition of $C(0) = C_o$, the solution of Equation 13 is

$$\frac{C}{C_o} = e^{\left(\left[\frac{A}{\beta D} + \frac{1}{\beta B} \right] \ln(B+D) - \frac{T}{B} - \left[\frac{A}{\beta D} + \frac{1}{\beta B} \right] \ln(B + D e^{(-\beta T)}) \right)} \quad (14)$$

where

$$A = \beta \rho_b (K_d^o - K_d^f)/n$$

$$B = 1 + (\rho_b K_d^f)/n$$

$$D = \rho_b (K_d^o - K_d^f)/n$$

The complicated appearance of Equation 14 is somewhat misleading. To predict contaminant concentration (C), as a function of pore volumes eluted (T), only three coefficients are needed in addition to initial pore water contaminant concentration, sediment water content, and sediment specific gravity. Initial leachate concentration can be estimated from column data or interstitial water measurements. The three adjustable parameters, β , K_d^o , and K_d^f , are obtained by curve fitting.

Figure 8 shows electrical conductivity, TOC, copper, and lead column elution curves for an estuarine sediment from San Francisco Bay. The observed data for duplicate columns are indicated by symbols. The fitted lines (no symbols) were obtained by trial and error using Equation 14 and porosity and bulk density values of 0.62 and 0.7 kg/ ℓ , respectively.

Although Equation 14 is simple in terms of column hydraulics, the equation has merit. This equation predicts increasing leachate contaminant concentrations in column leach tests as estuarine sediments are leached with fresh water. The equation also predicts occurrence of a peak value followed by a declining trend in leachate contaminant concentrations. These are the trends observed in SBLT and column leach tests for estuarine sediments. In addition, parameters needed for contaminant transport modeling can be obtained by fitting the equation to column data.

5 Conclusions

A thin-layer, column leach test has been developed to simulate contaminant leaching in CDFs. This test is recommended for leachate testing of estuarine sediments that are dredged and disposed in CDFs for which the primary source of water for leaching is low in ionic strength relative to the dredged material initial pore water ionic strength. Leaching of estuarine sediments and dredged materials with low-ionic strength water results in destabilization of the colloidal system as salt is washed out. Colloids are released and, along with the colloids, colloid-bound contaminants.

Elution curves obtained from thin-layer column leach tests simulate the salt washout effects to be expected in CDFs. From the elution curves, source terms for estuarine sediment leaching from a CDF can be evaluated, and predictions of contaminant concentration as a function of pore volumes eluted can be made.

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Appendix A

Thin-Layer Column Leach Apparatus Assembly and Loading

Scope

This standard operating procedure instructs the user on procedures for assembling, loading, and maintaining column leach apparatus. Shop drawings for fabricating the apparatus are provided in Figure A1.

Summary of Procedure

Contaminated sediment is mixed, weighed, and loaded into the column leach apparatus. Deoxygenated, distilled-deionized (DDI) water is introduced into the loaded column over an extended time interval. Water flow is controlled by a constant-volume flow pump. Leachate samples are collected at specified time intervals and are analyzed for specific parameters.

Materials and Apparatus

- Column leach apparatus (Figure A1).
- Kilogram weighing scale.
- Two 9/16-in. open-ended wrenches.
- One 10-in. crescent wrench.
- Mechanical mixer.
- Polyethylene beaker (5,000 ml).
- Stainless steel spatula, 12 in.
- Stainless steel spatula, 6 in.
- Polyethylene scoop.
- Paper towels.

