

# Environmental Effects of Dredging Technical Notes



# Synopsis of Hamlet City Lake, North Carolina, and San Francisco Bay Area, California, Sediment Leaching Studies

# Purpose

This note summarizes results from six laboratory leaching studies conducted on contaminated sediments. Laboratory batch and column leach tests were conducted on sediments from Hamlet City Lake, Hamlet, North Carolina; Inner and Outer Oakland Harbor, Oakland, California; Santa Fe Channel (Richmond Harbor), Oakland; and West Richmond and Pinole Shoal reaches of the J. F. Baldwin Channel, Oakland. These studies were conducted for the U.S. Army Engineer Districts, Wilmington and San Francisco. Implications of the results for development of predictive techniques for leachate quality in confined disposal facilities (CDFs) are discussed.

# Background

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When contaminated dredged material is placed in CDFs, contaminants may be mobilized by leachate generation and seepage. Therefore, techniques are needed for predicting leachate quality in CDFs and evaluating potential impacts on ground and surface waters. The U.S. Army Corps of Engineers has initiated development of laboratory tests for predicting leachate quality in CDFs under the Long-term Effects of Dredging Operations Program. The current status of leachate testing and the recent application of leachate tests under development to six sediments are reviewed in this technical note.

# **Additional Information**

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# Sediments

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Sediments from Hamlet City Lake, Hamlet, North Carolina (Brannon, Myers and Price 1992), Oakland Harbor, Oakland, California (Lee and others 1993a), Santa Fe Channel, California (Lee and others 1993b), and J. F. Baldwin Channel, California (Lee and others 1993c) were collected in sufficient volume to conduct tests identified in the Decisionmaking Framework (Lee and others 1991) for evaluating dredged material confined disposal alternatives. Hamlet City Lake sediment is a freshwater sediment, and the San Francisco Bay area sediments are estuarine sediments. Sediment was homogenized after collection, and leachate tests were conducted on a subsample of the homogenized sediment. Information on sediment collection and handling, sediment physical and chemical characterization, and other tests conducted is available in the above-named references.

## **Batch Leach Tests**

The sequential batch leach test (SBLT) used in the Hamlet City Lake and San Francisco Bay area sediment leaching studies was essentially the same as the test used in previous studies (Environmental Laboratory 1987, Palermo and others 1989, and Myers and

Brannon 1988) and discussed in a previous note (Myers and Brannon 1991). Figure 1 shows a schematic of the general test procedure. Kinetic batch and liquid-solid ratio batch tests were also conducted in these studies. Details on SBLT, kinetic, and liquid-solid ratio test procedures are available in the references previously cited.



## **Column Leach Tests**

Column leach tests were conducted in thin-layer columns designed specifically for low-permeability sediments and dredged material (Myers, Gambrell, and Tittlebaum 1991, and Myers, Brannon, and Price 1992).

Figure 1. Schematic of WES sequential batch leach test

The studies summarized in this note were the first sediment leaching studies conducted with thin-layer columns. Figure 2 is a schematic of the thin-layer column.





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Previous studies (Environmental Laboratory 1987, Myers and Brannon 1988, and Palermo and others 1989) have shown that conventional column designs could not fully satisfy testing requirements for low-permeability sediments (Louisiana Water Resources Research Institute 1990). The major problem was the time required to elute a meaningful number of pore volumes without using pore-water velocities that grossly exceed field pore-water velocities. In most field situations, pore-water velocities in CDFs containing fine-grained dredged material are not likely to be greater than 10<sup>-5</sup> cm/sec. The thin-layer column shown in Figure 2 was designed as a laboratory-scale physical model of leaching in a CDF. This design minimizes wall effects, elutes 10 or more pore volumes in six months while holding pore-water velocities to 10<sup>-5</sup> cm/sec or less, and produces sufficient sample for chemical analysis without having to elute more than one pore volume (Myers, Gambrell, and Tittlebaum 1991).

#### **Evaluation of Test Procedures**

Kinetic batch tests on Hamlet City Lake and San Francisco Bay area sediments indicated that the shake time used in the SBLT (24 hr) is long enough for leachate contaminant concentrations to reach steady state. With the six studies discussed in this report and three previous studies (Environmental Laboratory 1987, Myers and Brannon 1988, and Palermo and others 1989), a database consisting of nine sediments and a wide variety of inorganic and organic contaminants has been developed on leachate contaminant concentration versus shake time. This expanding database continues to indicate that 24 hr of shaking is adequate.

