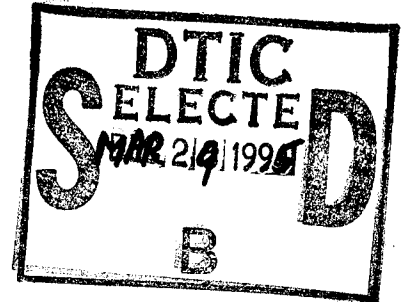




# *Environmental Effects of Dredging Technical Notes*

## **Factors Affecting the Behavior of Metals in Leachate**



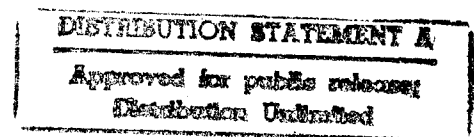
### **Purpose**

This technical note describes factors affecting batch leaching of metals from dredged material. Factors evaluated include time of sediment-water contact, sediment salinity regime, and sediment oxidation status.

### **Background**

Contaminated dredged material is often placed in confined disposal facilities where movement of contaminants by leachate is an important environmental concern. No laboratory testing protocol has been routinely applied to predict leachate quality and quantity from confined dredged material disposal facilities. In 1984, the US Army Corps of Engineers initiated investigations of confined disposal facility (CDF) leachate by developing a theoretical framework for prediction of leachate quality based on mass transport theory. The theoretical framework included both batch and column testing in an integrated approach. Batch testing provides a quick, relatively easy method for determining the distribution of contaminants between dredged material and leachate. Equilibrium distribution (partitioning) coefficients derived from batch tests can then be used to relate leachate contaminant concentrations to solid phase contaminant concentrations. Column testing more closely approximates contaminant losses under field conditions in a CDF than do batch tests. Leachate results predicted by batch tests can be compared to those observed from column leaching experiments by combining column tests results, distribution coefficients from batch tests, and mass transport theory.

The integrated approach was used in studies at Indiana Harbor, Indiana; Everett Harbor, Washington; and New Bedford Harbor, Massachusetts. Results of these studies were evaluated in 1988 at a workshop hosted by Louisiana State University



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in Baton Rouge. Among the recommendations of workshop participants was further investigation of metals in conjunction with other inorganic components of leachates. This Technical Note reports on the results of those investigations.

## **Additional Information or Questions**

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## **Introduction**

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

Experimental procedures for determining leachate quality have been used to evaluate the potential impacts of confined disposal of dredged material from Indiana Harbor, Indiana; Everett Harbor, Washington; and New Bedford Harbor, Massachusetts (Environmental Laboratory 1987, Palermo and others 1989, Myers and Brannon 1989). Results of these laboratory studies are summarized in Technical Note EEDP-02-7 (Myers and Brannon 1988). Technical Note EEDP-02-11 (Brannon and others 1989) reported results of an initial evaluation of the factors affecting leachate quality for polychlorinated biphenyls (PCBs).

This Technical Note reports on the results of investigations conducted on desorption kinetics and sequential batch leaching of metals from dredged material removed from freshwater and saline environments. The impacts of time of sediment-water contact, sediment salinity, and sediment oxidation status are examined.

## **Methods**

### **Desorption Kinetics**

Desorption kinetics have been determined using a variety of sediments, both freshwater and saline. A 4:1 water-to-sediment ratio by weight was used for kinetic batch testing, the details of which are described in Myers and Brannon (1989). As appropriate desorption times were reached, tubes were centrifuged and leachate was filtered through 0.45- $\mu$ m membrane filters. Subsamples of the leachate were analyzed for metals of interest and major anions and cations.

## Sequential Desorption

Anaerobic sediments subjected to kinetic batch testing were also used for sequential desorption batch testing. In addition, sediments that had been allowed to oxidize for six months under controlled conditions were also tested (Myers and Brannon 1989). A 4:1 water-to-sediment ratio and a shaking time of 24 hr were used in seven sequential cycles of the batch leach tests (Myers and Brannon 1989).

## Data Analysis

All statistical analyses were conducted using methods developed by the Statistical Analysis Systems Institute (Barr and others 1976). To test for differences between means, analysis of variance procedures were used.

Leachate ionic strength was determined by analysis of major anions and cations in leachate and the MINTEQA2 chemical equilibrium model.