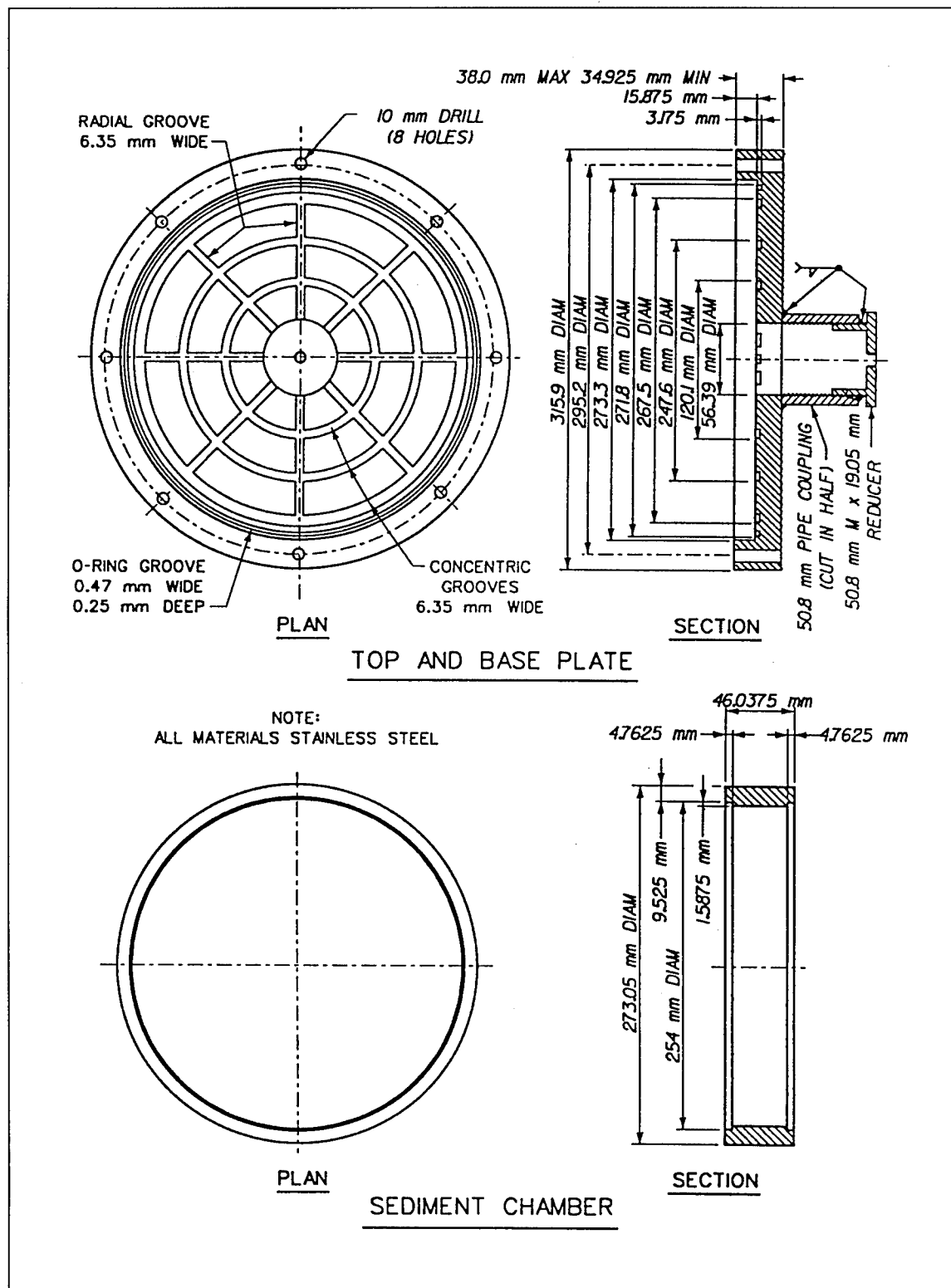


Figure A1. Shop drawing of thin-layer column

Glass fiber filter, 1 μm , 257-mm diam, binder free, (Gelman Type A/E or equivalent).
Polyethylene gloves.
Teflon tubing (ID 5/32 in., OD 1/4 in.).
Contaminated sediments.
Constant-volume metering pump (Example: Fluid Metering, Inc., Model #QG6-0-SSY and QG6-2-SSY).
Dial indicator kit (Example: Fluid Metering, Inc., Q485-1).
O-rings (ring diameter 10.75 in., OD 0.157 in.).
Stainless steel plug valve, (Example: Hoke #7312G4Y).
Stainless steel tubing, (OD 1/4 in., ID 1/8 in.).
Stainless steel tubing, (OD 1/8 in.).
Compression fittings, (1/4 by 1/2 in.) and (1/4 by 1/8 in.).
5-gal glass bottle.
Support table for columns.
Detergent.

Reagents

Deoxygenated, DDI water conforming to American Society for Testing and Materials (ASTM) Type II (ASTM D1193-77).

Procedure

Assemble the Fluid Metering Pump, and Dial Indicator Kit according to manufacturer's instructions.

Clean the column parts with a liquid, nonionic, metal-free, detergent solution, rinse thoroughly with DDI water, and let dry.

Screw the nuts onto the bottom of the threaded rods and insert the rods through the column base plate. Place the base plate in the 3-in.-diam hole on the table.

Using 1/4- by 1/2-in. compression fittings, attach a 2-in. piece of 1/4-in. stainless steel tubing to the inlet of the base plate. (Note: Use 1/4- by 1/2-in. compression fittings to make all stainless steel/Teflon tubing/plug valve/fluid pump connections.)

Connect a stainless steel plug valve to the 2-in. piece of stainless steel tubing. Use a suitable length of 1/4-in. OD, Teflon tubing to connect the plug valve to the outlet side of the Fluid Metering Pump.

Attach a suitable length of 1/4-in. OD, Teflon tubing to the inlet side of the pump, and insert the opposite end of this tubing in a 5-gal glass bottle filled with deaired, DDI water. Securely cover the mouth of the bottle with parafilm.

Open the plug valve, and turn on the fluid pump. When the water level reaches the grooves inside the base plate, turn off the pump.

Place an O-ring inside the base plate making sure the O-ring is properly seated to avoid water leakage. Place a distribution disk in the base plate. Place a glass fiber filter on top of the distribution disk. Place the sediment chamber in the base plate, properly aligning it on top of the O-ring.

On a mechanical mixer, carefully mix the sediment. Mixing under an oxygen-free atmosphere is recommended.

Weigh the 5,000-ml beaker, spatula, and scoop. Use the scoop to transfer approximately 4 kg of sediment to the beaker. Record the total weight of the sediment, beaker, spatula, and scoop.

Slowly fill the sediment chamber with sediment from the beaker, while carefully avoiding entrapment of air bubbles. When the sediment is level with the top part of the sediment chamber, carefully smooth the surface of the sediment with the spatula. (Note: In order to properly seat the top distribution plate, clean the groove in the sediment chamber.)

Place a distribution plate on top of the sediment chamber. Place a glass fiber filter on top of the distribution plate. Wet the O-ring before placing it in the top groove of the sediment chamber.

Carefully place the top plate on the sediment chamber, aligning the plate with the threaded rods in the base plate. Tighten all nuts. Connect 1/4-in. stainless steel tubing to the outlet of the top plate.

Connect a suitable length of stainless steel or Teflon tubing to the outlet of the top plate. (Teflon is recommended for leaching of metals.)

Set the dial indicator to obtain the correct flow rate for experimental conditions. Turn on the fluid pump, carefully check all areas for leaks, and tighten connections if necessary.

Reweigh the beaker, spatula, scoop, and sediment remaining in the beaker. Determine the weight of sediment in the column leach apparatus, by difference, and record this weight.

Appendix B

Collection and Preservation of Column Leachate Samples for Total Metal, Chloride Ion, Total Organic Carbon, pH, and Elec- trical Conductivity Analyses

Scope

This procedure describes the collection and preservation of samples generated from leaching of sediment and dredged material in laboratory column leaching apparatus.

Summary of Procedure

Column leachate samples are collected at a prescribed frequency, preserved with acid to $\text{pH} < 2$, and stored at 4°C prior to metals, chloride ion, and total organic carbon (TOC) analyses. The pH and electrical conductivity are determined on discrete nonacidified samples.

Materials

Analytical balance.
pH paper.
Parafilm, minimum 4 in. in width.
Labeling tape.
pH meter.
Electrical conductivity meter.
Clamp, large.
Ring stand.

Pipetter.

Pipet tips: 1 ml, 5 ml.

Polyethylene stirring rods.

Polyethylene bottles: 60, 250, 500, 1,000 ml.

Note: All plasticware must be prewashed with a metal-free, nonionic detergent solution, rinsed, soaked in 1 + 1 nitric acid for 24 hr, and rerinsed in distilled-deionized (DDI) water.

Reagents

DDI water conforming to American Society of Testing and Materials (ASTM) Type II Water (ASTM D1193-77).

Ultrax nitric acid, concentrated (J. T. Baker).

Ultrax sulfuric acid, concentrated (J. T. Baker).

Procedure

Sample preservation

Place two strips of labeling tape on each polyethylene sample collection bottle. Consult the sample collection chart in Table B1, then pipette 0.5 ml DDI water and 0.5 ml concentrated Ultrax nitric acid per 100 ml of leachate sample for metal analysis into the polyethylene bottle. For TOC analysis, pipette 0.5 ml DDI water and 0.5 ml of concentrated Ultrax sulfuric acid into the collection bottle. Weigh the bottle and lid, and record this weight on one strip of labeling tape.

On the other strip of tape, label each collection vessel with the sediment identification, column leach apparatus number, sample number, and parameter code. Suggested parameter codes are M = metals, C = chloride, T = total organic carbon, and PE = pH and electrical conductivity.

Remove the lid, and securely cover each bottle with parafilm. Puncture a small hole in the center of the parafilm with a pipette tip.

Attach a large clamp to a ring stand, and secure the collection bottle to the clamp. Place the bottle under the column leach apparatus, tilting and elevating the bottle in such a manner that the end of the outlet tubing is in contact with the acid solution in the bottle. Tightly seal the parafilm around the outlet tubing.

Table B1 Sample Collection Chart		
Sample Number	Approximate Sample Size, g	
	(Metals)	(TOC)
1	250	100
2	250	100
3	250	100
4	250	100
5	250	100
6	250	100
7	500	250
8	500	250
9	500	250
10	500	250
11	500	250
12	500	250
13	500	250
14	500	250
15	500	250
16	500	250
17	500	250
18	500	250
19	500	250
20	1,000	500
21	1,000	500
22	1,000	500
23	1,000	500
24	1,000	500
25	1,000	500
26	1,000	1,000
27	1,000	1,000
29	1,000	1,000
30	1,000	1,000

Sample collection

Collect leachate samples at a prescribed frequency. Recommended frequency is provided in the sample collection chart listed in Table B1.