The effect of liquid-solid ratio on batch leachate contaminant concentrations was investigated in these studies as in previous studies. Results continue to show that a 4/1 (mass/mass) liquid-solid ratio is probably the highest ratio than can be used without solids concentration effects becoming important. With the six studies discussed in this report and three previous studies (Environmental Laboratory 1987, Myers and Brannon 1988, and Palermo and others 1989), a database consisting of nine sediments and a wide variety of inorganic and organic contaminants has been developed on solids concentration effects in batch testing of sediments. This expanding database continues to indicate that a 4/1 liquid-solid ratio is the maximum ratio that can be used without introducing solids concentrations effects. A 4/1 liquid-solid ratio is also an operational minimum; that is, lower ratios introduce significant operational problems with sequential batch leach testing.

Thus, the kinetic and liquid-solid ratio testing conducted for Hamlet City Lake and San Francisco Bay area sediments indicated no need to alter the SBLT. The theoretical foundation of the SBLT and the specifics of the test procedures are anticipated to remain as first developed.

The improved column leaching apparatus performed as designed. In some cases, as many as 16 pore volumes were eluted, and in no case were less than 10 pore volumes eluted in six months. Pore-water velocities were about

10<sup>-5</sup> cm/sec or less. There was no evidence of solids washout, serious wall effects, or short-circuiting. Leachate volumes were adequate for analysis of analytes requiring 1 L of sample without having to elute more than one pore volume. The columns performed satisfactorily for sediments with low and high porosity. Although additional testing and evaluation are needed before the column test procedure is as well developed as the SBLT, further changes are anticipated to focus on refinements in loading and sample handling procedures.

# Integration of Batch and Column Tests

The integrated approach (Figure 3) was used in the Hamlet City Lake and San Francisco Bay area sediment studies to evaluate the applicability of SBLT data to prediction of contaminant leaching from dredged material in CDFs. In the integrated approach, information from SBLTs, soils tests, and column operating records is used in a contaminant transport equation to predict column elution curves. If predicted and observed column elution curves agree, the conclusion may be reached that the processes governing transfer of contaminants from dredged material solids to water have been adequately described. Agreement between predicted and observed column elution curves also indicates that SBLT data, when properly interpreted, can be used to predict contaminant leaching from dredged material for flow conditions that apply in the field.



Figure 3. Integrated approach

#### Hamlet City Lake Sediment Study

The Hamlet City Lake study showed that, for the most part, contaminant desorption could be modeled by linear equilibrium partitioning. Figure 4 shows observed and predicted column elution curves from Hamlet City Lake sediment for selected metals. The predicted curves were developed using distribution coefficients obtained from analysis of desorption isotherms prepared from SBLT data and an advection-diffusion equation with equilibrium-controlled desorption. No elution curves for organic contaminants are shown because the organics of interest in this sediment (polycyclic aromatic hydrocarbons) did not leach in detectable amounts in either batch or column leach tests. The agreement between predicted and observed elution curves in Figure 4 shows that linear equilibrium partitioning was a good model for desorption of arsenic, cadmium, nickel, and zinc in Hamlet City Lake sediment.



Figure 4. Predicted and observed column elution curves for Hamlet City Lake sediment

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The Hamlet City Lake study results are consistent with the results from a previous study involving a freshwater sediment from Indiana Harbor, Indiana (Environmental Laboratory 1987). The aggregate result of these studies suggests that linear equilibrium partitioning may be a satisfactory model of leaching from freshwater sediments for a variety of contaminants.

Equilibrium partitioning for organics is given by

$$q = K_d C$$

where

q = equilibrium sediment contaminant concentration, mg/kg

 $K_d = distribution coefficient, L/kg$ 

C = equilibrium leachate contaminant concentration, mg/L

and equilibrium partitioning for metals is given by

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

(1)

where q<sub>r</sub> (in milligrams per kilogram) is the sediment metal concentration in geochemical phases resistant to leaching.

Equations 1 and 2 have been presented previously as sediment desorption models (Environmental Laboratory 1987 and Myers, Brannon, and Price 1992).

Distribution coefficients (K<sub>d</sub>) and sediment metals concentrations in geochemical phases resistant to leaching (qr) are obtained by analysis of desorption isotherms constructed from sequential batch leach data. With these parameters, the time dependency of column leachate quality can be modeled. Similarly, these parameters can be coupled with field flow conditions to predict leachate quality with time. The most important feature of Equations 1 and 2 is that models constructed around these equations will always predict decreasing contaminant concentrations in leachate with time. The time dependency is a direct result of washing of dredged material solids by water that enters a CDF; it is not related to the kinetics of desorption. The tendency of contaminant concentrations to rapidly decrease or remain relatively steady for long periods of time is indicated by the value of the distribution coefficient. Contaminants with distribution coefficients between 1 and 10 L/kg will tend to decrease rapidly. Contaminants with distribution coefficients greater than 100 L/kg will tend to persist at initial pore-water concentrations (Environmental Laboratory 1987).