## Results and Discussion

### Time of Sediment-Water Contact

Tests have shown that metal concentration patterns vary dramatically as time of contact increases during batch testing. Metal concentration curves of the types commonly observed are presented in Figure 1a. Of these curves, types A and B are most commonly encountered. Type A curves involve no significant change in metal concentration over time, and type B curves show peak metal concentration following 1 or more days (predominately 1 day) of shaking. Regardless of the type of curve observed over time, however, leachate metal concentrations following 1 day of shaking have been generally comparable to interstitial water concentrations. When conducting sequential batch leaching tests for metals, one day (24 hr) of shaking has been used because of the predominance of type A and B curves and the comparability of 24-hr leachate concentrations to interstitial water concentrations.

Changes in leachate metal concentration as shaking time increases are related to changes in leachate composition over time. For example, Figure 1b presents results of kinetic testing for Baltimore Harbor sediment. For the first few days of shaking, iron and sulfate concentrations were relatively constant, but total inorganic carbon (TIC) was steadily increasing. Rapid sulfate disappearance was observed between days 5 and 10 and iron concentration increased from 11 to 31 mg/L between day 14 and day 30. Over a 30-day period, order of magnitude changes were observed for sulfate, that is, sulfate was reduced to sulfide, and a 3.5-fold increase in TIC was observed. These changes in leachate composition can greatly impact leachate metal concentrations as insoluble metal sulfides and carbonate compounds are formed, and metals coprecipitated with iron oxyhydroxides are released. The pronounced changes in leachate composition over time in conjunction with the predominance of type A and B curves, and the correspondence between 24-hr batch tests and interstitial water concentrations,

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indicates that a 24-hr shaking time should continue to be used in sequential batch tests for metals.

### **Sediment Salinity**

Results of sequential batch leaching of metals, as was the case for nonpolar organic compounds, are strongly affected by the salinity of the sediment being tested. Sediments from saline environments possess high pore-water concentrations of anions and cations such as sodium, chloride, potassium, and sulfate that increase the ionic strength of pore waters and leachate. Ionic strength is also strongly related to the activity of metals in solution (Garrels and Christ 1965). As shown in Figure 1c, ionic strength is much higher in leachate from a saline sediment (Baltimore Harbor) than from a freshwater sediment (Buffalo River). As sequential batch leaching with fresh water proceeds, the ionic strength of the fresh water Buffalo River leachate remained relatively constant, decreasing slightly from an initial value of 0.0037 M (Molar) to 0.0026 M following 7 sequential batch desorption cycles. Conversely, ionic strength of the Baltimore Harbor leachate decreased from 0.261 M to 0.0046 M following 7 cycles.

Metal release patterns typical of those obtained during sequential batch testing of freshwater and saline sediments are presented in Figure 2a for Baltimore Harbor and Buffalo River sediments. Leaching of lead and copper in the freshwater Buffalo sediment followed the expected pattern of decreasing leachate concentration during sequential batch desorption testing. Metal release patterns for lead and copper in saline Baltimore Harbor sediments showed peak concentrations during the fourth leaching cycle when ionic strength dropped to levels characteristic of freshwater environments. These peaks in metal concentrations are characteristic of leaching results from saline sediments and are postulated to be a result of destabilization of colloidal material as ionic strength decreases. Such pronounced peaks do not occur when saline sediments are leached with saline water (Myers and Brannon 1989).

The net differences in behavior of metals in saline and freshwater sediments are illustrated in Figures 2b and 2c. Figure 2b is a desorption isotherm for lead derived from sequential batch desorption of freshwater Buffalo River sediment. Batch testing of anaerobic Buffalo River sediment resulted in a well-behaved desorption isotherm ( $R^2 = 0.635$  for all data) that can be used in mass transport equations to predict the potential leaching of lead from Buffalo River sediment placed in a CDF. The desorption isotherm for lead in saline Baltimore Harbor sediment (Figure 2c) is double sided and does not behave according to theory until after the fourth desorption cycle (represented by the data point of 0.1 mg lead/L in Figure 2c). Such desorption isotherms greatly complicate prediction of potential leachate quality in CDFs containing saline sediments.

### **Sediment Oxidation Status**

Sediment oxidation status exerts pronounced effects on metals leaching from most saline sediments, for example, Baltimore Harbor sediment (Figure 3). In saline sediments, leachate pH generally shows a marked decrease following

6 months of oxidation (Figure 3a). In addition to the drop in pH brought about by sediment oxidation, leachate sulfate concentration increased by an order of magnitude due to oxidation of sulfur and sulfide compounds in the anaerobic sediment (Figure 3b). As sequential batch leaching progressed, leachate pH increased and sulfate concentrations decreased in the aerobic leachate. Aerobic conditions resulted in much higher concentrations of zinc in the leachate than anaerobic conditions. During the course of sequential batch testing, 7.7 percent of sediment zinc was lost under aerobic conditions compared to 0.4 percent under anaerobic conditions. These results are illustrative of the effects that sediment oxidation can exert on metal leachate concentrations. Care must be exercised to ensure that such effects are not overlooked when evaluating potential impacts of leaching of metals from dredged material placed in CDFs.