After collection, replace the lid, carefully mix the leachate sample, and reweigh. Determine the weight of sample collected, by difference, and record this weight.

Insert a polyethylene stirring rod in the sample, and check the pH of the sample with pH paper. If the pH of the sample is greater than 2, add concentrated Ultrex nitric acid in 0.1-ml increments until the pH is less than 2.

For chloride determination, weigh 40 g of leachate sample into a 60-ml polyethylene bottle. Label the bottle with the sediment identification, column leach apparatus number, sample number, and parameter code. Store samples at 4 °C.

After each metal/chloride and TOC leachate sample has been collected, place a labeled, preweighed 20-ml polyethylene bottle under the column outlet. Collect approximately 12 g of leachate. (Reweigh the bottle to determine the exact weight of leachate.) Check the pH and electrical conductivity of this sample on a pH meter and electrical conductivity meter.

Appendix C

Collection and Preservation of Column Leachate Samples for Analysis of Organic Constituents

Scope

This procedure describes collection and preservation techniques for samples generated from leaching of sediments and dredged materials in laboratory column leaching apparatus.

Summary of Procedure

Column leachate samples are collected in amber glass bottles, in a prescribed manner. The samples are stored at 4 °C, then analyzed for polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and other related organic constituents.

Materials

Analytical balance.

Labeling tape.

Fraction collector, with the capability of time-based sample collection in seconds or minutes (Example: Eldex Laboratories, Inc., Model UP-1A).

Silicone tubing, plasticizer-free, additive-free (1/8-in. ID by 1/4-in. OD and 1/4-in. ID by 3/8-in. OD).

Amber glass bottles with Teflon-lined lids, precleaned to U.S. Environmental Protection Agency Level 1: 1,000 ml.

Reagents

Distilled-deionized (DDI) water conforming to American Society of Testing and Materials (ASTM) Type II (ASTM D1193-77).

Methanol, pesticide grade or equivalent.

Procedure

Preparation of fraction collector

Assemble the fraction collector according to manufacturer's instructions, and place it on the table near the column leach apparatus described in Appendix B. Attach a 12-in. section of silicone tubing (1/8-in. ID by 1/4-in. OD, cleaned with methanol and rinsed repeatedly with DDI water) to the outlet tubing on the column leach apparatus.

Attach 1/8-in. ID silicone tubing to the bottom of the glass tubes on the fraction collector. (This silicone tubing will be later connected to 1/8-in. stainless steel tubing inserted in lids used to cover the amber bottles during sample collection.)

Remove the lids from two 1-ℓ amber bottles. Drill four 1/8-in.-diam. holes in each lid. Insert pieces of 1/8-in. stainless steel tubing, equal to the height of the amber glass bottle (plus about 2 in.) through each hole.

Sample collection

Place a strip of labeling tape on each amber sample collection bottle. Weigh the bottle and lid and record this weight on the tape.

Label each collection vessel with the sediment identification, column leach apparatus number, sample number, and parameter code. Suggested parameter codes are PAH = polycyclic aromatic hydrocarbons, PCB = polychlorinated biphenyls.

Remove the lids from the weighed bottle and replace them with the lids described above. Place the bottle on the base of the fraction collector. Connect the silicone tubing described above to the stainless steel tubing on top of the lids.

Set the time-based control module on the fraction collector to collect a minimum of 500 ml of leachate sample per collection vessel.

Sample preservation

After collection, place the original lid on each leachate sample and reweigh. Determine the weight of sample collected, by difference, and record this weight.

Immediately after collection, store samples at 4 °C.

Appendix D

Digestion of Samples for Total Metal Analysis

Scope

This digestion procedure is used to prepare aqueous leachate samples that may contain insoluble colloidal particulates for analysis by flame atomic absorption spectroscopy (FLAA) or inductively coupled plasma spectroscopy (ICP). The procedure is used to determine total metal content. (Reference SW-846 Method 3010, Test Methods for Evaluating Solid Waste, U.S. Environmental Protection Agency).

Summary of Test Method

Nitric acid is added to a specified volume of the sample. The sample is refluxed with additional portions of nitric acid until the digestate is clear or the color is stable. The sample is then refluxed with hydrochloric acid and brought up to volume. The digested sample is analyzed for cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc.

Materials and Apparatus

- Fume hood.
- Hot plate.
- Safety glasses and polyethylene gloves.
- Volumetric flasks, 100 ml.
- Qualitative filter paper (Whatman #40 or equivalent).
- Polyethylene bottles, 125 ml.
- Glass stirring rods.
- Glass filtering funnel.
- Teflon beaker covers.
- 250-ml Teflon beakers.

Pipetter.
Pipet tips.

Note: All glassware and plasticware must be prewashed, rinsed, soaked in 1:1 nitric acid, and rerinsed in DDI water.

Reagents

Ultrex nitric acid, concentrated (J. T. Baker).
Ultrex hydrochloric acid, concentrated (J. T. Baker).
Distilled-deionized (DDI) water conforming to American Society of Testing and Materials (ASTM) Type II Water (ASTM D1193-77).
1:1 nitric acid.

Digestion Procedure

Mix the aqueous leachate sample thoroughly. Pour a 100-ml aliquot into a 100-ml volumetric flask. Transfer the sample to a 250-ml Teflon beaker. Add 3 ml concentrated Ultrex nitric acid and partially cover the beaker with a Teflon beaker cover.

Place the beaker on a hot plate set at 95 °C. Cautiously evaporate the contents to < 10 ml, making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to evaporate to dryness.

Cool the beaker and add another 3-ml portion of nitric acid. Completely cover the beaker, return it to the hot plate, and allow the sample to reflux, gently.

Continue heating and adding additional acid in 3-ml increments until the digestion is complete, as evidenced by a light color or an unchanging color.

Cool the beaker and add 10 ml of 1:1 hydrochloric acid. Cover the beaker, and reflux for an additional 15 min to dissolve any precipitate or residue resulting from evaporation. Wash down the cover and walls of the beaker with small portions of DDI water.

Place a piece of filter paper in a filtering funnel. Prerinse the filter paper with 1:1 ultrex nitric acid and discard this rinsate.

Place a 100-ml volumetric flask under the filtering funnel. To remove silicates and other insoluble matter, filter the hot digested sample into the volumetric flask. Rinse the beaker with small portions of DDI water and pour this rinsate through the filter paper.

Let the sample cool to room temperature, then dilute to 100-ml volume with DDI water. Mix, then pour the sample into a prelabeled 125-ml polyethylene bottle.

Quality Control

For each analytical batch of samples processed, carry a blank consisting of 100 ml of DDI water through the entire digestion procedure.

With each set of samples, process a duplicate and spiked sample and a standard reference material.