Results from the Hamlet City Lake sediment, while generally consistent with Equations 1 and 2, showed complicated desorption isotherms requiring careful analysis to obtain proper distribution coefficients. Additional work is needed on standardization of interpretation protocols for desorption isotherms. Since Hamlet City Lake is only the second freshwater sediment for which SBLT and column leach data are available, it is still too early to adopt Equations 1 and 2 for routine application to freshwater sediments.

#### San Francisco Bay Area Sediment Studies

The San Francisco Bay area sediment leaching studies showed that Equations 1 and 2 were not applicable to these sediments. SBLT and column leachate contaminant concentrations did not decrease, as required by Equations 1 and 2, but increased after the salt in these estuarine sediments was removed by leaching. The salt washout effect was also observed in Everett Bay (Palermo and others 1989) and New Bedford Harbor (Myers and Brannon 1988) sediments. The association of increasing contaminant concentrations in leachate with salt washout was demonstrated by conducting SBLTs with distilled-deionized. water and artificial saline water (formulated to match the in situ salinity) (Myers and Brannon 1988).

The New Bedford Harbor studies led to development of a rational explanation for the salt washout effect (Brannon and others 1991). Salinity dependency is the result of increasing repulsive forces between sediment colloids as ionic strength decreases. As repulsive forces increase, sediment colloid deflocculation takes place, resulting in an increase of nonfilterable microparticulates (colloids) in the aqueous phase. These particulates act as carriers for many contaminants.

The San Francisco Bay area sediment leaching studies showed mobilization of various inorganic and organic contaminants consistent with the salt washout hypothesis developed for New Bedford Harbor sediment. Figures 5 and 6 show examples of predicted and observed column elution curves for San Francisco Bay area sediments. As shown in these figures, predicted and observed contaminant concentrations increase as electrical conductivity (a measure of ionic strength) decreases. The agreement between predicted and observed curves in Figures 5 and 6 is not always good, but the tendency observed during sequential batch leaching for contaminant concentrations to increase was also observed during column leaching.

The predicted curves shown in Figures 5 and 6 were developed using a complete mix model for the columns that accounts for the salt washout effect. The complete mix equation is given below.

$$C(T) = C_o \exp\left\{ \left( \frac{A}{\beta D} + \frac{1}{\beta B} \right) \ln (B + D) - \frac{T}{B} - \left( \frac{A}{\beta D} + \frac{1}{\beta B} \right) \ln \left[ B + D \exp \left( -\beta T \right) \right] \right\}$$
(3)

where

- C(T) = contaminant concentration in leachate as function of pore volumes eluted, mg/L
  - $C_0$  = initial leachate contaminant concentration, mg/L

- A = β  $ρ_b$  ( $K_d^o K_d^f$ )/n (variables are defined below)
- $\beta$  = empirical coefficient for change in K<sub>d</sub> with T, dimensionless
- $D = \rho_b (K_d^o K_d^f) / n$  (variables are defined below)

$$B = 1 + (\rho_{h} K_{d}^{t})/n$$

T = number of pore volumes eluted, dimensionless

- $\rho_b$  = bulk density, kg/L
- $K_d^o$  = initial distribution coefficient; that is, distribution coefficient before salt has been washed out, L/kg
- $K_d^f$  = final (freshwater) distribution coefficient; that is, distribution coefficient after salt has been washed out, L/kg
  - n = sediment porosity, dimensionless



Figure 5. Predicted and observed elution curves for sediment from the West Richmond reach of J. F. Baldwin channel

Equation 3 has not previously appeared in the literature, primarily because the significance of the salt washout effect on contaminant mobilization has not been previously recognized.

The complicated appearance of Equation 3 is somewhat misleading. To predict contaminant concentration, C, as a function of pore volumes eluted, T, only three coefficients from SBLT desorption isotherms are needed in addition to initial pore-water contaminant concentration, sediment water content, and sediment specific gravity. Porosity and bulk density are calculated from sediment water content and specific gravity. Initial leachate concentration can be estimated from column data or interstitial water measurements. The three coefficients needed from the SBLT data are  $\beta$ ,  $K_d^f$ , and  $K_d^o$ .