## Summary

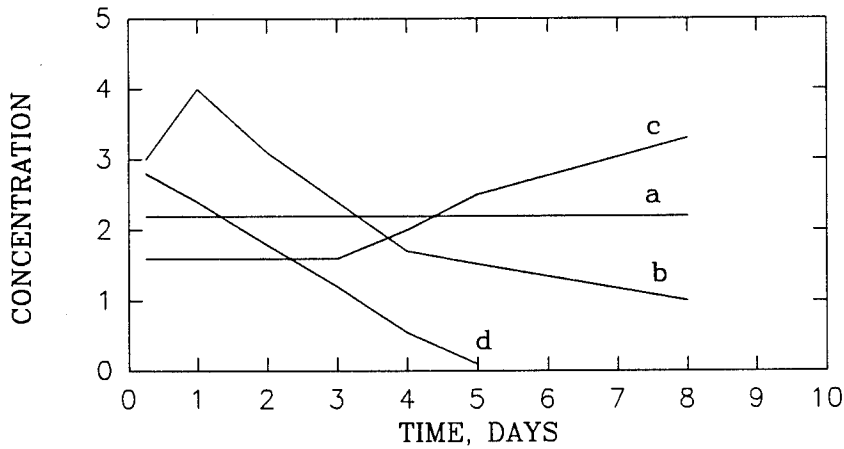
Results of batch testing with freshwater and saline sediments have shown that time of sediment-water contact, sediment salinity, and sediment oxidation status affect leaching of metals. Results of this study indicate that a 24-hr shaking time should continue to be used in sequential batch tests for metals. Sediments from freshwater environments generally behave according to theory and follow the expected pattern of metal releases, that is, decreasing concentrations during sequential batch leaching. However, leaching of sediment from saline environments with fresh water results in double-sided desorption isotherms that do not behave according to theory until after concentrations of metals in leachate peak. Oxidation of anaerobic sediment can result in decreased sediment pH which can greatly increase metal leaching compared to the unoxidized sediment.

## References

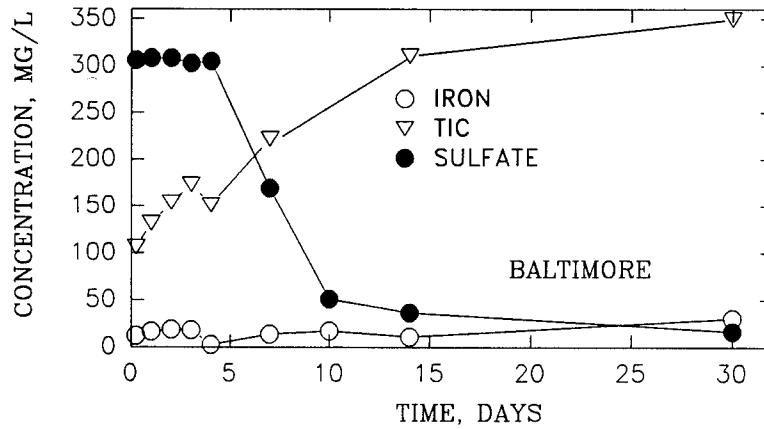
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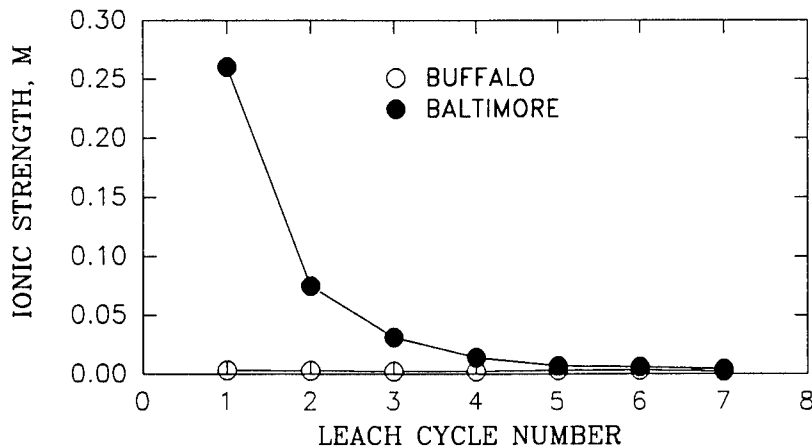
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a. Typical types of concentration curves observed during kinetic batch testing of dredged materials; concentration values are relative and show increasing and decreasing concentrations only

