



US Army Corps
of Engineers

Waterways Experiment
Station

Environmental Effects of Dredging

*Section 02 - Upland Disposal
Technical Notes
EEDP-02-1 through EEDP-02-20*

Compiled by
Dredging Operations Technical
Support Program

Section 02—Upland Disposal

EEDP-02-1 through EEDP-02-20

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Environmental Effects of Dredging Technical Notes



PLANT BIOASSAY OF DREDGED MATERIAL

PURPOSE: This note introduces the concept of using a plant as an indicator of the contaminants in dredged material. An example of the application of a plant bioassay procedure to saltwater dredged material placed in an upland disposal site was reported in a paper entitled "Contaminant Uptake by *Spartina alterniflora* from an Upland Material Disposal Site -- Application of a Saltwater Plant Bioassay," which was presented at the International Conference on Heavy Metals in the Environment in Heidelberg, Germany, and was published in the proceedings of the conference (Folsom and Lee 1983). The text of this note was taken from the paper.

BACKGROUND: Plant bioassay test procedures are being developed under the Long-Term Effects of Dredging Operations Program and are being field tested and verified under the "Interagency Field Verification of Testing and Predictive Methodologies for Dredged Material Disposal Alternatives," called the Field Verification Program (FVP). These procedures are relatively simple and can provide information that may be required in the ecological evaluation and environmental assessment of dredged material disposal. Based on laboratory results and limited field testing, the procedures can be applied to saltwater sediment or dredged material that requires placement in a wetland or upland environment. The concept presented in this note is the result of ongoing research under the FVP.

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Introduction

Recently, a solid-phase plant bioassay was developed to test sediment for contaminants that are potentially phytotoxic and may be bioaccumulated by plants (Folsom and Lee 1981a; Folsom, Lee, and Bates 1981). The solid phase plant bioassay was shown to be an excellent tool for predicting whether or not

contaminants (e.g., zinc and cadmium) were potentially bioaccumulated by the saltwater plant *S. alterniflora*. Folsom and Lee (1981a) pointed out, however, that the DTPA extraction data indicated that plant uptake from air-dried oxidized saltwater sediment would be substantially greater than from the same saltwater sediment under flooded reduced conditions. In addition, they suspected greater plant uptake once the excess salts were leached out and the sediments were dried. This technical note reports results of modifications to the original solid-phase plant bioassay to pursue this assumption.

Methodology

A sediment from Black Rock Harbor (BRH) in Bridgeport, Connecticut, was selected for this study due to its extremely high concentrations of one or more contaminants. The sediment was analyzed for texture, salinity, organic matter, conductivity, calcium carbonate equivalent, pH, total sulfur, oil and grease, and heavy metals (total nitric acid digestible and DTPA extractable).

The solid-phase plant bioassay was conducted in an experimental unit similar to the one shown in Figure 1, which was used in earlier studies (Folsom and Lee 1981a). Procedures for the flooded condition were essentially the same as those used previously. The upland condition was prepared by washing one volume (1 l) of original flooded sediment with three volumes (3 l) of reverse osmosis (RO) purified water. An electric stirrer was used to mix the sediment and water; the solids in the resulting suspension were allowed to settle out (about 4 days); and the supernatant was siphoned off. The sediment was washed two more times using the same procedure, and then the washed sediment was air-dried.

The washed air-dried (upland) sediment to be tested was placed into the inner container of the solid-phase bioassay apparatus. Water of appropriate salinity (15 parts per thousand) was added to the flooded sediment. RO water was added to the air-dried sediment initially to moisten the sediment and to promote seedling growth. Additional water was added only to meet the needs for plant growth. From this point on, the procedure of Folsom and Lee (1981a) was followed with the exception that only *S. alterniflora* was grown as the index plant.

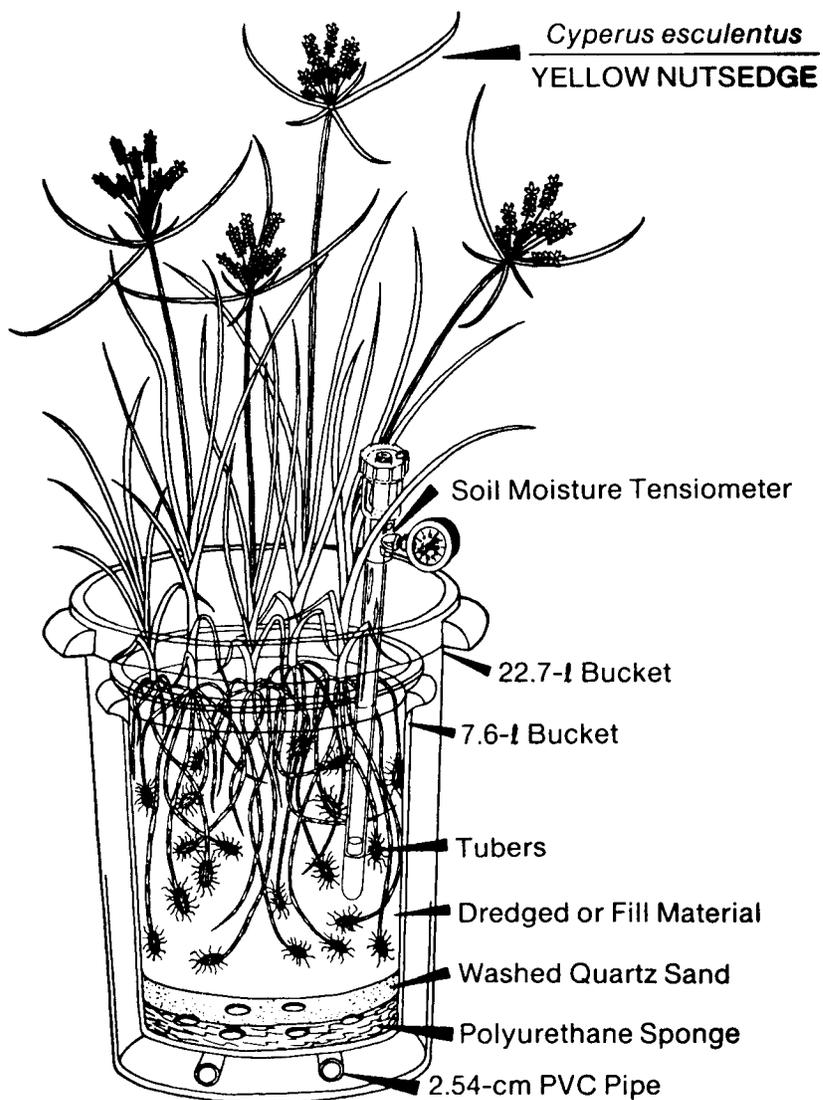


Figure 1. Schematic diagram of the experimental unit used for solid-phase plant bioassays

Results and Discussion

Selected physical and chemical parameters of the BRH sediment were determined to be as follows:

Organic matter, %	18.7
Salinity, ppt	25.3
Conductivity, dS/m	35.7
CaCO ₃ equivalent, %	1.0
pH: wet	7.6
reconstituted air-dried	6.6
Oil and grease, mg/g	5.3
Total Sulfur, %	1.3

The total amounts and DTPA-extractable heavy metal concentrations in BRH sediment are shown in the following tabulation:

Heavy Metal	Concentration, $\mu\text{g/g}$			
	Total Acid Digestible-Original Sediment	DTPA Extractable		
		Original Sediment Flooded	Upland	Washed Sediment, Upland
Zinc	1264	1.73	765	1017
Cadmium	16.7	<0.0005	22.0	24.7
Copper	2377	<0.005	701	235
Chromium	1346	0.18	1.45	1.62
Lead	330	0.01	14.3	23.2

The total sediment content of heavy metals was typical for that of contaminated saltwater sediment with the exception of copper, which was much greater (Folsom, Lee, and Bates 1981).

The data for the DTPA-extractable heavy metals in the BRH sediment showed that air-drying resulted in increased heavy metals extractability. Washing the sediment before air-drying had only a slightly increased effect on DTPA extractability of the heavy metals. The DTPA data would predict plant uptake of heavy metals to be greater from the air-dried upland sediment compared to the original flooded sediment.

Contents of the heavy metals in the leaf tissues of *S. alterniflora* grown in original sediment under both flooded and upland conditions and in upland washed BRH sediment are presented below:

Heavy Metal	Concentration, $\mu\text{g/g}$		
	Original Sediment		Washed Sediment,
	Flooded	Upland*	Upland
Zinc	13.0	219	341
Cadmium	0.04	0.91	4.65
Copper	3.77	18.7	36.2
Chromium	0.02	0.93	2.79
Lead	0.39	1.53	2.53

* Only one replicate supported plant growth.

Spartina alterniflora grew well and had low heavy metal contents under the flooded conditions. These results are typical for contaminated saltwater sediment placed under a flooded condition, and the data compared well with levels observed in plants from natural saltmarshes (Simmers et al. 1981). *S. alterniflora* did not grow well in the original air-dried (upland) sediment:

only one plant of one replicate survived. Decreased plant growth resulting in increased metal content could explain the elevated heavy metal content of the plant. Plants grown in washed sediment under an upland condition grew much better than under the unwashed upland condition. However, the heavy metal content of the plants was much greater compared to that of plants grown in the flooded condition. The same effect has been shown by Folsom and Lee (1981b) to occur with freshwater plants grown in freshwater sediment under flooded and upland disposal environments. Apparently, once the saltwater sediment is washed free of excess salt and plant growth occurs, the air-drying process results in increased availability of heavy metals. Removing excess salt from the sediment by washing simulated the natural salt-leaching process and can be used in a modified saltwater solid-phase plant bioassay to predict contaminant mobility into plants growing on saltwater dredged material deposited in upland disposal sites.

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Environmental Effects of Dredging Technical Notes



UPLAND ANIMAL BIOASSAYS OF DREDGED MATERIAL

PURPOSE: This note introduces the concept of using an upland animal as an indicator of the contaminants in dredged material (1) proposed for disposal in an upland environment or (2) already placed in an upland disposal facility. Examples of the applications of an animal bioassay procedure to estuarine and freshwater dredged material placed in an upland environment have been published in several recent papers. The text of this note is taken from a review prepared for the International Conference on Earthworms in Waste and Environmental Management, Cambridge, UK (Rhett, Simmers, and Lee In Press).

BACKGROUND: Animal bioassay test procedures are being evaluated, field tested, and verified under the "Interagency Field Verification of Testing and Predictive Methodologies for Dredged Material Disposal Alternatives," called the Field Verification Program (FVP). The FVP research is being conducted in conjunction with a scheduled dredging project in Black Rock Harbor (BRH) near Bridgeport, Conn. The bioassay test procedures are relatively simple and can provide information that may be required in the ecological evaluation and environmental assessment of dredged material disposal. Based on laboratory results and limited field testing, the procedures can be applied to contaminated sediment (dredged material) that requires placement in an upland environment. The concept presented in this note is the result of ongoing research under the FVP. The results of the field testing will be reported in a later Technical Note. Draft final guidance will be completed in September 1987.

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Introduction

The Clean Water Act in the United States requires that the environmental evaluation of dredged material prior to discharge or impacting the waters of the United States include the effects of disposal on concentrations of contaminants through biological processes. This results in a need for Corps of

Engineers districts to be able to predict the contamination of animals that may be associated with potential disposal alternatives: open-water disposal, upland disposal, and wetland creation. The following is a summary of the results of bioassay procedures using the earthworm *Eisenia foetida* to evaluate the potential contaminant mobility into soil-dwelling animals. These tests were derived from proposed Organization for European Common Development (OECD) and European Economics Commission (EEC) test procedures (evaluating the effects of new chemicals) and modified to consider accumulation and sublethal effects rather than toxicity.

The availability and animal uptake of heavy metals, polychlorinated biphenyls (PCBs), and polynuclear aromatic hydrocarbons (PAHs) from contaminated dredged material placed in upland disposal environments were evaluated with a solid-phase animal bioassay. The objectives of these studies were to apply, document, and verify existing terrestrial animal contact-bioassay procedures to predict movement of contaminants into soil-dwelling animals colonizing dredged material disposal sites.

The following dredged materials were chosen for testing: a highly contaminated estuarine sediment taken prior to dredging from BRH; dewatered dredged material from the Chicago River (Ill.) used to overlay a pyritic mine spoil; and dredged material from the Buffalo River (NY) confined in an upland disposal area. Each dredged material represented a different stage of aging and plant and animal colonization. The BRH dredged material represented time = 0 with no plant or animal colonization, and the material from the Chicago and Buffalo rivers represented aging of 7 and 9 years, respectively. The dredged materials also represented cases in which prediction of contaminant mobility is essential since confined disposal sites or other upland deposits of dredged material often become highly prolific wildlife habitats.

During the summer and fall of 1983, the earthworm *Eisenia foetida* was exposed to each substrate in a laboratory experimental chamber. After 28 days, the earthworms were removed and analyzed for heavy metals, PCBs, and PAHs. Comparisons were made of sediment levels of these contaminants with animal availability, bioaccumulation, and toxicity. The test procedures were intended to evaluate the potential movement of toxic heavy metals, PCBs, and PAHs from dredged material placed in an upland (oxidized) disposal area into soil-dwelling invertebrates as a first-step evaluation of contaminant mobility into animals that may colonize the dredged material.