Appendix E

Chloride Ion Determination by Ion-Selective Electrode

Scope

This test method covers the determination of chloride ion in aqueous leachate samples. Samples containing 2- to 1,000-mg/l chloride ion may be analyzed by this procedure. Samples containing higher concentrations of chloride ion may be analyzed after dilution of an appropriate aliquot of the sample.

Summary of Test Method

Chloride ion is measured potentiometrically using a chloride-ion-selective electrode in conjunction with a double junction, sleeve-type reference electrode. An equal volume of chloride ionic strength adjuster (CISA) is added to an equal volume of standard and sample. Potentials are measured on an ion-selective meter. (Reference American Society of Testing and Materials (ASTM) Method D 512-89.)

Interferences

The CISA minimizes interferences from up to 500-mg/l sulfide, 1,000-mg/l bromide or iodide, a hundredfold excess of cyanide over chloride, and 1,000-mg/l ammonia.

Materials and Apparatus

Ion-selective meter, (Example: Orion Model 720A).
Chloride-ion-selective electrode (Orion 9417B or equivalent).
Double-junction reference electrode (Orion 90-02 or equivalent).

Chloride-ion filling solutions (Outer chamber, Orion 900003 or equivalent;
Inner chamber, Orion 900002 or equivalent).

Magnetic stirrer.

Teflon-coated magnetic stir bars.

Magnetic stir bar retriever.

Analytical balance.

Oven.

Protective gloves.

1,000-ml volumetric flasks.

1,000-ml polyethylene jars.

30-ml glass beakers.

1-, 2-, 10-, 25-, 50-, and 100-ml volumetric pipets.

1,000-ml glass beaker.

Fume hood.

Reagents

Distilled-deionized (DDI) water conforming to ASTM Type II water (ASTM D1193-77, 1983).

Instrument performance check (IPC), (3,000-mg/l chloride). In a 1-ℓ volumetric flask, dissolve 6.31 g of reagent grade potassium chloride (dried for 1 hr at 500 °C) and dilute to volume with DDI water.

Quality control (QC) sample, (300-mg/l chloride.) Pipet 100 ml of the 3,000-mg/l chloride into a 1-ℓ volumetric flask and dilute to volume with DDI water.

CISA. Weigh 15.1 g of reagent grade sodium bromate (dried for 1 hr at 100 °C), and dissolve in 800 ml water. Pipet 75 ml of concentrated nitric acid. Stir well. Transfer to a 1-ℓ volumetric flask and dilute to volume with DDI water. Store CISA in a polyethylene bottle. (CAUTION: Sodium bromate is a strong oxidant and should be handled appropriately. Preparation and dilutions of CISA should be made in a fume hood.)

Chloride stock solution (1,000-mg/l chloride.) In a 1-ℓ volumetric flask, dissolve 1.648 g of reagent grade sodium chloride (dried for 1 hr at 600 °C) in DDI water and dilute to volume.

Chloride standard solutions (1-, 2-, 10-, 50-, 100-, and 500-mg/l chloride). Using volumetric pipets, transfer 1, 2, 10, 50, 100, and 500 ml of the 1,000-mg/l chloride stock solution into separate 1-ℓ volumetric flasks. Dilute each to 1 ℓ with DDI water.

Calibration Curve Preparation

Following the manufacturer's instructions, fill the inner and outer chamber of the double-junction reference electrode. Connect the electrodes to the ion-selective meter.

Pipet 10 ml of the 2-, 10-, 50-, 100-, 500-, and 1,000-mg/l chloride solutions in separate 30-ml beakers containing magnetic stirring bars. Add 10 ml of the CISA reagent. Stir each for 2 min magnetically.

Remove each beaker from the stirrer, retrieve the magnetic stir bars, and wait 30 ± 2 min before inserting the electrodes in each standard. Wait for a stable reading, then record the potential of each standard, in millivolts. Between each measurement, thoroughly clean the electrodes with DDI water.

Prepare a spreadsheet consisting of the logarithm of the standards prepared two steps above and corresponding millivolt values. Construct a standard calibration curve by plotting log concentration on the x-axis versus millivolt readings on the y-axis.

To determine the concentration of unknown samples, calculate the linear regression of concentration on the x-axis versus millivolt readings on the y-axis. Set up a formula that calculates x-intercept values from corresponding y values:

$$y = mX + b$$

$$mX + b = y$$

therefore

$$X = (y - b)/m$$

where

Y = known millivolt values

m = coefficient of X

b = constant

X = unknown concentration

Procedure for Measuring Samples

Place a magnetic stir bar in a 30-ml beaker with 10 ml of the sample and 10 ml of CISA reagent. Follow the instructions given in the second and third paragraphs under Calibration Curve Preparation above.

Calculate chloride concentration of the sample, in mg/ℓ, according to the last paragraph under Calibration Curve Preparation above.

If the chloride concentration is greater than 1,000 mg/ℓ, dilute an appropriate aliquot of the sample into a 100-ml volumetric flask with DDI water.

Pipet 10 ml of the diluted sample into a 30-ml beaker containing 10 ml of CISA into the beaker. Measure the sample according to the second and third paragraph under Calibration Curve Preparation above.

Calculate the concentration of the diluted sample as follows:

$$C = A \times B$$

where

C = concentration, mg/ℓ

A = calculated concentration value, mg/ℓ
(last paragraph under Calibration Curve Preparation above)

B = dilution ratio

Quality Control

Instrument performance check

Each time the ion-selective meter is operated, monitor performance by measuring the potential of the IPC. Do not add CISA to the IPC sample.

Quality control sample

Prior to analyzing samples, analyze the 300-mg/ℓ chloride quality control sample in the same manner as samples are analyzed.

Duplicates and spikes

After every 10th sample, analyze a duplicate and a spiked sample.

Standard reference material

Analyze a standard reference material with each batch of samples analyzed.

Contamination evaluation

Following the instructions given in this section, evaluate contamination each time a group of samples are analyzed.

Into a 30-ml beaker, pipet 10 ml DDI water and 10 ml CISA reagent. (Note: This solution is the reagent blank used for contamination evaluation of the reagents.)

Into another 30-ml beaker, pipet 10 ml of 1-mg/l chloride standard solution and 10 ml CISA reagent. Place a stir bar in each solution. Place each solution on the magnetic stirrer, stir for 2 min, remove the beakers from stirrer, and wait 30 ± 2 min.

Place the electrodes in the water/CISA solution. Record the millivolt reading. (This solution contains no added chloride, and the potential reading will not be very stable.)

Rinse the electrodes thoroughly, and place them in the 1-mg Chloride/CISA mixture. Wait 1 to 2 min, measure, and record the results in millivolts.

(NOTE: If the difference in readings between the water/CISA solution and the 1-mg/l chloride solution is less than 10 mV, the reagents are contaminated with chloride that will affect low-level concentrations. Uncontaminated reagents must be obtained.)

Appendix F

Bromide Ion Determination by Ion-Selective Electrode

Scope

This test method covers the determination of bromide ion in aqueous leachate samples. Samples containing 1 to 1,000 mg/l bromide may be analyzed by this procedure. Samples containing higher concentrations of bromide ion may be measured after dilution of an appropriate aliquot of the sample.