Figure 6. Predicted and observed elution curves for Richmond Harbor sediment, Santa Fe channel

Equation 3 does not explicitly account for colloid deflocculation as salt is washed out. This effect is accounted for by making the distribution coefficient nonconstant as indicated in the SBLT data. Since the nonconstant characteristic of  $K_d$  is related to salt elution, and salt elution is a decaying exponential,  $K_d$  as a function of the number of pore volumes eluted is written as

$$K_{d}(T) = K_{d}^{f} + (K_{d}^{o} - K_{d}^{f}) \exp(-\beta T)$$
(4)

Additional work is needed on the development of standard protocols for analyzing desorption isotherms for estuarine sediments and obtaining the model parameters in Equations 3 and 4.

Although there may be practical and theoretical issues related to application of Equations 3 and 4 that have not been investigated, Equations 3 and 4 appear to have substantial merit. These equations predict increasing leachate contaminant concentrations in SBLT and column leach tests as estuarine sediments are leached with freshwater. They also predict 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.

The value of the thin-layer columns for confirming contaminant elution trends predicted in SBLT was demonstrated in the San Francisco Bay area studies. If the type of column used in previous studies had been used in the San Francisco Bay area sediment leaching studies, several years of column leaching would have been required to observe the trends shown in Figures 5 and 6.

## **Future Directions**

In the leachate studies conducted to date, major differences in the leaching characteristics of freshwater and estuarine sediments have been observed. Initial leachate quality will probably represent worst-case leachate quality for freshwater dredged material. The available information suggests that equilibrium-controlled desorption with constant coefficients can predict leachate quality in freshwater dredged material. Because only two freshwater sediments have been tested, additional testing of freshwater sediments is needed to confirm the preliminary observations of leaching characteristics of freshwater sediments. In estuarine dredged material, initial leachate quality will not represent worst-case leachate quality if fresh water infiltrates a disposal site containing estuarine dredged material. Studies on estuarine sediments show that additional research is needed to develop quantitative predictive techniques that account for contaminant mobilization due to salt washout effects.

Future study should build on the lessons learned thus far. Directions for needed research are described in the following sections.

### **Test Development**

Additional kinetic batch tests are needed to describe short-term kinetics associated with approaching steady-state in 24 hr. Previous tests have focused on showing that shake times longer than 24 hr were not necessary for batch testing. Investigation of desorption kinetics at times less than 24 hr is needed in order to estimate the maximum pore-water velocities that can be used in column tests and still satisfy equilibrium assumptions. It may be possible to conduct the column leach test at pore-water velocities higher than 10<sup>-5</sup> cm/sec. Conducting the test at higher pore-water velocities would shorten the time required to conduct the test. Column tests at several pore-water velocities are also needed to investigate mass transfer limitations that may affect column elution curves. Column flow tests are planned for some of the sediments discussed in this note.

#### **Database Expansion and Development**

Additional studies on freshwater sediments are needed to confirm preliminary findings on leaching characteristics of freshwater sediments. In addition, the existing information on desorption coefficients for freshwater and estuarine sediments should be compiled and expanded through additional testing. Such a database is needed to provide default desorption coefficients for a priori prediction of leachate quality. A priori predictive techniques are needed for development of a tiered approach to evaluating leachate testing requirements. Tier I would involve estimation of leachate quality on the basis of bulk sediment chemistry. Tier I results would indicate the need for Tier II testing (laboratory leach tests). A limited effort in database compilation is planned.

#### **Colloid Destabilization**

Further testing of the colloid destabilization hypothesis for the salt washout effect in estuarine sediments is needed. Follow-on column leaching studies for the San Francisco Bay area sediments are currently under way in which colloidal mass, fraction organic carbon, and size distribution are being measured during column leaching. Colloid destabilization studies are planned for batch tests using radiolabeled tracer studies. The batch studies will focus on measuring partitioning between water and colloids.

#### **Field Verification**

Sufficient data have been collected to indicate, in a qualitative sense, significant differences in leaching of freshwater and estuarine sediments. These findings need to be field verified. However, field verification studies involving groundwater monitoring wells at numerous CDFs are not likely to yield meaningful results for tens to hundreds of years. The feasibility of using pilot-scale field leaching facilities for verification should be investigated. Currently, the U.S. Army Engineer District, Buffalo, has initiated such a project. SBLT and column leach tests are planned for the dredged material placed in the pilot-scale facility so that batch, column, and pilot-scale field leachate quality can be compared. These studies will add to the database on freshwater sediments.

#### **Predictive Equations for Estuarine Sediments**

The complete-mix equation discussed in this technical note for estuarine dredged material should be replaced with a more general equation that includes advective and dispersive processes important in predicting column elution curves. Column parameter estimation techniques are also needed to compare SBLT desorption coefficients with column best-fit coefficients. The required development effort has been initiated.

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