General Test Description

The earthworms used for testing were purchased from a local worm grower and placed in a 1.8 m × 1.5 m × 0.3 m wood-frame container with a plywood base. The worm beds were located in a partially shaded greenhouse where temperatures did not exceed 27° C. During summer months, the worm beds were watered daily to prevent drying. The worms were fed horse manure and chicken meal mash.

When worms were needed for testing purposes, they were hand sorted, rinsed in distilled water, and placed on paper towels until any excess water had drained off. About 20 to 40 g (fresh weight) of worms were added to 6 \times of test material contained in a 7.5- \times plastic bucket (Figure 1). During the exposure period (usually 28 days), distilled water was added to the substrates as necessary to maintain optimum moisture. Also, a nylon insect screen material was placed over the drain holes in the base and in the lid to prevent earthworm escape.

Upon completion of the exposure period, the earthworms were sorted from the material, rinsed in distilled water, blotted with paper towels, and weighed before and after a 48-hr purging at 10° C on wet filter paper. Purged

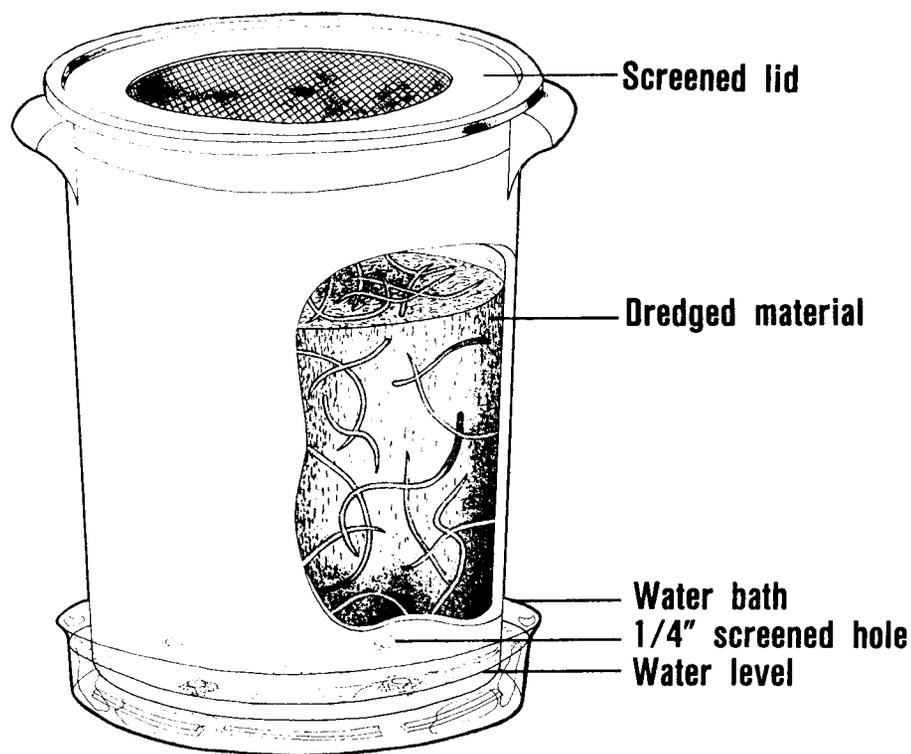


Figure 1. Setup for laboratory experimental chamber

worms were homogenized using a stainless steel Sorvall Omni-Mixer (DuPont Co.) and placed in acid-washed hexane-rinsed glassware. Samples of 5 g fresh weight for heavy metal analysis were oven-dried at 80° C for 24 hr and digested with nitric acid. Metal concentrations were measured using atomic absorption spectrometry. Organic compounds were extracted with hexane from 25-g fresh-tissue samples and measured using gas chromatography/mass spectrometry. Tabulations of test results are given in Appendix A.

Test Results

Example 1: Highly Contaminated Estuarine Sediment. In this case the earthworm bioassay procedure was used to predict the contaminant mobility for an upland (oxidized) disposal alternative prior to a dredging project. A highly contaminated sediment from the BRH FVP dredging site was collected and transported to the WES for growth-chamber bioassay tests. In order to simulate salt leaching due to rainfall and to enhance earthworm survivability, the sediment was washed until wash water indicated 0 ppt salt. The sediment was air-dried, pulverized, and rewet with distilled water to field capacity before the animals were added. As used here, field capacity is defined as the maximum amount of water that can be held within the pores of a soil after excess water has drained, usually for 24 hr.

Initial screening tests indicated that the BRH sediment was quite toxic to the worms while a similarly prepared reference sediment collected at the mouth of BRH was not. A series of toxicity tests indicated that survival for 7 days could be obtained only if the BRH sediment were diluted. A local woodland soil at the US Army Engineer Waterways Experiment Station (WES) was chosen as the dilution medium. Mixtures of 10 percent BRH sediment and 90 percent WES soil were used for the 7-day test. About 40 g (fresh weight) of earthworms were placed in approximately 1 kg each of the following substrates: 10 percent BRH sediment + 90 percent WES soil; 100 percent BRH reference sediment; and 100 percent WES soil. The tests were conducted in a controlled-temperature growth chamber at 20° C. No supplemental food was provided during the 7-day test period.

Total worm weights recovered from each of the three substrates decreased during the test period (Table A1). Although the worms were not counted, it was apparent that the 56-percent decrease in animal weight recorded in the BRH sediment + WES soil mixture was largely due to the reduction

in numbers of worms. The reduced weights from the other two substrates (16 and 12 percent) appeared to be due to starvation rather than die-off.

Results from the analysis of the earthworm tissue for cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), and mercury (Hg) in relation to substrate levels indicated that bioaccumulation was not demonstrated (Table A2). Some accumulation of Cr, Cu, Ni, and Pb was expected due to the high concentrations of these metals in the substrate material; however, the concentrations of these elements in the worm tissues were quite low. In contrast, Cd was found to be consistently higher in the worm tissue than in the substrate material. This may have been due to a higher-than-desirable background level of Cd (4.55 $\mu\text{g/g}$) in the worms prior to the test period or to the potential for the earthworm to accumulate Cd from low levels in the media (Hartenstein et al. 1980). The values reported in the literature for various earthworm species (Table A3) indicated Cd levels in worm tissues that were generally greater than those of the soil.

The earthworm bioassay was successful in determining that the BRH sediment is quite toxic to earthworms under upland conditions. However, there appears to be no indication that Cd or any other toxic heavy metal will accumulate to significant elevated levels in soil-dwelling invertebrates if the material, placed in an upland disposal environment, is diluted with uncontaminated soil. Therefore, the observed toxicity appears not to be solely related to metal concentrations.

Example 2: Restoration of Pyritic Mine Spoil Using Contaminated Dredged Material. In many locations there are large areas of unvegetated mine spoil adjacent to waterways where dredging is necessary and disposal areas must be found. It was proposed that such dredged material could be used for the restoration of abandoned mine spoil areas. The Ottawa, Ill., strip-mine reclamation project was initiated in 1978 as a demonstration of the feasibility of using a cover of dewatered dredged material to reclaim pyritic surface-mine spoil (Perrier et al. 1980). The main objectives of the reclamation were abatement of erosion and acid mine drainage by using dredged material as a medium for vegetation. The dredged material used in the demonstration was found to contain toxic heavy metals (Cd, Cu, Pb, and Ni); consequently, contaminant-mobility monitoring was necessary after vegetation became established (Simmers et al. 1984).

This study was designed to determine the major routes of contaminant mobility using the earthworm as an indicator in computing the bioavailability

of metals in the leaf litter, the surface layer of dredged material (30 cm), and a deep layer of dredged material near the mine spoil (100 cm). Also, these data were needed to clarify the contaminant mobility aspects of the restoration technique in relation to management of large-scale disposal operations.

Comparisons of the earthworm tissue levels of metals from the three test media and the two dominant plants at the site are shown in Table A4. The dominant plants, smooth brome grass *Bromua inermia* and tall fescue *Festuca elatior*, the source of the thick leaf litter (duff) layer on the site, were collected and analyzed. The main source of Cd appeared to be the leaf litter layer while Cu and Ni were apparently more bioavailable in the dredged material. Lead was apparently equally available in all three media.

Although the plants did not show an appreciable uptake of Cd, the earthworms exposed to the leaf litter indicated enhanced Cd availability. This is of critical concern in the management of such sites in the future. Removal of the duff of the grassland ecosystem by fire or mechanical harvesting may be a potential solution to reduce contaminant mobility via soil invertebrates in dredged material disposal sites such as this one. These data clearly show the need to examine all components of an ecosystem in order to fully describe routes of contaminant mobility, and that the evaluation of plant uptake alone may not address the bioavailability of contaminants from the duff or leaf litter.

Example 3: Confined Disposal Site. Between 1972 and 1976, about 720,000 m³ of dredged material from Buffalo Harbor was placed in an artificial lagoon on the New York shore of Lake Erie at Times Beach. The dredged material was heavily contaminated as a result of the activities of several industries including an oil refinery, steel plants, and an aniline dye chemical plant on the water front adjacent to the dredging site. The disposal operation resulted in the creation of an area composed of an aquatic, a wetland, and an upland environment, and prolific wildlife developed at the disposal site.

This site was selected for investigation because of the recognized ecological value of a continuous sediment/soil interface gradient from a pond with a maximum depth of about 2 m to a woodland at about 2 m above groundwater levels. This situation also provided an unique opportunity to study the interactions between the combination of physical conditions and biotic development on the one hand and contaminant mobility on the other hand.

Figure 2 is a sketch map indicating some of the vegetation present nine years after disposal was terminated and the location of the sampling stations (Marquenie et al. In Press).

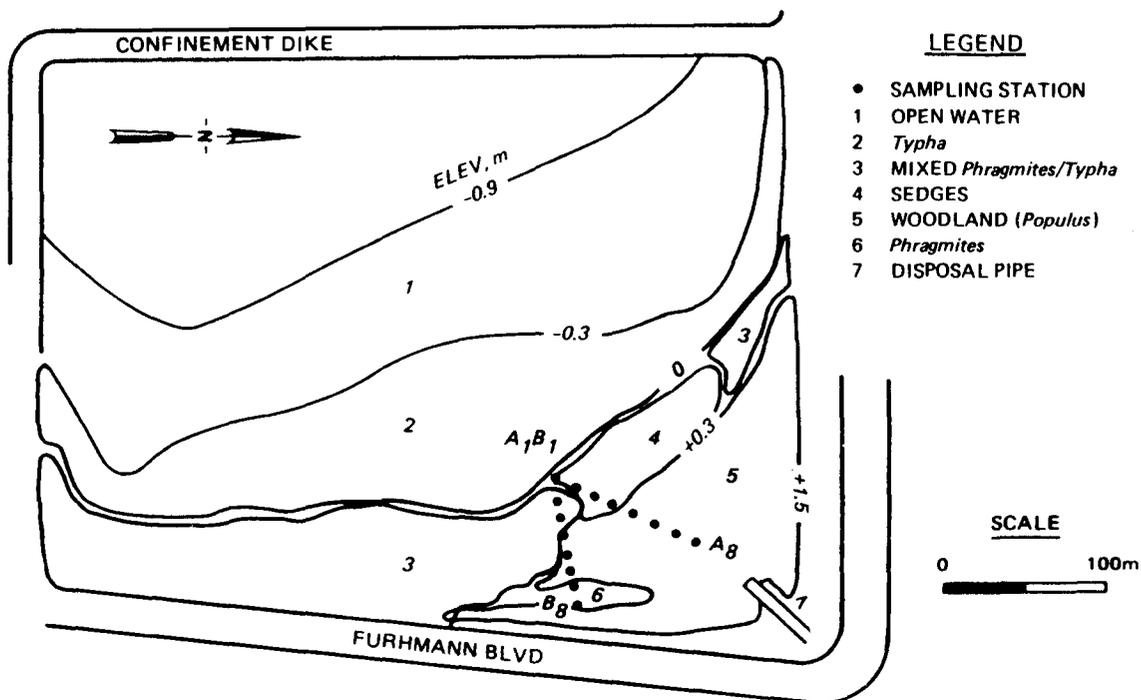


Figure 2. Locations of sampling stations and vegetative types at Times Beach confined disposal site

The results of the bioassay analyses are shown in Table A5. It is evident that the disposal site is relatively contaminated and that there appears to be a variation in the concentration of metals and organic contaminants along the transects. The highest soil concentrations of contaminants generally were found in the A₂B₂ wetland region but also were high in the A₈ and B₈ upland regions. Exposed earthworms also showed varied values of bioaccumulation in these areas as reflected in tissue concentrations of heavy metals and total PCBs (Table A5) and individual PAHs (Table A6). Transect A was found to most accurately follow the soil/water gradient and, therefore, showed a more distinct pattern of substrate concentration and bioavailability than did Transect B.

Conclusions

The results of the animal bioassay were found to be useful in the evaluation of the contaminant mobility from dredged material placed in upland disposal facilities and in the prediction of contaminant mobility as part of the

decision-making process prior to selection of a disposal alternative, such as upland disposal or wetland creation. The earthworm *Eisenia foetida* showed a high level of sensitivity as a bioassay animal in its ability to bioaccumulate various heavy metals, PCBs, and PAHs from a variety of contaminated substances. The animal bioassay procedure appears to be a valuable tool for predicting and evaluating the contaminant availability from dredged material of either freshwater or marine origin before or after its upland disposal.