Summary of Test Method

Bromide ion is measured potentiometrically using a bromide-ion-selective electrode in conjunction with a single-junction, sleeve-type reference electrode. The electrodes are calibrated in bromide solutions of known concentrations. An ionic strength adjuster (ISA) is added to both standards and samples. Potentials, in millivolts, are measured on an ion-selective meter.

Interferences

Reference American Society of Testing and Materials (ASTM) D 1246-88.

Materials and Apparatus

Ion-selective electrode meter (Example: Orion Model 720A).
Bromide-ion-selective electrode (Orion 9435B or equivalent).
Single-junction sleeve-type reference electrode (Orion 90-01 or equivalent).
Single reference electrode filling solution (Orion 900001 or equivalent).
Ionic strength adjuster (Orion 940011 or equivalent).
Magnetic stirrer.
Teflon-coated magnetic stir bars.

Magnetic stir bar retriever.
Analytical balance.
Oven.
Polyethylene gloves.
1,000-ml volumetric flasks.
1,000-ml polyethylene jars.
30-ml glass beakers.
1/2-, 1-, 5-, 10-, 25-, 50-, and 100-ml volumetric pipets.

Reagents

Distilled-deionized (DDI) water conforming to ASTM Type II water (ASTM D1193-77).

Instrument performance check (IPC) sample, (4,000 mg/l bromide.)
Dissolve 5.1514 g of potassium bromide (dried for 1 hr at 500 °C) in DDI water in a 1-ℓ volumetric flask. Dilute to volume with DDI water.

Quality control (QC) sample, (400 mg/ℓ bromide.) Pipet 100 ml of 4,000-mg/ℓ bromide solution into a 1-ℓ volumetric flask and dilute to volume with DDI water.

Bromide stock solution, (1,000 mg/ℓ bromide.) In a 1-ℓ volumetric flask, dissolve 1.288 g of sodium bromide (dried for 1 hr at 500 °C) in DDI water and dilute to volume.

Bromide standard solutions: (1, 5, 10, 50, and 100 mg/ℓ bromide.)
Using volumetric pipets, transfer 1, 5, 10, 50, and 100 ml of the 1,000-mg/ℓ bromide stock solution into separate 1-ℓ volumetric flasks and dilute each to 1 ℓ with DDI water.

Preparation of Calibration Curve

Following the manufacturer's instructions, fill the outer chamber of the single-junction reference electrode with filling solution. Connect the electrodes to the ion-selective meter.

Pipet 25 ml each of 1, 5, 10, 50, 100 and 1,000-mg/ℓ bromide standard solutions into separate 30-ml beakers containing magnetic stir bars. Add 0.5 ml ISA reagent and stir magnetically for 2 min.

Remove the beakers from the stirrer, retrieve the stir bars, and wait 15 ± 2 min before inserting the electrodes in each standard. When the reading stabilizes, record the potential of each standard in millivolts. Between each measurement, thoroughly clean the electrodes with DDI water.

Prepare a spreadsheet of the data from the logarithms of the standards prepared as described two paragraphs above and corresponding millivolt values. Calculate regression data. Construct a standard calibration curve by plotting log concentration on the x-axis versus millivolt readings on the y-axis.

To determine the concentration of unknown samples, use the regression data to set up a formula that calculates x-intercept values from corresponding y values:

$$\begin{aligned}y &= mX + b \\mX + b &= y \\ \text{therefore} \\ X &= (y - b)/m\end{aligned}$$

where

y = known millivolt values

m = coefficient of x

b = constant

X = unknown concentration

Procedure for Assaying Samples

Pipet 25 ml of leachate sample into a 30-ml beaker. Add 0.5 ml of the ISA reagent and stir on a magnetic stirrer for 2 min.

Remove the beaker from the stirrer, wait 15 ± 2 min, then insert the electrodes in the beaker. Wait 1 to 2 min for the reading to stabilize, then record.

To determine the bromide concentration in the sample, refer to the last paragraph under Preparation of Calibration Curve.

If the bromide concentration is higher than 1,000 mg/l, dilute an appropriate aliquot of the sample into a 100-ml volumetric flask with DDI water.

Pipet 25 ml of the diluted sample into a 30-ml beaker. Add 0.5 ml of the ISA reagent. Measure the sample according to the second and third paragraphs in this section.

Calculate the concentration of the diluted sample as follows:

$$C, \text{ mg/l} = A \times B$$

where

C = concentration, mg/ℓ

A = calculated concentration value, mg/ℓ

B = dilution ratio

Quality Control

Instrument performance check

Each time the ion-selective meter is operated, monitor instrument performance by measuring the potential, in millivolts, of the 4,000-mg/ℓ bromide sample. Do not add ISA to the IPC sample.

Blank determination

Analyze a blank, daily.

Quality control sample

Prior to analyzing samples, analyze the 400-mg/ℓ bromide quality control sample in the same manner as samples are analyzed.

Duplicates and spikes

Analyze a duplicate and spiked sample after every 10th sample.

Standard reference material (SRM)

Analyze an SRM with each set of samples.

Appendix G

Anaerobic Sequential Batch Leach Test

Scope

This appendix provides the user with detailed guidance on the conduct of the anaerobic sequential batch leach test (SBLT).

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 section on recommended procedures. A relationship between q and C is needed to evaluate the source term S in the mathematical model shown in Figure 2 in the main text. The source term is obtained by using the chain rule as follows:

$$S = - \frac{\rho_b}{n} \frac{\partial q}{\partial t} = - \frac{\rho_b}{n} \frac{\partial q}{\partial C} \frac{\partial C}{\partial t} \quad (G1)$$

The term $\partial q / \partial C$ represents the functional dependence of leachate quality on contaminant levels in the dredged material solids. The SBLT provides 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 SBLTs for sediments (Environmental

Laboratory 1987; Myers and Brannon 1988b; Palermo et al. 1989; Brannon, Myers, and Price 1990; Myers, Brannon, and Price 1992).¹

Summary of Procedure

Sediment is prepared and loaded into centrifuge tubes under anaerobic conditions at a 4:1 water to sediment ratio, then sequentially leached for 24 hr with distilled-deionized (DDI) water. Leachate is separated from sediment by centrifugation, and the leachate is chemically analyzed. Fresh DDI water is added to the centrifuge tube to replace that removed, and the process is repeated a minimum of four complete cycles.

Materials and Apparatus

- 450-ml stainless steel centrifuge tubes for organic contaminants.
- 250-ml polycarbonate centrifuge tubes with leakproof caps for metals.
- Weighing scale with sufficient capacity to accurately weigh centrifuge bottle, cap, and added sediment and water.
- Glove box of sufficient size to contain centrifuge bottles, sediment, and scale.
- High-purity nitrogen gas.
- Vacuum source.
- Mechanical mixer.
- Stainless steel spatula.
- Paper towels.
- Glass fiber filter, 1 μm , 47-mm diam., binder free, (Gelman Type A/E or equivalent).
- Glass fiber prefilters, 4 μm , 47-mm diam., binder free, (Whatman Type GD/F or equivalent).
- Cellulose acetate filters, 0.45 μm , 47-mm diam., (Millipore or equivalent).
- Filtration manifolds for organics and metals.
- High-capacity tumbler.
- Muffle furnace.
- Oxygen meter.
- 1-l amber glass sample bottles for organic contaminants.
- 250-ml plastic sample bottles for metals.
- Contaminated sediment.