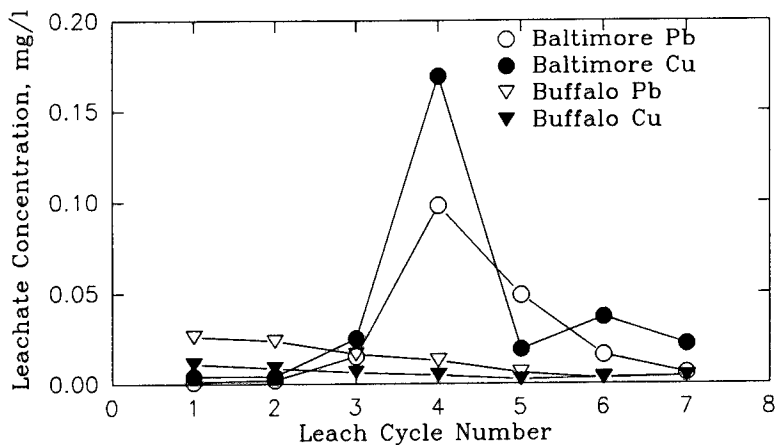


b. Changes in Baltimore Harbor leachate as a function of sediment-water contact time during batch leaching

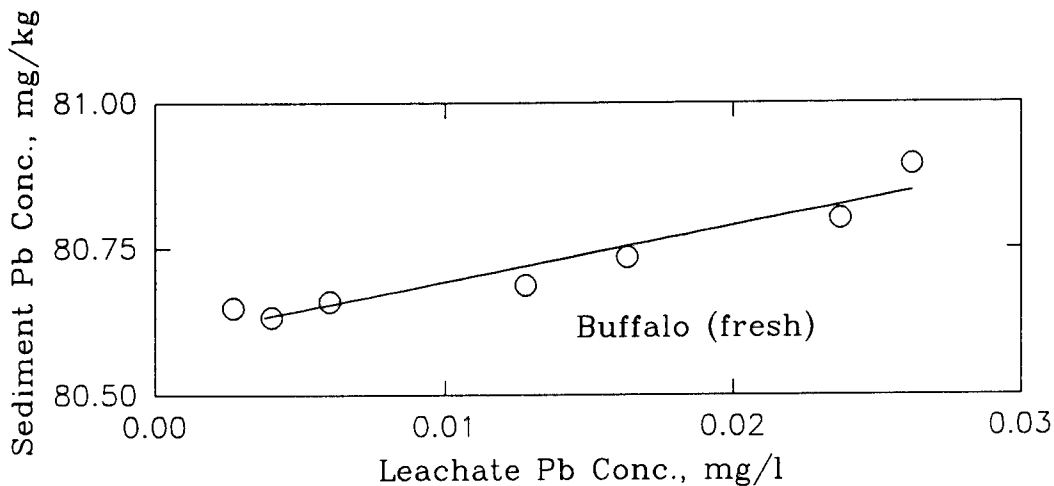


c. Ionic strength changes during sequential batch leaching of saline Baltimore Harbor sediment and freshwater Buffalo River sediment

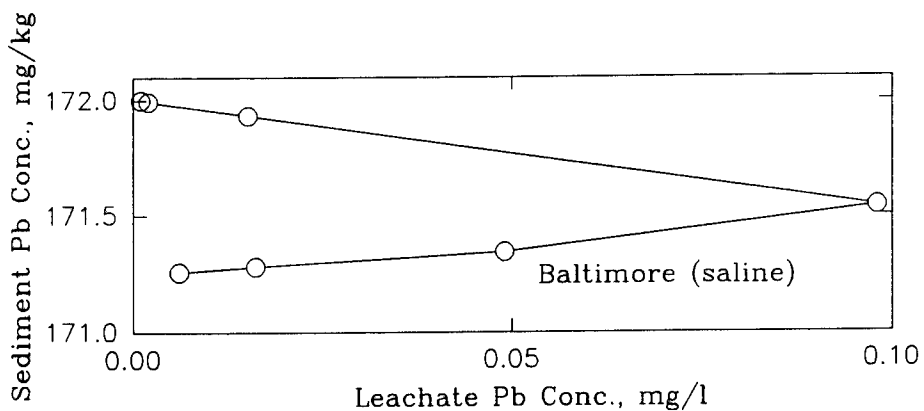
Figure 1. Sediment-water time of contact test results



a. Changes in leachate concentrations of lead and copper during sequential batch leaching of freshwater and saline sediment



b. Desorption isotherm for lead with regression line of best fit derived from sequential batch leaching of freshwater Buffalo River sediment



c. Desorption isotherm for lead derived from sequential batch leaching of saline Baltimore Harbor sediment