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Table A1
Weight Changes of Earthworms after 7-day Exposure
to Various Substrates (BRH)

<u>Substrate</u>	<u>Weight of Worms, g (wet wt)</u>		<u>Weight Loss in 7 Days, %</u>
	<u>Initial</u>	<u>Final*</u>	
10% BRH Sediment + 90% WES Soil	40	17.4 ± 5.4	56
BRH Reference Sediment	40	33.7 ± 1.8	16
WES Soil	40	35.0 ± 1.5	12

* Mean of 3 replications ± standard deviation.

Table A2
Contaminant Concentrations in Earthworms after Exposure to Various Substrates (BRH)

Contaminant	Type of Substrate - Contaminant Concentration, $\mu\text{g/g}$ (dry wt)						
	10% BRH Sediment + 90% WES Soil		BRH Reference Sediment		WES Soil		Background Worm Tissue*
	Substrate	Tissue*	Substrate	Tissue*	Substrate	Tissue*	
Cd	2.9	5.83 \pm 0.80	2.9	4.26 \pm 0.55	0.2	3.80 \pm 0.34	4.55 \pm 0.21
Cr	191	4.73 \pm 1.55	314	6.96 \pm 0.28	8.07	2.53 \pm 0.06	1.90 \pm 0.20
Cu	330	34.1 \pm 1.4	438	33.8 \pm 1.3	9.86	12.0 \pm 0.60	11.25 \pm 0.52
Ni	29.6	6.03 \pm 2.97	45	3.07 \pm 0.84	15.0	3.33 \pm 1.18	0.49 \pm 0.46
Pb	63.5	7.6 \pm 0.13	135	5.13 \pm 0.63	10.3	4.7 \pm 0.10	5.23 \pm 0.40
Zn	176	110.5 \pm 2.3	329	112.3 \pm 1.5	29.5	102.6 \pm 0.6	118.5 \pm 2.9
Hg	0.19	<0.050	0.475	<0.050	<0.049	<0.050	<0.050

* Mean of 3 replications \pm standard deviation.

Table A3
Cadmium Levels in Earthworms and Soils Reported in Literature

Reference	Locality	Species	Cadmium Levels µg/g (dry wt)	
			Tissues	Soil
Andersen (1979)	Denmark	<i>Allolobophora longa</i>	5.7 - 11.8	0.14 - 0.99
		<i>A. caliginosa</i>	6.9 - 10.9	0.14 - 0.99
		<i>A. rosea</i>	10.9 - 26.9	0.14 - 0.99
		<i>A. chlorotica</i>	10.9 - 16.2	0.14 - 0.99
		<i>Lumbricus terrestris</i>	8.8 - 16.9	0.14 - 0.99
Czarnowska and Japkiewicz (1978)	Poland	Unidentified	3.5 - 17.0	0.11 - 1.10
Gish and Christensen (1973)	USA	<i>A. species</i> and <i>L. terrestris</i> combined	5.9 - 14.4	0.66 - 1.59
Van Hook (1974)	USA	<i>A. species</i> , <i>L. species</i> and <i>Octolasion</i> species combined	3.1 - 9.3	0.23 - 0.80
Ireland (1979)	Wales	<i>Eiseniella tetraeda</i>	3.0 ± 0.3	4.0 ± 0.2
		<i>Dendrobaena veneta</i>	7.0 ± 1.0	4.0 ± 0.2
		<i>L. rubellus</i>	15.0 ± 5.0	2.0 ± 0.1
		<i>L. rubellus</i>	4.0 ± 0.1	4.0 ± 0.2
		<i>L. rubellus</i>	2.5 ± 3.0	4.0 ± 0.3
Beyer et al. (1982)	USA	<i>Aporrectodea tuberculata</i> , <i>Ap. turgida</i> , <i>Ap. longa</i> , and <i>L. terrestris</i> combined	4.8	0.1

Table A4
Contaminant Concentrations in Earthworms, Plants, and Substrates
from Mine Spoil Restoration Site, Ottawa, Ill.

Variable	Material Tested	Concentration, $\mu\text{g/g}$ (dry wt)			
		Cd	Cu	Pb	Ni
Background	Earthworm tissue	3.67 \pm 0.51	9.55 \pm 1.00	1.50 \pm 0.65	2.00 \pm 0.77
	Brome grass plant tissue*	0.78	8.09	6.06	4.47
	Tall fescue plant tissue*	0.73	7.83	27.16	11.00
Bioassay substrate:					
Leaf litter	Earthworm tissue	14.07 \pm 5.37	9.17 \pm 1.56	2.17 \pm 0.46	1.87 \pm 0.46
	Substrate	3.27 \pm 0.73	15.66 \pm 1.65	-	5.89 \pm 0.20
Dredged material surface layer**	Earthworm tissue	9.03 \pm 0.89	25.83 \pm 4.20	2.87 \pm 0.69	5.23 \pm 0.61
	Substrate	10.00 \pm 0.50	127 \pm 8.60	620 \pm 69.9	51.50 \pm 3.20
Dredged material deep layer†	Earthworm tissue	8.23 \pm 0.21	25.37 \pm 1.03	5.27 \pm 2.00	5.33 \pm 0.31
	Substrate	9.18 \pm 1.63	116.7 \pm 10.3	585 \pm 22.8	50.13 \pm 2.16

* Simmers et al. (1984)

** 30 cm.

† 100 cm.

Table A5
Contaminant Concentrations in Earthworms after Exposure to
Various Times Beach Substrates

<u>Transect Location</u>	<u>Component</u>	<u>Concentration, $\mu\text{g/g}^*$</u>					
		<u>Cd</u>	<u>Cu</u>	<u>Hg</u>	<u>As</u>	<u>PCBs (10 isomers)</u>	<u>PAHs (22 compounds)</u>
A8 (upland)	Substrate	2.10	116.0	2.10	25.0	0.462	40.93
	Tissue	8.86	27.7	0.48	21.1	3.950	21.06
A6 (transition)	Substrate	0.76	60.0	1.52	20.0	0.712	7.03
	Tissue	6.54	17.3	0.98	17.5	4.426	1.95
A2 (wetland)	Substrate	2.73	148.0	4.22	38.5	1.004	45.52
	Tissue	11.70	32.1	1.39	24.0	4.520	11.78
B2 (wetland)	Substrate	9.61	334.0	8.50	72.4	0.961	63.96
	Tissue	10.80	57.6	0.81	23.9	6.720	38.88
B6 (transition)	Substrate	5.33	228.0	4.78	58.8	0.743	32.09
	Tissue	17.60	36.2	1.14	35.3	3.620	7.46
B8 (upland)	Substrate	7.74	269.0	7.45	53.0	0.480	35.10
	Tissue	16.0	46.7	1.77	53.8	3.125	8.49
Reference	Substrate	0.39	16.5	0.74	3.40	<0.128	\leq 3.49
	Tissue	3.04	10.1	0.06	8.72	<0.410	\leq 0.77

* Concentrations in substrates reported as dry weight; concentrations in tissues reported as ash-free dry weight.

Table A6
Significant PAHs in Worm Tissue and Times Beach Substrates*

Transect Location	Component	Concentration, $\mu\text{g/g}^{**}$							
		Pyrene	Tri-phenylene	Benzo(e) Pyrene	Benzo(b) Fluoranthene	Benzo(k) Fluoranthene	Benzo(a) Pyrene	Benzo (g,h,i) perylene	Ideno (1,2,3-c,d) Pyrene
A8	Substrate	2.9	≤ 0.15	1.8	3.0	1.7	3.8	3.4	3.0
	Tissue	3.9	≤ 0.015	1.5	2.1	1.3	2.8	1.5	1.3
A6	Substrate	0.53	≤ 0.15	0.32	0.43	0.25	0.56	0.26	0.47
	Tissue	0.14	0.074	0.099	0.15	0.11	0.16	0.19	0.21
A2	Substrate	2.7	≤ 0.15	2.1	3.5	1.9	5.2	4.5	3.1
	Tissue	0.53	1.6	0.75	1.3	0.65	1.8	1.1	1.1
B2	Substrate	2.5	≤ 0.15	4.0	5.6	2.9	8.6	7.6	6.7
	Tissue	≤ 0.015	3.6	4.2	5.4	2.6	7.4	3.2	5.0
B6	Substrate	1.5	≤ 0.15	2.1	2.3	1.2	3.6	3.7	2.9
	Tissue	0.093	0.57	0.65	0.54	0.24	0.93	0.93	1.6
B8	Substrate	2.1	≤ 0.15	2.1	2.4	1.4	3.6	3.9	3.1
	Tissue	0.15	0.69	1.1	0.67	0.37	1.3	1.5	0.83
Reference	Substrate	≤ 0.15	≤ 0.15	≤ 0.2	≤ 0.025	0.032	≤ 0.02	0.80	≤ 1.01
	Tissue	≤ 0.15	0.021	≤ 0.02	≤ 0.002	0.0047	≤ 0.002	0.160	0.029

* Summary of preliminary data.

** Concentrations in substrates reported as dry weight; concentrations in tissues reported as ash-free weight.



Environmental Effects of Dredging Technical Notes



UPLAND DISPOSAL SITE MANAGEMENT FOR SURFACE RUNOFF WATER QUALITY

PURPOSE: This technical note describes how the results of the surface runoff water quality test can be used to predict the water quality of surface runoff from confined upland disposal sites and to develop appropriate management plans before dredging. This procedure was developed as part of the Field Verification Program (FVP) and is based on (a) test data collected from Black Rock Harbor, Conn., dredged material using the surface runoff water quality test in a laboratory environment and (b) the results of field studies that tested techniques for controlling surface runoff water quality from an upland disposal site that contained the same contaminated dredged material from Black Rock Harbor used in the laboratory study.

BACKGROUND: Contaminated dredged material is often placed in confined upland disposal sites where movement of contaminants by surface runoff during storms is an important environmental concern. When dredged material is first placed in a confined upland disposal site, it is usually anaerobic with a near-neutral pH (7.0) and a high moisture content (>40 percent). Under these conditions, many contaminants such as heavy metals remain tightly bound to particulates and are poorly soluble. As the dredged material dries and oxidizes, physicochemical changes occur in the material that may increase the solubility of many heavy metals. The more soluble forms of the heavy metals then have a greater potential for causing adverse environmental effects due to increased mobility through surface runoff and increased bioavailability.

The surface runoff water quality test was developed by the Environmental Laboratory to provide Corps of Engineers (CE) Field Operating Agencies (FOAs) with a method for evaluating surface runoff water quality from contaminated dredged material before dredging and disposal. This test can be used in conjunction with plant and animal bioassay, leachate, and effluent tests to evaluate upland disposal of contaminated dredged material. If needed, effective control measures and restrictions can be identified before disposal. Upland disposal can also be evaluated in relation to other disposal alternatives such as open-water or wetland disposal to select the most environmentally sound disposal alternative.

ADDITIONAL INFORMATION OR QUESTIONS: Contact one of the authors, Mr. John G. Skogerboe (601) 634-3716 (FTS 542-3716) or Dr. Charles R. Lee (601) 634-3585 (FTS 542-3585), or the EEDP Program Manager, Dr. Robert M. Engler (601) 634-3624 (FTS 542-3624).

Introduction

The surface runoff water quality test was developed under the Environmental Impact Research Program (EIRP) to predict soil loss and surface runoff water quality from CE construction sites (Lee and Skogerboe 1984). The test was further refined and field verified for confined upland disposal of contaminated dredged material under the FVP (Skogerboe et al. 1987).

The surface runoff water quality test uses the Waterways Experiment Station (WES) rotating disk rainfall simulator designed to duplicate the kinetic energy of natural rainfall (Westerdahl and Skogerboe 1982) and laboratory lysimeters placed in a temperature-controlled greenhouse. Sediment is collected from a proposed dredging site, brought to the WES, and tested during both the wet anaerobic stage and the dry oxidized stage. Results are then statistically compared to water quality criteria chosen by the agency sponsoring the study. This technical note reports results collected from surface runoff water quality tests conducted on contaminated dredged material from Black Rock Harbor.

Results of field tests conducted to evaluate methods for controlling surface runoff water quality are also presented. Soil amendments such as lime, sand, gravel, and horse manure were incorporated into field plots to reduce the solubility of heavy metals, increase establishment of vegetation, and reduce erosion of contaminated material from the FVP upland disposal site. The soil amendments along with several tolerant plant species were selected from an instruction report, "Restoration of Problem Soil Materials at Corps of Engineers Construction Sites," developed by Lee et. al. 1985. Surface runoff water quality tests were conducted on the field plots to test the effectiveness of the amendments for controlling surface runoff water quality.

Methods

Dredged material from Black Rock Harbor was brought to WES and tested using the surface runoff water quality test. The laboratory lysimeter had a surface area of 4.5 by 1.5 m and was filled to a depth of 0.3 m. A series of rainfall simulations were applied to the dredged material while wet and anaerobic. Approximately 6 months later, another series of rainfall simulations

were applied to the dry oxidized dredged material. Each rainfall simulation was 5.1 cm/hr for 0.5 hr. Runoff samples were collected during each storm and analyzed for suspended solids (SS), cadmium (Cd), copper (Cu), chromium (Cr), manganese (Mn), nickel (Ni), and zinc (Zn) in unfiltered and filtered water samples.