¹ References cited in this appendix are located at the end of the main text.

Reagents

Deoxygenated, DDI water conforming to American Society of Testing and Materials (ASTM) Type II (ASTM D1193-77).

Concentrated HCl.

Concentrated Ultrex HNO₃.

Procedure

For organic contaminant leaching, use clean stainless steel centrifuge tubes, stainless steel spatulas, and glass filtration apparatus according to instructions for analysis of organic contaminants in SW-846, Test Methods for Evaluating Solid Waste, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC 20460. Combust glass fiber filter, and prefilter at 400 °C for 15 min.

For metal contaminant leaching, use clean polycarbonate centrifuge tubes, stainless steel spatulas, and polycarbonate filtration apparatus according to instructions for metals analysis in SW-846.

Prepare forms and labels. Conduct percent solids determination on mixed sediment sample and calculate solids and water content and required weights of water and sediment to achieve a water to solids ratio of 4:1 (weight of pore water + weight of DDI water/dry weight of sediment).

Seal the glove box and, using alternate vacuum and nitrogen addition, purge and vent until the oxygen meter registers 0 percent. Ensure that a slight overpressure of nitrogen exists inside the glove box. This can be determined by observation of a slight expansion of the rubber gloves attached to the glove box.

Add all necessary equipment to the glove box through the airlock. Cycle as necessary to remove any residual oxygen.

In the glove box, remix the sediment to ensure uniformity. Place a centrifuge bottle with cap on the balance and record the weight. Tare the centrifuge bottle and cap and load with sediment to the desired weight. Record the weight of the sediment added. Tare the centrifuge bottle, cap, and added sediment and add DDI water to bring the final water to sediment ratio to 4:1. Wipe sediment from any surface that contacts the O-ring of the leakproof top. Record the weight of DDI water, then zero the balance and record the weight of bottle, cap, sediment, and leachwater. Bottles should be loaded such that pairs of bottles balance to within 2 g. For organic contaminants, multiple bottles may be required to obtain sufficient leachate (1 ℓ) for chemical analysis.

Ensure that all centrifuge bottles are sealed, then remove the bottles from the glove box and transfer them to a tumbler. Tumble the samples for 24 hr at a rate of 40 revolutions per minute. Record the time tumbling starts and stops.

Remove the centrifuge bottles from the tumbler and place paired bottles opposite one another in a refrigerated centrifuge. Centrifuge stainless steel tubes for organic contaminant analysis at $6,500 \times g$ for 30 min. Note: Stainless steel centrifuge tubes are heavy, limiting the speed of centrifugation. Leachates for metals are centrifuged at $9,000 \times g$.

Assemble the decontaminated filtration apparatus. For organic contaminants, the $4\text{-}\mu\text{m}$ prefilter is placed over the $1\text{-}\mu\text{m}$ glass fiber filter. Filter the samples, maintaining a nitrogen atmosphere over the samples while filtration is ongoing. Acidify leachate for organic analysis with 1 ml of concentrated HCl per liter of leachate to prevent iron precipitation and organic scavenging, then transfer sample to a precleaned, 1-*l* amber glass bottle. Bottles for analysis of organic contaminants should be filled to the top. For metals, much the same procedure is followed. Filter the sample through a $0.45\text{-}\mu\text{m}$ filter and acidify with 1 ml of concentrated Ultrex nitric acid per liter of leachate. Transfer leachate samples to plastic bottles for storage and analysis.

In the deoxygenated glove box, record the weight of the centrifuge bottle with lid and sediment after filtering. Repeat with remaining samples.

Add DDI water to the centrifuge tubes to bring them back to the same water to solids ratio of 4:1. Record the weight of bottle with lid, DDI water, and sediment. Repeat with remaining samples.

Tumble samples and centrifuge as described above. Repeat a minimum of four times.

Using DDI water, prepare and run a procedure blank according to the procedure described above for one cycle.

Using DDI water, prepare a laboratory blank.

Appendix H

Determination of Total Organic Carbon in Estuarine Leachate Samples



Environmental Effects of Dredging Technical Notes



Determination of Total Organic Carbon in Estuarine Leachate Samples

Purpose

This technical note describes an analytical procedure for determining total organic carbon (TOC) in multiphase leachate samples containing microparticulates, details the techniques used to obtain analytical results and ensure data validity, and presents performance statistics on accuracy, precision, and bias.

Background

Dredging operations of the U.S. Army Corps of Engineers may result in disposal of dredged material in a confined disposal facility (CDF). Dredged material may contain various types of inorganics (metals), oils, and organic contaminants. When placed in a CDF, dissolved organic matter and microparticulates may facilitate leaching of contaminants into surface water or groundwater. Column leach tests under development by the Corps of Engineers provide a controlled laboratory mechanism for simulating the leaching process in a CDF. Collection and evaluation of leachate samples provide quantitative information needed to assess potential water quality impacts of the confined disposal alternative.

Testing of estuarine leachate samples containing colloids and microparticulates requires special analytical techniques. A procedure detailing the determination of TOC concentration in estuarine leachate samples is described in this technical note.

Additional Information

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3909 Halls Ferry Road, Vicksburg, MS 39180-6199



the Environmental Effects of Dredging Programs, Dr. Robert M. Engler, (601) 634-3624.

Introduction

Distinct differences in leaching characteristics of freshwater and estuarine sediments have been observed and documented (Brannon and others 1991; Lee and others 1993a,b,c; Myers and Brannon 1993). Anaerobic leaching of freshwater sediments with distilled-deionized (DDI) water produces aqueous leachate samples relatively free of microparticulates (Brannon, Myers, and Price 1992). Conventional liquid injection procedures (American Public Health Association 1989, U.S. Environmental Protection Agency 1986) for TOC determination are analytically sound for these leachate samples.

Column leaching of estuarine sediments with DDI water initially produces microparticulate-free leachate samples. After leaching several pore volumes, leachate samples containing nonfilterable colloids and nonsettleable microparticulate matter are obtained (Lee and others 1993a,b,c). Analysis of these samples for metals and organic species using standard procedures presents no major obstacles. However, analysis of these samples for TOC using standard techniques has been subject to error due to the nonhomogeneity of the samples and the dispersion of TOC in both water and colloid phases.

Preliminary testing of estuarine leachate samples by a modified ampule method resulted in a fivefold increase in TOC over identical samples tested by standard liquid injection techniques. These highly disparate results indicate that quantitation of TOC in estuarine leachate samples by liquid injection techniques is problematic, and may yield erroneously low results. Separate analysis of liquid and microparticulate phases after filtration is an alternative. However, possible losses during filtration and the attendant problems associated with multiple sample analyses justify the development of an analytical technique for whole sample testing, that is, without microparticulate separation.