Figure 2. Batch leaching test results

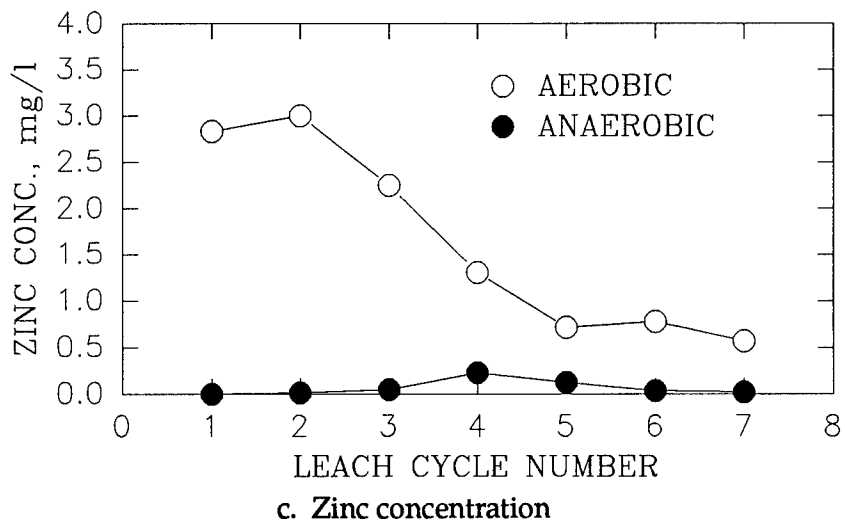
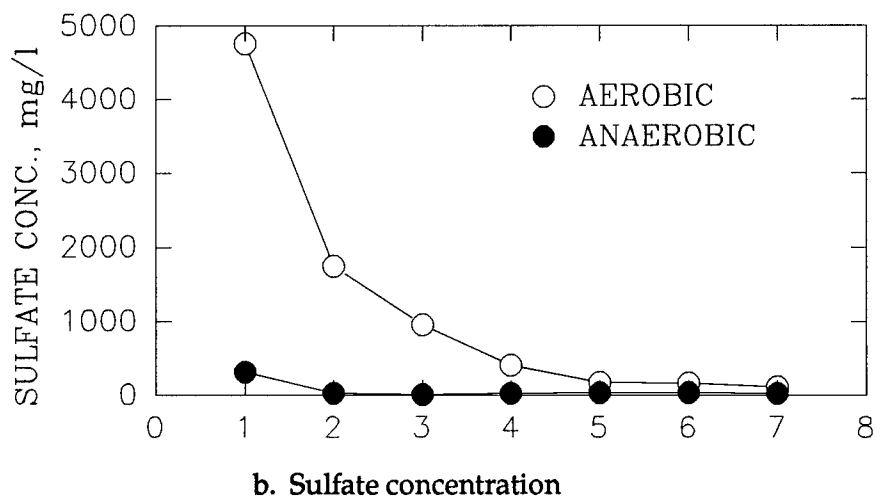
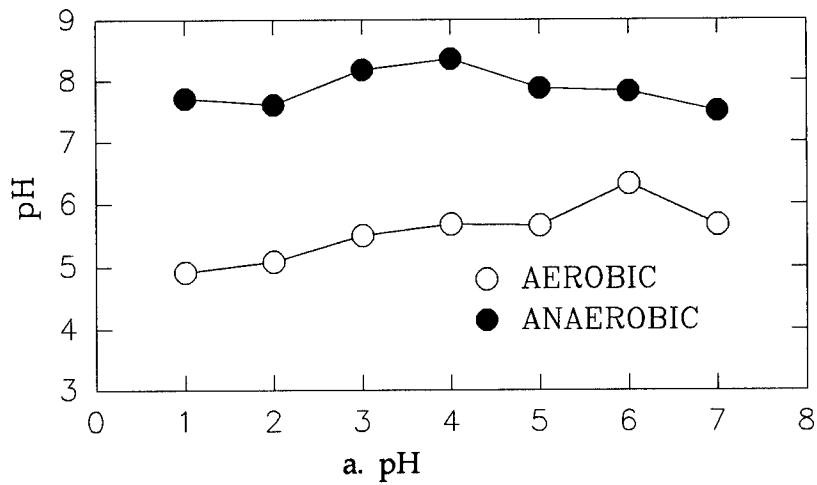


Figure 3. Relationship between oxidation state in Baltimore Harbor sediment and leachate