The results of the tests were compared to the US EPA Water Quality Criteria for the Protection of Aquatic Life. Criteria (such as the Lake Michigan Water Quality Standards for receiving water quality or background water quality) have been used for similar evaluations of other contaminated dredged material. All of these criteria were used for comparison to filtered or soluble contaminants in surface runoff. No criteria currently exist for comparison to unfiltered or total heavy metal concentrations in water samples.

Methods for controlling surface runoff water quality from the contaminated Black Rock Harbor dredged material were tested at the upland disposal site in Bridgeport, Conn. The test plots (2 by 6.1 m), which included five soil treatments and four plant species, were established 2 years after disposal when the dredged material had dried and oxidized.

a. Treatments.

1. Control, no amendments
2. Lime, 28.2 mt/ha (metric tons/hectare)
3. a. Lime, 28.2 mt/ha
b. Sand, 13 cm surface layer
c. Limestone gravel, 6.6 cm surface layer
4. a. Lime, 28.2 mt/ha
b. Horse manure, 112 mt/ha
5. a. Lime, 28.2 mt/ha
b. Sand, 13 cm surface layer
c. Limestone gravel, 6.6 cm surface layer
d. Horse manure, 112 mt/ha

b. Plant Species.

1. *Agropyron elongatum* (Tall Wheatgrass) 'Alkar'
2. *Festuca arundinacea* (Tall Fescue) 'Alta'
3. *Puccinella distans*
4. *Sporobolus virginicus*

One year after the test plots were established, surface runoff water quality tests were conducted at the upland disposal site on control plots; plots amended with lime, sand, and gravel; and plots amended with lime, sand gravel, and manure. The rainfall simulator was transported to the field site for the tests. Simulated storms were identical in duration and

intensity to those used in the greenhouse lysimeter surface runoff water quality tests.

Results and Discussion

Laboratory lysimeter tests

During the wet anaerobic period, heavy metals were poorly soluble in surface runoff (Table 1). Concentrations of metals in unfiltered water

Table 1
Surface Runoff Water Quality from Black Rock Harbor Dredged Material

Condition of Dredged Material	Parameter	Concentrations, Mg/ℓ		EPA Criteria mg/ℓ
		Unfiltered	Filtered	
Wet anaerobic	SS	10,326	N	N
	Cd	0.328	0.005	0.0015-0.0024
	Cu	34.6	0.011	0.012-0.043
	Mn	3.83	0.112	N
	Ni	2.04	0.013	1.3-3.1
	An	16.0	0.120	0.180-0.570
	Cr	19.3	0.004	2.2-9.9
Dry oxidized	SS	167	N	N
	Cd	0.133	0.112*	0.0015-0.0024
	Cu	0.970	0.622*	0.012-0.043
	Mn	0.190	0.158	N
	Ni	0.183	0.128	1.3-3.1
	Zn	3.62	1.06	0.180-0.570
	Cr	0.255	0.008	2.2-9.9

* Filtered concentrations statistically greater than the EPA criteria (P = 0.05).

N Indicates that no values are available.

samples exceeded the concentrations in filtered samples by 1 to 3 orders of magnitude, indicating that the heavy metals were tightly bound to the particulates. During this period, the dredged material was highly erosive so that high concentrations of insoluble heavy metals would have been discharged from a disposal site if the SS were not removed from the surface runoff.

As the dredged material dried and oxidized, many of the heavy metals became more soluble in surface runoff. Except for Cr, filtered concentrations were not significantly different (P = 0.05) from the unfiltered

concentrations, indicating that the metals were present in mostly soluble forms. The SS and metal concentrations in the unfiltered surface runoff from the dry oxidized dredged material were significantly less than concentrations from the wet anaerobic dredged material. Filtered heavy metal concentrations from the dry oxidized dredged material, however, were equal to or greater than the filtered concentrations from the wet anaerobic dredged material.

Results of the surface runoff water quality test on the Black Rock Harbor dredged material showed that very different management strategies would be required for controlling contaminants in surface runoff during the wet anaerobic period and during the dry oxidized period. During the wet anaerobic period, most of the heavy metals in surface runoff could be removed by trapping the SS before the runoff is discharged from the disposal site. Concentrations of Cd, Cu, Cr, Ni, Mn, and Zn in filtered surface runoff from the wet anaerobic Black Rock dredged material were statistically equal to or less than the EPA criteria and would require no restrictions or control measures. If the values had exceeded the criteria, additional restrictions or control measures would have been required.

After the dredged material dried and oxidized, the management strategy changed for controlling surface runoff water quality. Heavy metals were no longer tightly bound to the particulates and had become mostly soluble. Trapping of particulates could, therefore, no longer contain the contaminants in the disposal site. Comparing of metal concentrations in filtered surface runoff to the EPA criteria showed that concentrations of Cd, Cu, and Zn exceeded the criteria. Concentrations of Cd, in particular, exceeded the criteria by two orders of magnitude. Management practices under these conditions might include selecting one or more restrictions or control measures: capping, containment of all runoff on the site, runoff treatment, or soil amendments to reduce the solubility of the contaminants. (The FVP field upland disposal site was managed to contain most of the contaminants and surface runoff in the disposal site.)

Field tests

Because of the high salinity in the dredged material, establishment of vegetation on the upland Black Rock Harbor disposal site was difficult. No vegetation grew on the control plots, lime plots, or lime, sand, and gravel plots. Some vegetation was established on plots amended with lime and manure and on the plots amended with lime, manure, sand, and gravel. Vegetation on

these plots grew mostly in cracks in the dredged material where the amendments had accumulated.

Results of surface runoff water quality tests conducted on the site management test plots are presented in Table 2. Heavy metal concentrations in

Table 2
Effect of Soil Amendments on Heavy Metal Concentrations in Filtered
and Unfiltered Samples

Sample Type	Treatment	Parameter - Concentration, mg/l*					
		Cd	Cu	Cr	Ni	Mn	Zn
Unfiltered	Control	0.55 A	57 A	12 A	3.5 A	4.1 A	40 A
	Lime, sand, gravel	0.40 AB	38 AB	7.9 AB	2.7 AB	3.4 A	27 AB
	Lime, sand, gravel, manure	0.06 B	10 B	3.9 B	0.95 B	0.85 B	3.7 B
Filtered	Control	0.56 A#	47 A#	0.49 A	3.1 A	3.1 A	40 A#
	Lime, sand, gravel	0.36 AB#	31 A#	0.23 AB	2.2 A	2.6 A	27 AB#
	Lime, sand, gravel, manure	0.02 B#	2.0 B#	0.004 B	0.21 B	0.33 B	2.3 B#

* Treatments with the same letters were not significantly different (P = 0.05).

Value exceeds the EPA criteria (P = 0.05).

surface runoff from plots amended with lime, sand, and gravel tended to be lower than concentrations in surface runoff from the control plots but were not significantly different. The addition of horse manure to lime, sand, and gravel did, however, significantly reduce concentrations of Cd, Cu, Cr, Ni, Mn, and Zn in unfiltered and filtered water samples. The addition of horse manure also significantly reduced the solubility of Cd, Cu, Ni, and Zn in surface runoff (Table 3).

Table 3
Percentage of Soluble Heavy Metals in Surface Runoff from Field
Plots Treated with Different Soil Amendments

Treatment	Parameter - Concentration, mg/l*					
	Cd	Cu	Cr	Ni	Mn	Zn
Control	104 A	73 A	5 A	77 A	69 A	100 A
Lime, sand, gravel	99 A	72 A	3 A	73 A	66 A	92 A
Lime, sand, gravel, manure	47 B	15 B	1 A	22 B	35 A	57 B

* Treatments with the same letters were not significantly different (P = 0.05).

Discussion

Heavy metal concentrations in surface runoff from the field plots were greater than those of the laboratory lysimeter tests. The field plots contained dredged material that had undergone considerable weathering beyond that of the dredged material tested in laboratory lysimeters and earlier field verification test plots (Skogerboe et al. 1987). The field plots were established 2 years after the dredged material was placed in the upland disposal site, and the surface runoff tests were conducted 3 years after disposal. During the 3 years, a control measure based on the laboratory lysimeter data was implemented by maintaining weir structures to prevent contaminants from being discharged from the site. This control measure had significant effects by containing salts, eroded particulates, surface runoff water, and soluble and insoluble heavy metals within the disposal site.

Soil amendments were effective in reducing heavy metal concentrations in filtered and unfiltered surface runoff from the Black Rock Harbor dredged material. Filtered metal concentrations were reduced by an order of magnitude by the addition of the horse manure but still exceeded the EPA criteria and required additional restrictions or control measures. If a mixing zone were being considered in the receiving water body outside of the disposal site, the size of the required mixing zone could be reduced by an order of magnitude. If heavy metal concentrations in surface runoff had been reduced to levels equal to or less than the selected criteria, then no additional control measures or restrictions would have been required.

The previous discussion illustrates how surface runoff water quality tests can be used to evaluate potential contaminant mobility from upland disposal sites and the influence of selected restrictions or control measures such as soil amendments and the use of tolerant plant species to control soil erosion and surface water quality.

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Environmental Effects of Dredging Technical Notes



UPLAND ANIMAL BIOASSAYS OF DREDGED MATERIAL

PURPOSE: This note follows Technical Note EEDP-02-2 on this subject and provides additional information concerning the concept of using an upland animal as an indicator of bioavailable contaminants in dredged material. The relationship of the WES index species *Eisenia foetida* to field earthworm species likely to colonize an upland dredged material environment is important to the interpretation and prediction of disposal consequences.

This note relates heavy metal uptake by four earthworm field species on eight substrates, which were previously used in WES plant bioassay studies in Europe, to the WES index earthworm *E. foetida*. This is necessary for several reasons. First, the Field Verification Program (FVP) upland animal bioassay must be field verified with a colonizing species and not the laboratory index species. Second, Corps of Engineers District/Division personnel need to know that field species colonizing a site can be related to WES index species. Third, the data presented here will permit the WES plant bioassay data to be related to the animal data in the FVP.

The text of this note was prepared by Dr. E. A. Stafford, Rothamsted Experimental Station, Harpenden, United Kingdom. It is a summary of a report entitled "Comparison of Heavy Metal Uptake by *E. foetida* with That of Other Common Earthworms" prepared by Dr. Stafford in cooperation with Dr. C. A. Edwards, who is now at Ohio State University, through a research contract issued by the European Research Office, US Army Research, Development and Standardization Group, United Kingdom.

BACKGROUND: Animal bioassay test procedures were evaluated, field tested, and verified for dredged material of marine origin under the "Interagency Field Verification of Testing and Predictive Methodologies for Dredged Material Disposal Alternatives" (FVP). The bioassay procedure is not only a relatively simple method for ecological evaluation and environmental assessment of potential upland placement of dredged material, it is a useful postdisposal bio-monitoring procedure as well.

The initial laboratory evaluations indicated that the FVP dredged material was toxic to earthworms, and this result was subsequently verified in the field. As the index earthworms did survive in washed FVP Black Rock Harbor (near Bridgeport, Conn.) dredged material, it was suspected that the observed toxicity was directly related to salinity and not to a contaminant.

Conditions favorable for the colonial establishment of earthworms at the FVP upland field site currently do not exist and probably will occur only when the salinity of the dredged material decreases. At that time, the accumulation of contaminants by the earthworms that form an important part of the terrestrial food web can be related to that predicted by the WES index species. However, the index species functions only as a "white rat" or surrogate in the laboratory and never a prevalent colonial species.

Additional calibration of the upland animal bioassay to biomonitoring procedures, particularly concerning upland habitats on dredged material of marine origin, will be reported in later technical notes.

ACKNOWLEDGMENTS: The author wishes to thank Mr. V. Cosimini and Mr. M. Fearnhead for operating the ICP instrument, the Soil Survey of England and Wales for analysis of soil properties and Dr. S. P. McGrath of Rothamsted Experimental Station, Harpenden, United Kingdom, for helpful discussion and collaboration during the study. This research was funded by the Field Verification Program, Dr. R. M. Engler, Program Manager, through the European Research Office, US Army Research, Development and Standardization Group, U. K. under Contract Number DAJA 45-84-C-0027.

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Introduction

Earthworms have great potential for use as bioassay/biomonitor organisms in studies of contaminant uptake and possess many characteristics that make them ideally suited for this purpose (Ma 1982). Studies have demonstrated that native species of earthworms, collected at contaminated sites, can be used to indicate biologically available levels of these contaminants (Helmke et al. 1979, Ireland 1983, Pietz et al. 1984). However, it is the species *Eisenia foetida* (which does not naturally colonize these sites) which has been recommended for use in the laboratory for the ecotoxicological testing of agricultural and industrial chemicals (European Economic Community (EEC) 1984), proposed as a bioassay species for assessing contaminant availability in waste materials, and used to determine the bioavailability of contaminants in dredged material (Marquenie and Simmers 1984).

Correlations between total and DTPA-extractable metal concentrations in contaminated substrates and the concentrations in the tissues of earthworms exposed to these substrates over a 28-day period may be used to establish their potential as biomonitor organisms. Due to differences in physiology and feeding behavior between earthworm species, the use of a surrogate species,

such as *E. foetida*, in studies of contaminant bioavailability needs to be validated by making interspecific comparisons of metal uptake.