The TOC concentration in nonhomogeneous, aqueous-based, multiphased, estuarine leachate samples is more appropriately determined by the modified ampule method described in this technical note.

Sediment Leaching

Two estuarine sediments were tested in this study: Outer Oakland Harbor (Oakland, CA) and Pinole Shoal (Baldwin Harbor, California). Sediments were mechanically mixed under a nitrogen atmosphere, weighed, and loaded into the column leach apparatus described in Brannon, Myers, and Tardy (1994). Leaching tests were performed in duplicate for all sediments.

DDI water was transported to each column in an upflow mode. Water flow rates providing average pore water velocities of about 1×10^{-5} cm/sec were

controlled by constant-volume metering pumps. Leachate samples were collected at specified time intervals, weighed, preserved to $\text{pH} \leq 2$ with concentrated sulfuric acid, and stored as described in Brannon, Myers, and Tardy (1994). Sediment leaching generated 230 samples that were used to develop the modified ampule method described in the following section.

Sample Preparation

Five representative analytical subsamples were prepared by mixing each leachate sample on a magnetic stirrer. During mixing, 0.25- to 1.0-ml aliquots of the samples were transferred (using 10-ml pipet tips with a minimum opening of 3 mm) into tared, precombusted, 10-ml glass ampules and weighed on an analytical balance. Acidification of the analytical subsamples with 1 ml of 5-percent phosphoric acid was followed by addition of 2 ml of DDI water. After 30 min, 0.2 g potassium persulfate and 2 ml DDI water were added to the ampules. Removal of inorganic carbon from the samples was accomplished by placing the ampules on an Ampule Purging and Sealing Unit (Oceanographics International Corporation) and sparging with carbon-free oxygen at a rate of 60 ml/min for 6 min. After sealing, the ampules were placed in a digestion chamber at 105 to 115 °C for 30 min. Nonpurgeable organic carbon remaining in the sample was converted to carbon dioxide by the action of persulfate at the elevated temperature. Identical procedures were followed in the preparation of standards and quality control samples.

Preparation of Standards, Calibration Curve, and Quality Control Samples

A 1,000- $\mu\text{g}/\text{ml}$ carbon stock solution was prepared by dissolving 0.2128 g anhydrous potassium hydrogen phthalate in DDI water and diluting to volume in a 100-ml volumetric flask. Carbon standard solutions (5, 10, 20, 30, 40, 60, and 80 $\mu\text{g}/\text{ml}$ carbon) were prepared by pipetting 0.5, 1.0, 2.0, 3.0, 4.0, 6.0, and 8.0 ml carbon stock solution into separate 100-ml volumetric flasks and diluting to volume with DDI water. Carbon standard solutions (1-ml aliquots) were analyzed, and a calibration curve was constructed by plotting micrograms of carbon in the standards versus millivolt values from the instrument (Figure 1). The linear range of the instrument was established from the calibration curve. The linear range of the method was 5 to 80 $\mu\text{g}/\text{ml}$ carbon. Leachate samples exceeding the linear range were reanalyzed after subsequent weighing of a smaller subsample.

A 50- $\mu\text{g}/\text{ml}$ instrument calibration check standard (ICCS) was prepared by pipetting 5.0 ml Carbon Stock Solution into a 100-ml volumetric flask and diluting to volume with DDI water.

A quality control (QC) sample containing 40 $\mu\text{g}/\text{ml}$ carbon was prepared by dissolving 0.125 g tartaric acid in DDI water in a 1-L flask, then diluting to volume.

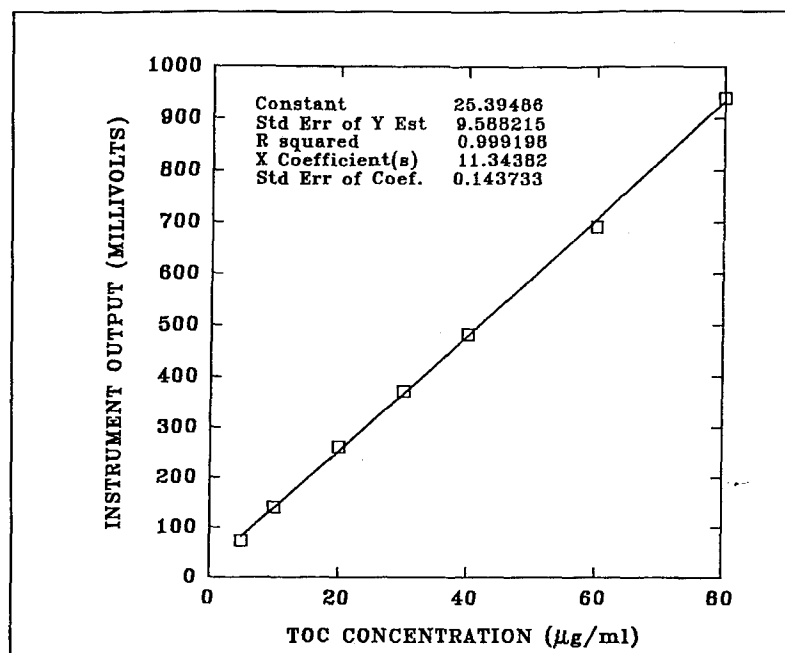


Figure 1. Total organic carbon standard calibration curve

A certified reference material (CRM) (No. 03042 from Environmental Resource Associates) was prepared as instructed in the Certificate of Analysis accompanying the CRM.

Quantitative Analysis of Standards and Samples

An Oceanographics International Corporation model 700 TOC Analyzer was used to quantitate the organic carbon content of samples and standards. After breakage of the ampules on the cutter assembly, the carbon dioxide formed was carried by an inert, nitrogen gas stream to the nondispersive infrared detector and measured. Carbon dioxide detected was a quantitative measurement of TOC in the sample.

Quality Control

Prior to analyzing samples, the instrument was calibrated using a DDI water blank and the 50-µg/ml ICCS. Instrument performance was monitored

throughout the analytical run, by periodically reanalyzing the ICCS. Prior to sample testing, a method blank and QC sample were analyzed. Precision measurements were obtained by replicate analysis of leachate samples at a frequency of 10 percent. Matrix interference was investigated by spiking samples with 0.25 or 0.5 ml of a 50- μ g/ml carbon standard solution at a 10-percent frequency rate. Method accuracy and bias were determined by analyzing the CRM at the beginning and end of each analytical run. Statistical computations (American Public Health Association 1989, Taylor 1987) were used in evaluating chemical measurement data.

Results and Discussion

Performance Characteristics

QC sample analysis results are shown in Figure 2. The center line represents the mean; the two outer lines represent the upper (UCL) and lower (LCL) control limits, or 99-percent confidence level corresponding to ± 3 standard deviations (SD). The two lines closest to the mean line are the upper (UWL) and lower (LWL) warning limits, or 95-percent confidence level (± 2 SD). The mean value for the quality control sample was 41.0 μ g/ml carbon with a standard deviation of 2.22 μ g/ml carbon. One data point is outside the lower warning limit. However, one analysis result outside the 95-percent confidence level and within the 99-percent level is normal, and is expected to occur approximately once in every 20 analyses. At the 99-percent confidence level, no data points are outside the upper or lower control limits. Nearly symmetrical distribution of data points around (19 above and 18 below) the mean value indicates absence of trending toward high or low bias results (Taylor 1987).