Materials and Methods

Substrates

Eight substrates consisting of four soils, three dredged materials, and a river sediment were selected which contained elevated levels of at least one of the elements zinc (Zn), copper (Cu), cadmium (Cd), and lead (Pb) as well as a reference soil (Frongoch) with relatively low levels of heavy metals. The soils, dredged material, and sediment were similar to those used previously in bioassays using the WES index plant species. All substrates were air dried and sieved (<2 mm). Their chemical and physical properties are summarized in Table 1.

Earthworms

Four field species of earthworms were selected for comparison with *E. foetida*. These were *Lumbricus terrestris*, *Allolobophora longa*, *Allolobophora caliginosa*, and *Allolobophora chlorotica*. Earthworms were collected using formalin vermifuge from a substrate of similar metal composition to the reference soil (Frongoch). An initial sample of these earthworms was taken for chemical analysis; a subsample of the *E. foetida* was also analyzed to ensure low background concentrations of heavy metals. Only mature, clitellate earthworms were selected for experimental use in order to ensure comparable age and physiological condition.

Experimental procedure

Based on European Economic Community test stipulations (EEC 1984) and the results of other research, a stocking density of 1 g (wet weight) of earthworms per 40 g air-dry substrate was used. For the 28-day experimental period, 1,200 g of substrate (air-dry weight) was rewetted to field capacity, and the appropriate number of earthworms (to produce 5 g of tissue at the end of the test period) of each species was added. Each combination of substrate and earthworm species was assayed in triplicate.

After 28-day exposure to the substrates, earthworms were separated from the substrate by hand, weighed, and immediately dried and finely ground for the determination of heavy metal content and acid-insoluble residue. Bioavailability of heavy metals in the substrate was assessed in terms of uptake

Table I
Physical and Chemical Characteristics of the Soils

Soil (<2 mm)	Particle Size ^{1/}				Organic Carbon (%) ^{2/}	pH (1:2.5) in Water	C.E.C. ^{3/}	Zn	Cu	Cd	Pb
	200 µm- -2 mm	50 µm- -200 µm	2 µm- -50 µm	<2 µm							
Frongoch ^{4/}	14	6	56	24	4.3	6.0	20.8	116 ^{5/} (3.96) ^{6/}	22.9 (5.83)	0.91 (0.11)	75.9 (21.9)
Ystwyth ^{7/}	36	<1	55	9	2.0	6.2	7.3	790 (184)	34.7 (9.42)	3.02 (1.06)	1,442 (525)
Halkyn Mt. ^{7/}	6	5	58	31	2.5	8.1	18.4	1,383 (332)	120 (45.2)	3.40 (2.33)	945 (195)
Shipham ^{7/}	50	22	27	1	0.7	7.6	7.7	142,674 (637)	207 (1.50)	1,616 (25.8)	22,531 (64.8)
Parys Mt. ^{7/}	31	11	45	13	3.6	3.9 ^{8/}	23.5	249 (0.86)	483 (9.22)	2.73 (0.02)	1,443 (1.68)
Broekpolder ^{9/}	2	9	57	32	5.7	7.4	29.2	829 (239)	154 (50.8)	10.5 (5.56)	222 (20.3)
Oostabtpolder ^{9/}	6	<1	60	34	4.3	7.5	22.8	446 (126)	85.9 (29.5)	9.23 (3.47)	118 (15.5)
Spieringpolder ^{9/}	8	16	47	29	3.2	7.8	25.0	731 (110)	88.9 (27.1)	5.02 (2.11)	201 (40.4)
Neckar River Sediment	4	11	55	30	3.6	7.4	25.9	521 (129)	202 (79.4)	27.7 (13.99)	155 (33.2)

^{1/} Particle size separates as a percentage of oven-dry peroxidized substrate <2 mm.

^{2/} Other percentages based on oven-dry substrate <2 mm.

^{3/} C.E.C. = cation exchange capacity, measured in milliequivalents/100 g.

^{4/} Reference soil.

^{5/} Total (HNO₃/HClO₄) metal concentration in substrate.

^{6/} DTPA-extractable metal concentration in substrate in parentheses.

^{7/} Soil contaminated by metal mining waste.

^{8/} Parys Mt. substrate was initially toxic to earthworms, and this toxicity was reduced by addition of lime to raise the pH to 6.0.

^{9/} Contaminated dredged material.

into the earthworm tissue. It was therefore essential to distinguish between metal concentration in the earthworm tissue and metal concentration due to substrate in the earthworm gut. The acid-insoluble residue content of the earthworm sample was used as an inert marker to calculate the substrate content of the sample, and a correction factor was then applied to eliminate the heavy metal concentration resulting from substrate within the earthworm gut. This method has been described by Stafford and McGrath (1986).

Chemical analysis

Physical and chemical analysis of the samples was carried out using oven-dried samples of <2-mm particle size. DTPA-extractable metals were measured using a procedure based on the method of Lindsay and Norvell (1978) and modified by Lee et al. (1978). Total metal concentrations were determined after digestion in concentrated nitric and perchloric acids. Concentrations of total and extractable metals were determined by inductively coupled plasma emission spectrometry (ARL® 3400 instrument) with background correction using standards prepared in the appropriate solution. Acid-insoluble residue was determined gravimetrically after digestion in concentrated hydrochloric acid (Stafford and McGrath 1986).

Statistical methods

Linear regression analyses and associated correlation coefficients were calculated to determine the significance of the relationship between substrate metal levels (total and DTPA-extractable) and metal concentrations in the earthworm tissue, and to compare uptake of metals by *E. foetida* and each of the field species of earthworms.

Results and Discussion

The percent survival of earthworms over the 28-day period was high, with an overall mean of 92.3 percent (by weight). Metal concentrations present in the earthworm tissue were correlated with metal concentrations (total and DTPA-extractable) in the substrates to which the earthworms were exposed. The linear relationships are plotted in Figure 1, along with correlation coefficients. Data for Zn, Cd, and Pb concentrations showed a skewed distribution and were therefore converted to natural logarithms before carrying out statistical analysis.

Substrate physicochemical variables have been demonstrated to influence

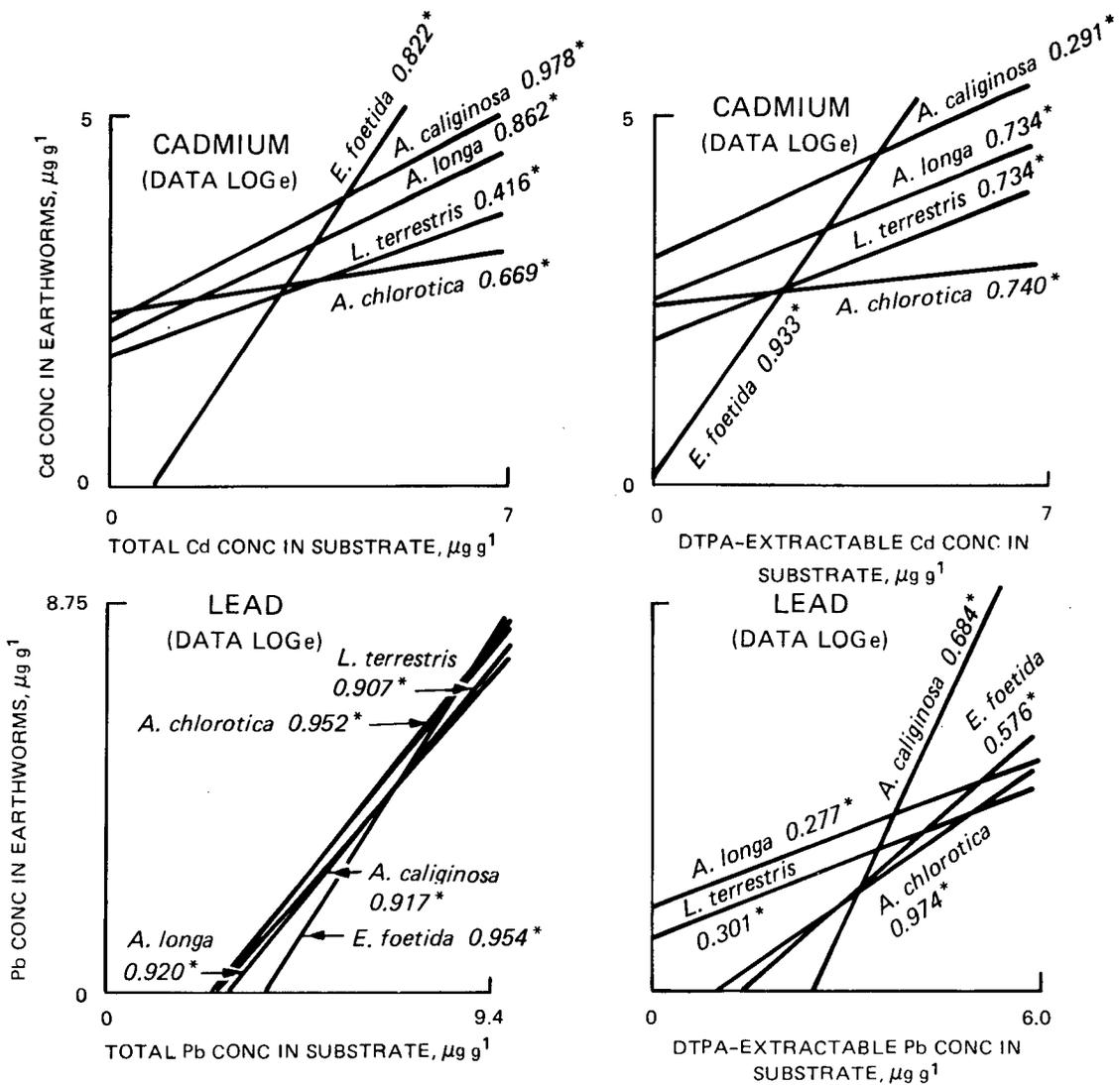


Figure 1. Relationship between metal concentration in earthworms and soil (*mean values significantly correlated within 95-percent confidence limits) (Continued)

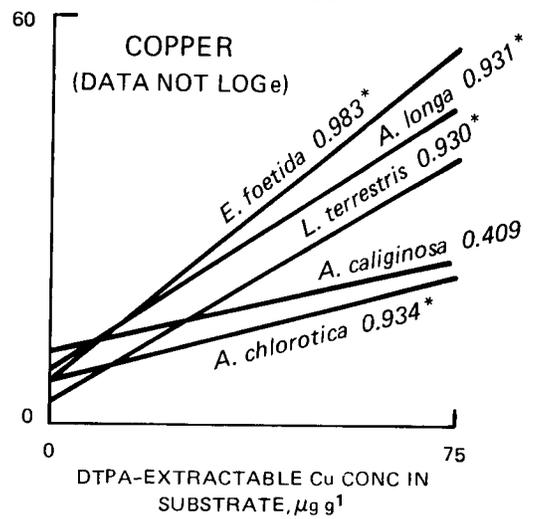
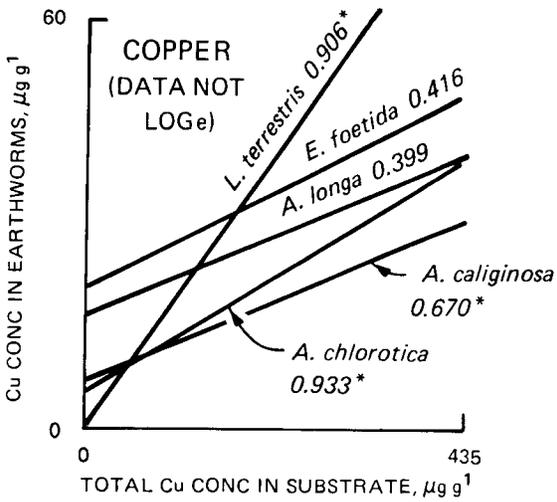
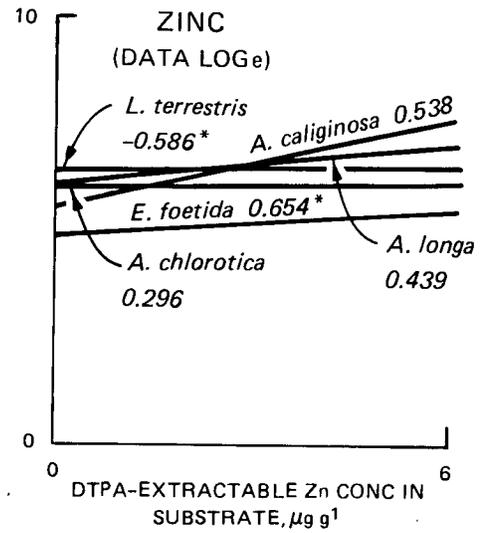
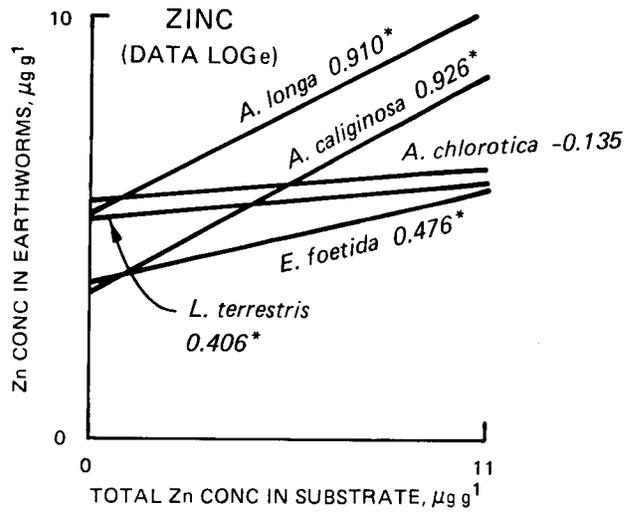


Figure 1. (Concluded)

metal uptake by earthworms (Ma 1982, Ireland 1983); however, despite these additional differences (Table 1), positive linear relationships were observed between earthworm Cu concentrations and DTPA-extractable substrate Cu levels for all species except *A. caliginosa*, between Cd concentrations in most of the earthworm species and total and DTPA-extractable Cd in the substrate, and between Pb concentrations in earthworms and total Pb in the substrate (Figure 1). Cu concentrations in earthworm tissue were more closely correlated with DTPA-extractable Cu in the substrate compared with total Cu in the substrate, while the opposite result emerged for the relationship between earthworm and substrate Pb concentrations. This may have been a result of the chemical extraction procedure used. The DTPA-extraction procedure was developed to assess possible deficiency of Zn, Fe, manganese (Mn), and Cu in the substrate and may provide a good indication of the availability of the elements for which it was developed. However, it is rarely used to assess Pb availability due to the poor results obtained.

Generally, the results obtained from the bioassay suggest that earthworm tissue concentrations of the elements Cu, Cd, and Pb represented a good indication of the bioavailability of these elements in the substrate. In contrast, no consistently significant relationship was evident between Zn concentrations in the earthworm tissue and the substrate. The slope of the line of best fit indicated that Zn concentrations in earthworm tissues increased only slowly with increasing substrate Zn levels (Figure 1). Similar results have previously been reported (Roberts and Johnson 1978, Martin and Coughtry 1982) and suggest that earthworms may have limited application in assessing the bioavailability of Zn in the substrate.

Metal concentrations present in the earthworm *E. foetida* were also correlated with metal concentrations measured in each of the field species studied. The linear relationships and correlation coefficients are shown in Figure 2. For the majority of combinations, a statistically significant ($p < 0.05$) linear correlation was observed between *E. foetida* and the field species. Although absolute concentrations of metals within the earthworm tissue may differ between species, a close, positive relationship in metal uptake between species, as observed in the present experiment (Figure 2), would suggest that one species can serve to indicate metal availability to the others. As a screening tool, the surrogate species selected for use in laboratory bioassays should represent the most consistency in specific

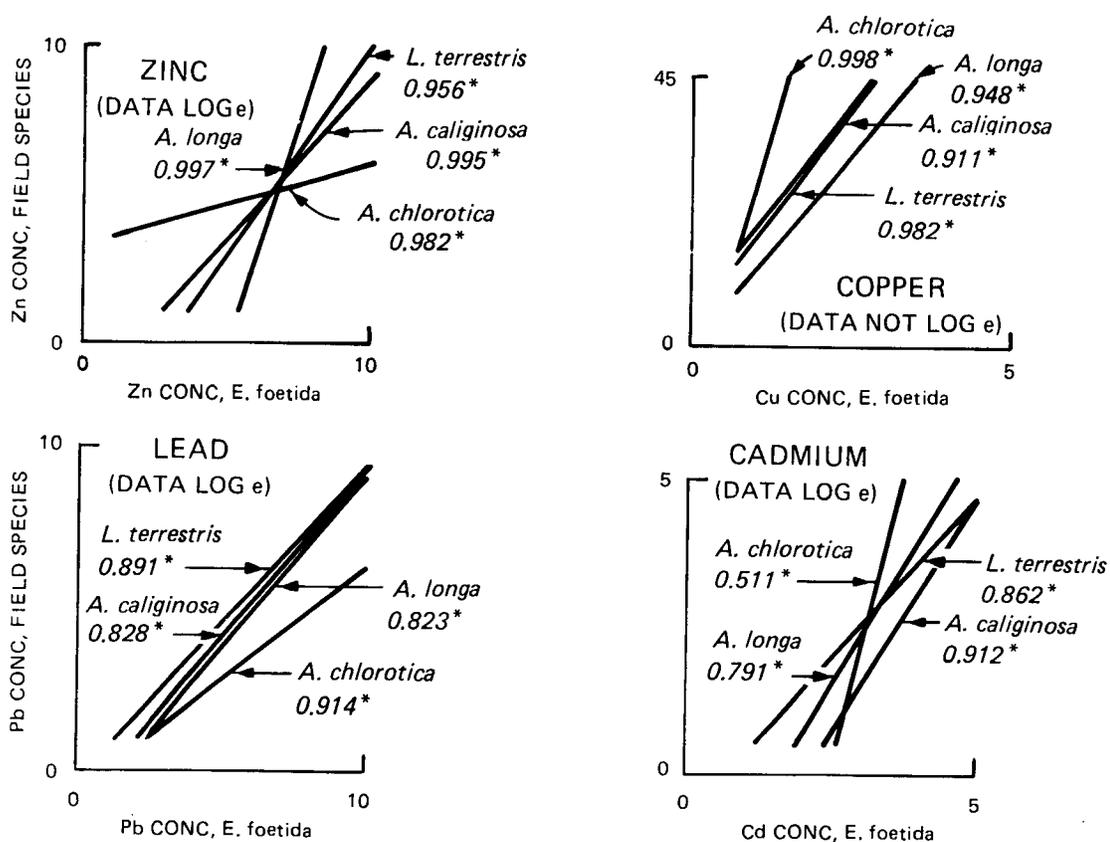


Figure 2. Relationship between metal concentrations in *E. foetida* and field species of earthworm (*mean values significantly correlated within 95 percent confidence limits)

contaminant uptake of the group. Figure 1 generally indicates a high rate of metal uptake by *E. foetida* compared with the field species of earthworm. In addition, Figure 1 shows that there was a consistently significant correlation ($p < 0.05$) between metal concentration in *E. foetida* and increasing metal concentrations in the substrate.

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Environmental Effects of Dredging Technical Notes



REFINEMENT AND SIMPLIFICATION OF COLUMN SETTLING TESTS FOR DESIGN OF DREDGED MATERIAL CONTAINMENT AREAS

PURPOSE: This note provides background and theory concerning the settling of dredged material slurries, a description of the evolution of column settling test procedures, and the technical basis for certain simplifications to the test procedures that are not contained in other published reports.

This note does not repeat the detailed instructions for conducting column settling tests that are contained in the recently issued Engineer Manual (EM) 1110-2-5027, "Confined Disposal of Dredged Material" (Office, Chief of Engineers (OCE) US Army 1987).

BACKGROUND: Confined dredged material containment areas (DMCAs) must be designed to provide the storage volume required for both dredged solids and the removal of suspended solids from the effluent discharged from the area. Various settling processes occurring in the DMCA control the initial solids removal, compaction, and fractional retention of solids. EM 1110-2-5027 provides design guidance for DMCAs. Laboratory column settling tests are an integral part of these design procedures.

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Settling Processes in Dredged Material Disposal Areas

Four types of settling are generally recognized. The type that occurs in any given suspension is a function of both the type of particle involved, particularly its surface characteristics, and the concentration of particles at a given time. The four types are listed below.

- I. Discrete Settling - The particles do not interact during settling. Each particle maintains its individuality and does not change in size, shape, or density while settling. Each particle settles as if it were alone and isolated.

- II. Flocculent Settling - The particles flocculate and agglomerate during settling. As the particles grow in size, they decrease in density because of entrained water, but they usually settle faster.
- III. Zone Settling - The concentration of particles is so great that they touch adjacent particles in all directions and maintain their spatial relationship, settling as a mass or open matrix. They usually exhibit a definite interface between the settling particles and the clarified liquid above. The particle matrix settles more slowly than the individual particles of the same size and density because the quantity of water being displaced by the settling particles is so great that the resulting upward velocities of the displaced water reduce the effective downward velocity of the particle mass.
- IV. Compression Settling - The concentration is so great that the particles rest on each other and mechanically support each other. The weight of the particles above slowly compresses the lower layers, increasing the pore pressure and squeezing out the water. This is also sometimes called thickening. In treatment plants, the settling is sometimes aided by slow stirring to break up the bridging action of the particles.

The relation of the different types of settling to type of particle and concentration of particles is shown in Figure 1.

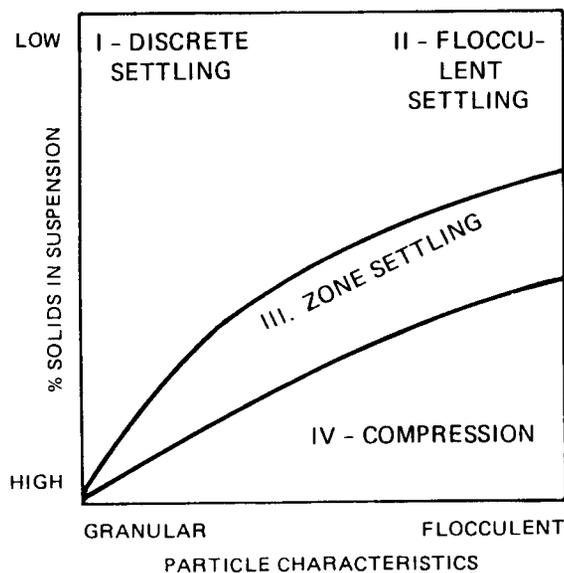


Figure 1. Types of settling

From Figure 1 it can be seen that discrete settling occurs only in suspensions with low concentrations of granular particles. This occurs in a DMCA with a small fraction of larger particles (sand and gravel) occasionally

encountered, or with bricks, crockery, shells, broken tools, and household items, etc., that were thrown or washed into the waterway. It never happens with hydraulically placed fine-grained dredged material, because the concentrations in the influent are so high (50 to 200 g/l) and because most of the particles (clay, silt, organic matter) are naturally flocculent. All of the other three settling processes may occur simultaneously in a DMCA, and any one may control the design of the DMCA.

Dredged material slurries will initially exhibit either flocculent settling or zone settling, depending primarily on the slurry concentration, particle type, and the salinity of the water. Slurries with salinity greater than 3 ppt will usually exhibit zone settling, because the dissolved ions act as a coagulant. These ions compress the electrical double layer, reduce the effective distance over which the natural repulsive surface forces are effective, and allow sediment particles to touch enough adjacent particles that a loose open matrix is formed, which settles as a mass. Freshwater slurries usually exhibit flocculent settling, but may exhibit zone settling if concentrations are high enough or if the particle surface characteristics are flocculent enough.

Regardless of whether the upper layers of the settling material in the containment area initially exhibit flocculent or zone settling, the bottom layers of settled material will exhibit compression settling, or thickening. As material accumulates and the concentration rises, successive layers will begin to rest on and be supported by the bottom of the disposal area and then each other, much like an accordion being slowly let down onto a hard surface. The change from flocculent or zone settling to compression settling, at which the bottom begins to provide some physical support, occurs at a concentration of approximately 200 to 300 g/l for most dredged material slurries.

Development of Procedures

The development of initial guidance for designing DMCA's was described by Montgomery (1978); Montgomery, Thackston, and Parker (1983); and Palermo, Montgomery, and Poindexter (1978). Montgomery (1978) developed laboratory test procedures for characterizing the settling properties of dredged material slurries and provided step-by-step instructions and example design calculations. These procedures allow the prediction of the concentration of

suspended solids in the effluent of a DMCA in which flocculent settling is occurring. The effluent from a DMCA in which zone settling is occurring (the clarified supernatant above the interface) was said to contain less than 1 g/l, but no procedure to quantify it further was suggested.

Palermo (1984, 1986) and Palermo and Thackston (in preparation) extended the work of Montgomery by applying the flocculent settling tests to the particles in the supernatant above the interface. These procedures may be used to predict the concentration of particles in the effluent to within a few milligrams per liter.

Field verification of these laboratory tests, along with the results from project studies and the experience of both WES and Corps District personnel in using the laboratory test and design procedures, is described by Averett, Palermo, and Wade (in preparation). These studies, plus additional simplifications and refinements described in this technical note, led to the testing and design procedures now contained in EM 1110-2-5027 (OCE 1987). The procedures originally recommended by Montgomery (1978) for designing DMCA's to ensure sufficient solids storage capacity, based on the results of the long-term compression settling test, have not been changed, and are included in EM 1110-2-5027 in their original form.

Testing Column

Both Montgomery's (1978) work with dredged material slurries and the pioneering work of Vesilind (1968) showed conclusively that wall effects in small columns will greatly affect the settling rate, sometimes positively and sometimes negatively, depending on solids concentrations and characteristics. Montgomery's (1978) work showed that 20 cm (8 in.) was the smallest diameter column in which settling would be comparable to that occurring in the field. A schematic of the standard testing column recommended by Montgomery is shown in Figure 2.