Replicate leachate sample analysis results were evaluated to determine method precision. In theory, replicate calculations based on the difference of two measurements (the range) cannot be less than zero since it is the absolute difference between two positive numbers (Dux 1990). In practice, since bias may represent both positive and negative interferences, expression of relative percent difference having positive and negative values permits evaluation of precision, bias, and data distribution.

Relative percent difference (RPD), shown in Figure 3, was calculated using the formula

$$\pm RPD = \frac{\text{Original result} - (\text{Replicate result})}{\text{Mean}} \times 100$$

All resulting data were within the 25 percent upper laboratory acceptance limit (ULAL) and -25 percent lower laboratory acceptance limit (LLAL). Precision calculated from the SD of the results of duplicate sample analyses was 4.5 μ g/ml.

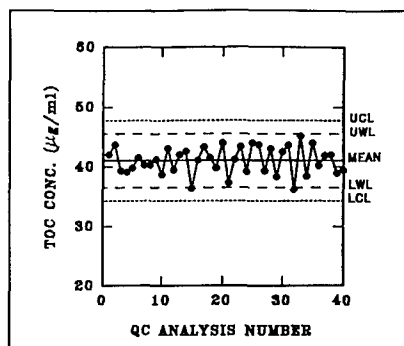


Figure 2. Quality control sample results

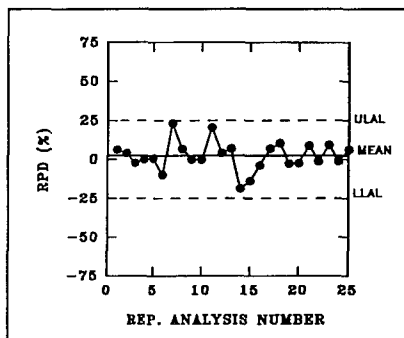


Figure 3. Replicate results for relative percent difference

Percent recovery of spiked samples is presented in Figure 4. Control lines correspond to the mean recovery (97.9 percent) and the ULAL and LLAL values of 125 and 75 percent, respectively. Absence of matrix effects was verified by spike recoveries all within the laboratory acceptance range of 75 to 125 percent, with no data outliers.

Results for the CRM analyzed with this batch of samples are shown in Figure 5. The center line represents the mean value; the outer lines correspond to the upper (UCV) and lower (LCV) control values recommended by the vendor. The mean value for the CRM was 66.6 µg/ml TOC compared with a certified mean value of 67.9 µg/ml with an LCV of 58 µg/ml and a UCV of 78 µg/ml. The standard deviation was 3.2 µg/ml, with a method bias of 1.3 µg/ml, single operator bias of 0.8 µg/ml, and net bias of 1.9 percent. Comparison of the results obtained using this method with the published values for the CRM

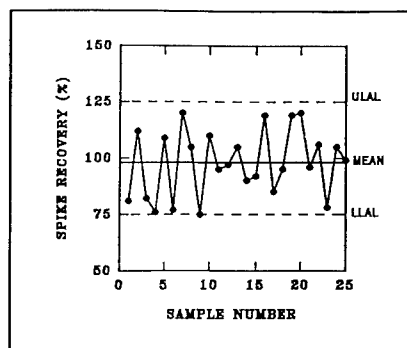


Figure 4. Spike recovery results

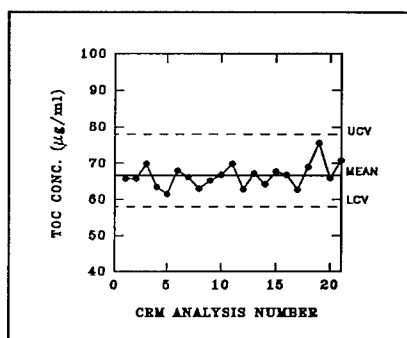


Figure 5. Analytical results for certified reference material

validates the analytical procedure. The CRM data confirm method accuracy and further authenticate the measurement process.

Application

Elution curves depicting TOC released during column leaching of Outer Oakland Harbor sediment with DDI water are shown in Figure 6. TOC concentrations in leachate steadily increased to peak concentrations and then tended to decline. These curves are typical of the elution behavior of contaminants in estuarine sediments when leached with DDI water (Lee and others 1993a,b,c). They show that initial leachate quality is not the worst quality that can be expected when estuarine dredged material is placed upland and leached with low-ionic strength water.

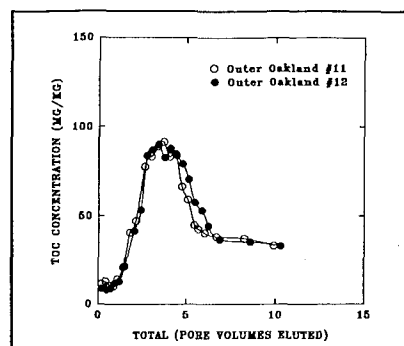


Figure 6. Total organic carbon elution curves

Companion analysis of contaminant concentrations and TOC was not possible in the previous studies by Lee and coworkers (1993a,b,c) because suitable analytical techniques were not available for TOC analysis of samples with significant amounts of nonsettleable microparticulates. Application of the analytical technique presented in this note shows that TOC elution generally correlates to the contaminant elution behavior previously reported and therefore may be instrumental in governing contaminant elution.

Conclusion

The test procedure described in this technical note can be used to make accurate and reproducible measurements of TOC concentrations in estuarine leachate samples. Acceptable bias, precision, and accuracy can be obtained with the procedure. Thus, this method eliminates the need to separately determine TOC in liquid and microparticulate phases of aqueous samples.

In addition to the analysis of leachate samples containing nonsettleable microparticulate matter, the analytical procedure described in this technical note may be applicable to determination of TOC in solid and semisolid materials containing moderate to large amounts of organic carbon. TOC determination in samples of this nature presently requires sample predrying and sieving, which may introduce errors resulting in unacceptable bias, accuracy, and precision results. The procedures described in this technical note eliminate these steps and could provide more accurate and precise results.

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13. ABSTRACT (Maximum 200 words) Contaminated dredged material is sometimes placed in confined disposal facilities (CDFs) where the potential for movement of contaminants to groundwater and surrounding surface water by leaching is an important environmental concern. Column leach tests have been developed as laboratory-scale physical models of contaminant leaching in a CDF that include advective-dispersive and other mass transfer effects. Column leach tests are recommended for predicting leachate quality in CDFs containing estuarine dredged material leached by low-ionic strength water. Under the influence of decreasing ionic strength, contaminant release from estuarine dredged material is complicated by destabilization of the sediment colloidal system. These effects are better predicted with the column leach test described in this report than with the sequential batch leach test previously recommended for leach testing of freshwater sediments. This report describes procedures for conducting column leach tests and provides guidance on interpretation of results for estuarine sediments. Mathematical formulation of sorption descriptors that account for salt washout effect is also described.				
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