Pilot Test

The earlier works of Montgomery (1978) and Palermo, Montgomery, and Poindexter (1978) provided guidance on how to conduct both zone settling and flocculent settling tests on the bulk slurries, and how to distinguish between

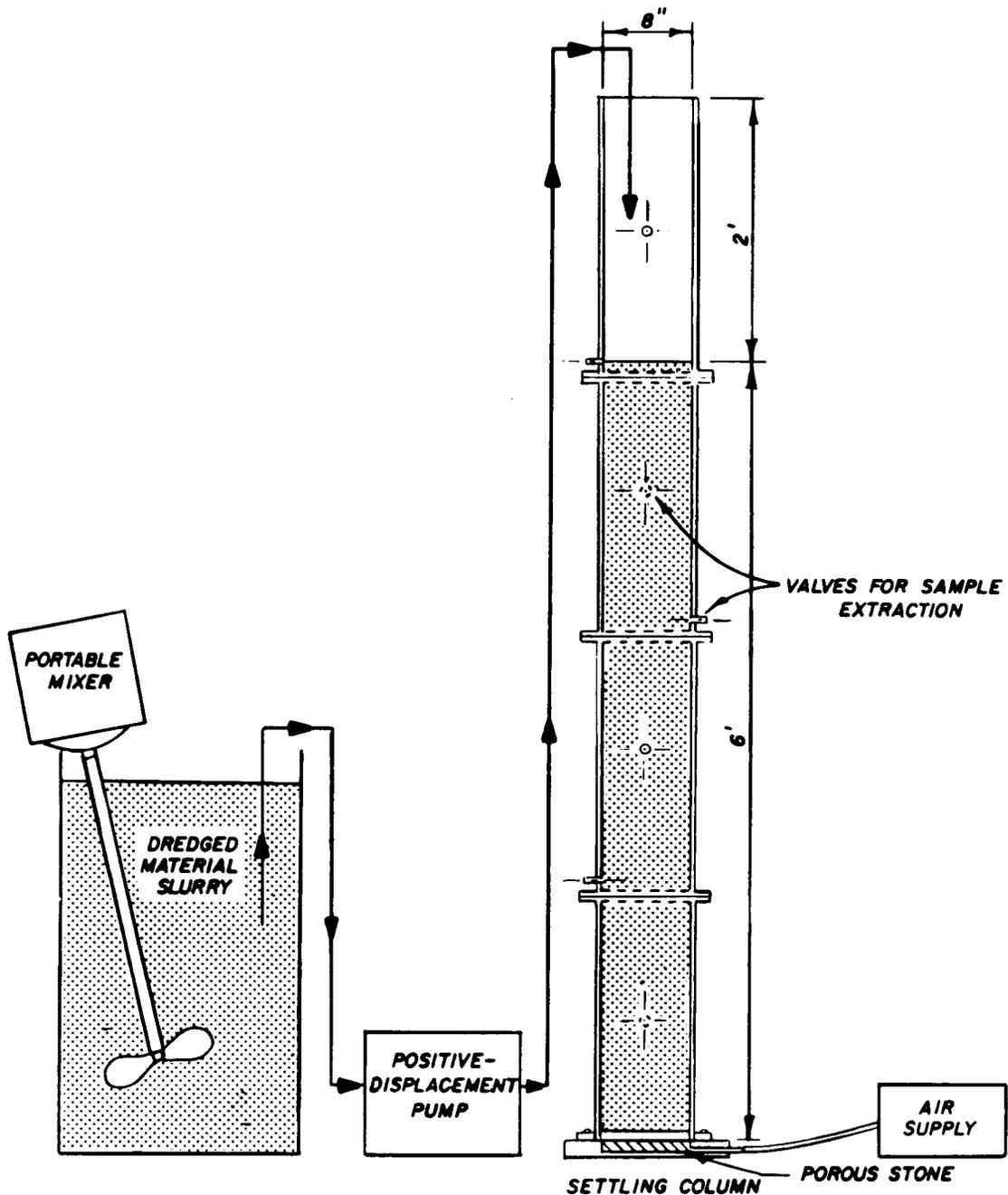


Figure 2. Schematic of apparatus for settling tests

them once the lab test had begun. (Zone settling produces a sharp interface.) However, no method to predict which type of settling would occur was discussed, other than the observation that saltwater sediments usually exhibited zone settling and freshwater sediments usually exhibited flocculent settling.

EM 1110-2-5027 recommends the use of a pilot test in a 4-l graduated cylinder before the main test in the 20-cm column is conducted. This pilot

test allows lab personnel to identify the type of settling occurring, to estimate how many suspended solids determinations will need to be conducted, to estimate how many samples will need to be taken simultaneously (during a flocculent settling test, four to six samples, but during a zone settling test, only one to three samples above the interface), and to decide what kind of data analysis will be needed. With this information, sufficient supplies can be procured, oven space reserved, etc., before the full-scale test begins.

It is important to remember that settling rates observed in the 4- λ test cylinder are not representative of those to be expected in the field, although the settling processes should be. EM 1110-2-5027 recommends a 4- λ graduated cylinder because it is the largest standard size "small" vessel readily available. A smaller cylinder could be used, but wall effects would be much more severe, and settling rates would be even less representative of actual field conditions.

Simplification of Zone Settling Test

For the case of zone settling of the slurry, the test developed by Montgomery (1978) consists of the following stages:

- a. Placing the slurry in the settling column.
- b. Observing the fall of the interface formed between the semiclarified supernatant and the more concentrated slurry.
- c. Repeating the test several times using a specific range of slurry concentrations.
- d. Computing the limiting solids flux for zone settling using procedures described by Yoshioka et al. (1957).

These procedures have been simplified in EM 1110-2-5027 so that only one zone settling test is now required. The single test is to be conducted at the slurry concentration expected in the influent to the DMCA in the field (the highest average concentration expected to prevail for several hours at a time), or at 150 g/ λ if the expected influent concentration is not known. This should produce a sufficiently conservative design, since zone settling velocities are inversely proportional to slurry concentration, and 150 g/ λ is the highest average concentration usually encountered for several hours at a time. The technical basis for the simplification is given in the following paragraphs.

This recommendation of a single test is a significant simplification compared to the original procedure (Montgomery 1978; Palermo, Montgomery, and Poindexter 1978). The original procedure required a series of zone settling tests with initial slurry concentrations ranging from 50 to 200 g/l. The results from these tests were used to calculate the solids flux (lb/hr-ft²),

$$S_i = C_i v_i$$

where C_i (lb/ft³) is the slurry concentration and v_i (ft/sec) is the zone settling velocity, so that a plot of solids flux versus slurry concentration could be made as recommended by Yoshioka et al. (1957). This plot, shown as Figure 3, was used to find the limiting solids flux, S_L , as a function of the selected design solids concentration, C_d , to be achieved in the lower layers of the DMCA at the end of the filling operation. The value of C_d is determined from the compression settling test and is the average solids concentration in the containment area at the end of the dredging operation.

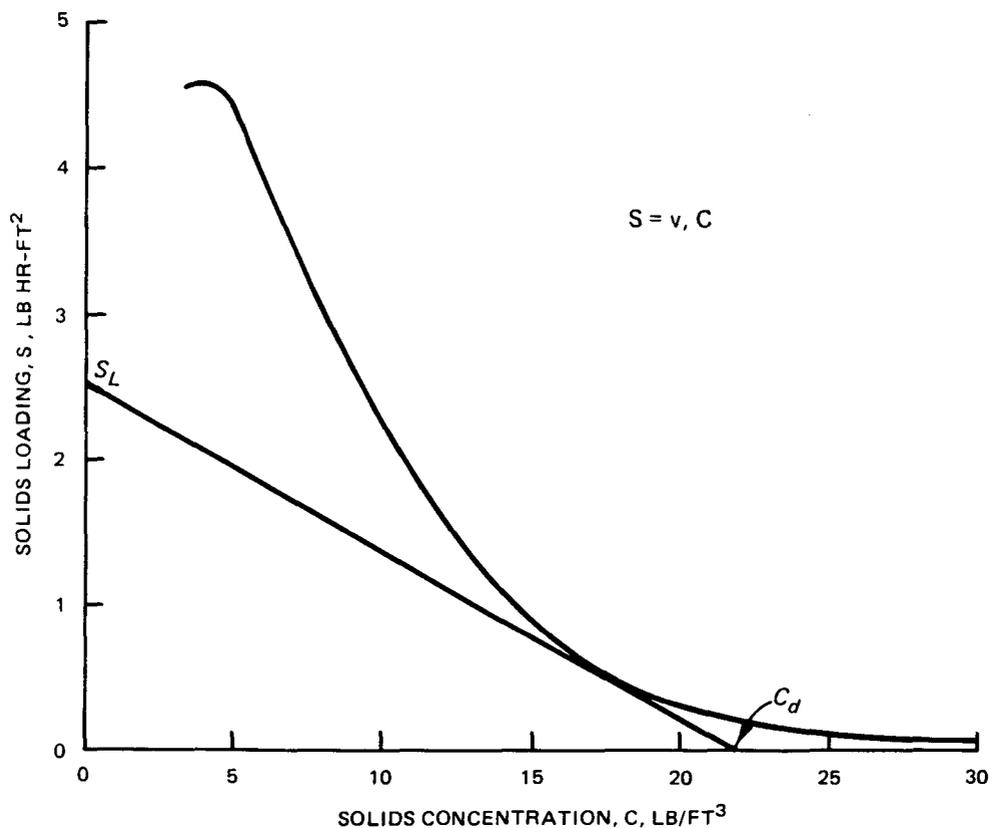


Figure 3. Typical solids loading curve for dredged material

The value of S_L is determined by drawing a line from C_d on the horizontal axis tangent to the solids flux curve and intersecting the solids loading scale on the ordinate as shown in Figure 3.

This is a standard design procedure used in environmental engineering practice for continuous thickeners, in which C_d represents the desired underflow concentration. A very good explanation of this procedure was given by Dick (1972).

In applying this procedure to DMCA's, in which there is no underflow, the implicit assumption was made that the average concentration of material in the containment area at the end of dredging, C_d , could be used to represent the underflow concentration. This assumption does not imply that the "bottom" (the boundary between the zone settling phase and the compression or thickening phase) will be stationary and not rise during filling of the DMCA as occurs in a continuous thickener, in which the depth of settled solids is kept constant. A stationary interface could occur only if there were a downward velocity created by an underflow equivalent to the upward movement of the boundary between phases caused by the continual addition of more solids settling from above. Selection of a limiting solids loading only limits the upward movement of the boundary to a tolerable amount. Since bottom buildup is controlled by storage volume design, not settling velocity, this precaution and the attendant elaborate design procedure have now been found to be unnecessary in most cases.

First, zone settling velocity is usually not the limiting factor in sizing a DMCA. Solids storage capacity usually is. Second, it has been found that it is unnecessary to limit the rate of rise of the "bottom." All that is necessary to prevent unacceptably high effluent solids concentrations is that solids be removed from the overlying surface water and deposited on the "bottom" faster than (or at least as fast as) the maximum rate at which they can be transported downward by zone settling. This criterion may be met by using the minimum value of solids flux produced by the maximum probable value of influent slurry concentration as used in the lab test.

If the "bottom" elevation rises far enough to cause the "clarified" surface layer to be too shallow for effective solids removal (because of high advective flow velocities or wind-generated turbulence in the too-shallow surface layer), the elevation of the water surface can be raised, adding to the thickness of the surface layer. This can easily be done by adding boards

to the adjustable-height outlet weir if the dikes have been correctly designed to be strong enough and high enough for the expected solids volume plus settling volume plus freeboard.

In addition, there are frequently situations in which Montgomery's (1978) design procedure cannot be applied. For some slurries, C_d is so close to (not much greater than) C_i , the influent slurry concentration, that a tangent to the solids flux curve cannot be drawn. This occurs when the influent slurry concentration is high, but thickens slowly, so that the design solids concentration, or solids concentration at the bottom of the test column at a time equal to one-half the expected time of filling of the DMCA, is below the steeply sloping part of the solids flux curve.

Referring to Figure 3, one can see that, if the design solids concentration from the long-term consolidation test were 12.5 lb/ft^3 , no tangent to the solids flux curve could be drawn. If the design solids concentration were 15 lb/ft^3 , the tangent line could be drawn, but would produce an intercept on the ordinate, or value of S_L , that is so high that it is meaningless, because it is higher than any possible value on the solids flux curve.

Extension of Flocculent Settling Test

For the case of flocculent settling of the slurry, the tests developed by Montgomery (1978) generally consist of the following steps:

- a. Placing the slurry in the settling column at the expected influent solids concentration.
- b. Extracting samples of the settling slurries at various times and at various depths in the column.
- c. Analyzing the samples for solids concentrations.
- d. Computing the weighted fractions of solids removed at each sampling time by settling using procedures described by McLaughlin (1959).

EM 1110-2-5027 recommends no changes in the regular flocculent settling test devised by Montgomery (1978). This test is similar to the standard multiheight column settling test common in environmental engineering, but uses a much simpler and more straightforward method of analysis that was originally proposed by McLaughlin (1959). However, EM 1110-2-5027 does contain an extension of the flocculent settling test to the semiclarified supernatant above the interface in zone settling tests, based on the work of Palermo (1984).

When slurries undergo zone settling in a laboratory test column, almost

all of the solids are entrapped in a loose, open matrix that settles as a single mass. However, a few colloidal solids that are not trapped in the matrix remain in the semiclarified supernatant above the interface. In addition, as the mass settles, it displaces water from below, which must move upward through the voids in the settling mass. This upward water velocity shears some loosely bound colloids from the settling mass and carries them into the supernatant, causing the suspended solids concentration to rise during the initial stages of settling. The higher the slurry concentration, the smaller the void spaces, the higher the resulting upward water velocities, and the more solids that are carried into the semiclarified supernatant.

Montgomery (1978) did not propose any method of quantifying the total suspended solids (TSS) concentration in the supernatant, which in a DMCA becomes the effluent concentration. He only stated that the effluent concentration from DMCA's designed using his procedure and properly operated should be below 1 to 2 g/l, low enough to satisfy most of the effluent discharge permit standards common at that time. However, many current discharge permits limit effluent TSS to below 0.1 g/l, so this approach is not sufficient. Therefore, Palermo (1984) devised a method to predict the TSS in the supernatant as a function of retention time, based on the application of the flocculent settling test.

Palermo (1984, 1986) showed that the solids in the supernatant always undergo flocculent settling, whether the slurry undergoing zone settling is from fresh water or salt water. He also showed that the normal flocculent test procedures could be used, except that there is no true initial concentration to be used to calculate normalized concentrations. As explained above, there are two sources of solids in the supernatant under laboratory test conditions--one (the solids not originally trapped in the settling mass) decreasing with time because of flocculation and settling, and one (the solids carried into the supernatant from the settling mass by the upward-flowing displaced water) increasing with time.

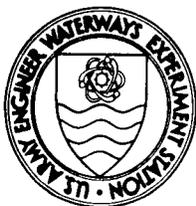
Palermo (1984, 1986) analyzed the effects of several possible assumptions regarding the magnitude of the value to be used as the initial concentration in the laboratory test, and showed that all gave essentially the same final result. Therefore, he recommended that, for simplicity, the concentration in the first sample taken at the highest sampling port be used as the initial concentration.

Summary

Several additions and modifications have been made to the recommended column settling test and design procedures for dredged material containment areas since the first guidance was published (Montgomery 1978; Palermo, Montgomery, and Poindexter 1978). These changes have been incorporated into the procedures described in the newly issued design manual, EM 1110-2-5027. This technical note provides the design engineer with an explanation of the major changes and why they were made. The engineer is referred to the EM itself for a detailed outline of the procedures.

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Environmental Effects of Dredging Technical Notes



HEAVY METAL UPTAKE BY AGRONOMIC CROPS AND *CYPERUS ESCULENTUS* GROWN ON OXIDIZED AND REDUCED SOILS CONTAMINATED WITH METAL-MINING WASTES

PURPOSE: This note expands the scope and utility of the Waterways Experiment Station (WES) plant bioassay procedure by using *Cyperus esculentus* (yellow nut-sedge) as an index plant to link an existing agronomic data base to that of the WES data base. Relating contaminant uptake and mobility by the index plant grown on dredged material to that of an existing agricultural data base may show that levels of contaminant uptake by plants and subsequent mobility into the food web from dredged material may be compared to what is normally acceptable in agricultural products. Therefore, contaminant uptake and mobility may not be as harmful to the environment as often projected (i.e., absence of "unacceptable adverse effect").

This technical note is a synopsis of a contract report prepared under the Toxic Substances Bioaccumulation by Plants work unit in the Long-Term Effects of Dredging Operations Program. Dr. Brian E. Davies and Ms. Nicola J. Houghton of the University College of Wales, Aberystwyth, Great Britain, conducted the study.

BACKGROUND: WES has developed a plant bioassay procedure using the freshwater plant *C. esculentus* to evaluate the mobility of contaminants from dredged material into the environment. The utility and scope of the procedure are being expanded and evaluated by using *C. esculentus* as an index plant to link several large agronomic data bases. One of these large data bases describes vegetable crop production on metal-contaminated mining wastes in the United Kingdom. The plant bioassay procedure was tested by researchers from the University College of Wales, Aberystwyth, Great Britain. Specific objectives of this study were to implement the plant bioassay procedure using metal-contaminated mining wastes from old mining sites and to relate the resulting plant uptake data to the Welsh data base.

ADDITIONAL INFORMATION: This note was written by Dr. Bobby L. Folsom, Jr., Environmental Laboratory, and Dr. Brian E. Davis and Ms. Nicola J. Houghton of the University College of Wales, Aberystwyth, Great Britain. For additional information contact Dr. Folsom, commercial or FTS: (601) 634-3720; or the manager of the Environmental Effects of Dredging Programs, Dr. Robert M. Engler, (601) 634-3624.

Approach

Contaminated soils were collected from areas in Wales and western England where base metals had been mined in the nineteenth century. Two of these areas were near Liverpool, two near Aberystwyth, and one near Bristol. Each soil contained high levels of one or more of the following heavy metals: lead (Pb), zinc (Zn), copper (Cu), and cadmium (Cd). A silty soil from the WES reservation served as a reference soil. Heavy metal uptake from each of the soils by the WES index plant, *C. esculentus*, was investigated in a controlled greenhouse environment under reduced (flooded) and oxidized (upland) conditions. The effect of liming the soils on heavy metal uptake by the agronomic crops was investigated since increased soil pH was necessary for crop growth. The agronomic crops included lettuce (*Lactuca sativa* var. Paris White), radish (*Raphanus sativus* L. var. Webb's French Breakfast), wheat (*Triticum aestivum* var. Timmo), red fescue (*Festuca rubra* var. Merlin), and Italian ryegrass (*Lolium multiflorum* S23). Each crop was grown in each of the contaminated soils until full vegetative growth had been reached, at which time the crops were harvested. Each treatment was replicated three times.

The plants were analyzed for acid (HNO_3) extractable Cd, Cu, Zn, and Pb. The soils were analyzed for HNO_3 , diethylene triamine pentaacetic acid (DTPA), and ethylene diamine tetraacetic acid (EDTA) extractable Cd, Cu, Zn, and Pb. DTPA had been used extensively in the WES plant bioassay procedure, while EDTA had been used in Wales to estimate mobility of heavy metals. Extracting the same soils with both extracts provided a link between the WES and the Welsh soil-extraction procedures.

Results

DTPA and EDTA extractable heavy metal levels were higher from the aerobic soils than from the flooded soils. Folsom, Lee, and Bates (1981) had found the same result with DTPA when flooded sediments were drained and allowed to oxidize. They attributed this behavior to oxidation of heavy metal-organic matter complexes into simpler more soluble and more mobile forms. Increased mobility subsequently increased plant availability of the metals. However, the soils used in the present study were oxidized prior to flooding. When an oxidized soil is flooded, the reduction process converts inorganic

sulfates into sulfides and results in the formation of less soluble heavy metal sulfides (Gambrell et al. 1977). Reduced solubility of the heavy metals in the flooded soils is reflected in reduced heavy metal concentrations in both DTPA and EDTA extractions and implies reduced plant availability of heavy metals. However, when heavy metal levels obtained by DTPA extraction were correlated with plant uptake levels, Cd was the only metal significantly less available from flooded soil.

Significant positive correlation was found between DTPA extractable Cd and plant uptake of Cd by agronomic crops. DTPA extractable Cd accounted for over 92 percent of the variability ($r^2 = 0.92$) of Cd in tissue of radish leaves, radish bulbs, lettuce, and *C. esculentus*. DTPA extractable Cd accounted for 81 percent of the variability in tissue of Italian ryegrass. DTPA extractable Cd accounted for only 61 percent of tissue Cd in red fescue, while that of wheat was less than 45 percent. The correlation between DTPA extractable Cu and Zn and plant uptake was positive but was not as significant as for Cd. DTPA extractable Cu, however, accounted for 84 percent of the variability in *C. esculentus*, while DTPA extractable Zn accounted for only 31 percent. The correlation between DTPA extractable Pb and plant uptake was marginal (generally, $r^2 < 0.50$). DTPA extractable Pb accounted for only 40 percent of tissue Pb in *C. esculentus*.

Significant positive correlations were found (Figures 1 and 2) between *C. esculentus* and agronomic crop heavy metal uptake and established the link between the Welsh and WES data bases. The correlations varied between metals and plant species. Cadmium and zinc correlation between *C. esculentus* and agronomic crops were not as strong, however, as those found by van Driel, Smilde, and van Luit (1985).

Reduced uptake and subsequent reduced correlation between plant heavy metals in agronomic crops and *C. esculentus* could have resulted from liming the soils. Liming was necessary to support plant growth of the agricultural crops. Liming did not affect *C. esculentus*. Increased crop growth may have masked increased metal uptake since increased plant dry matter may have resulted in a dilution effect (i.e., because the increased plant growth was not proportional to increased metal uptake). When these same crops were grown on contaminated sediments (pH of 7.0 or greater), highly significant correlations between the heavy metal status of *C. esculentus* and the crops were found (van Driel, Smilde, and van Luit 1985). Bingham et al. (1979) found that Cd

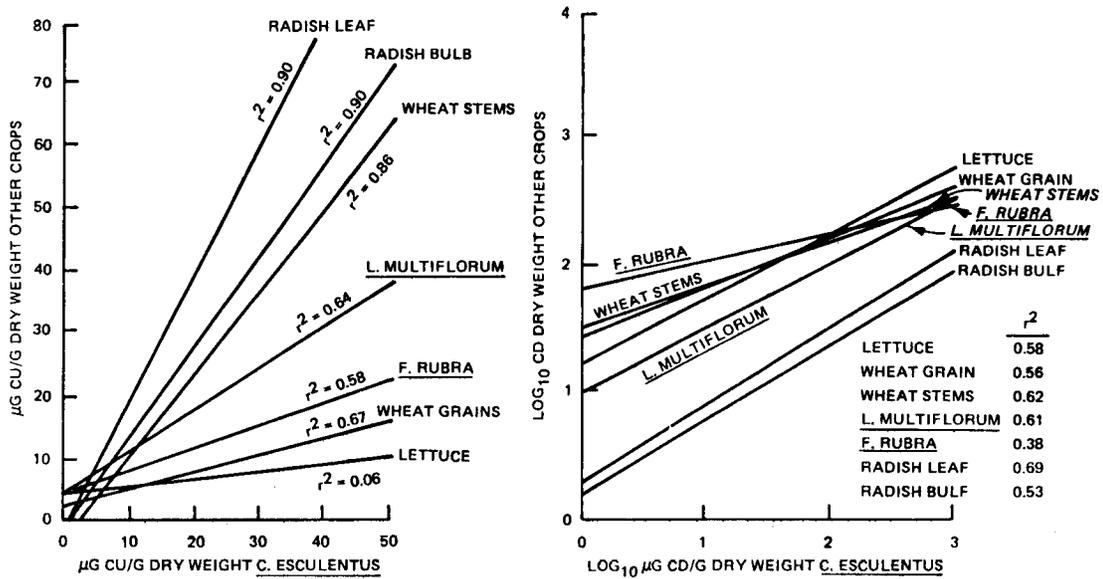


Figure 1. Correlation between heavy metal uptake (Cu and Cd) by *C. esculentus* and other agronomic crops

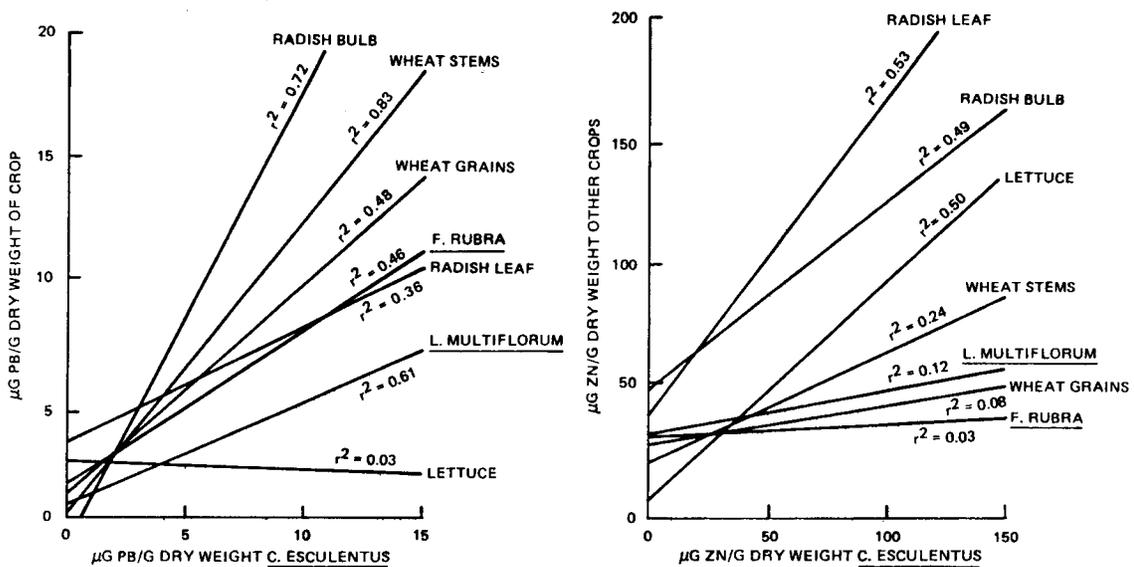


Figure 2. Correlation between heavy metal uptake (Pb and Zn) by *C. esculentus* and other agronomic crops

was phytotoxic (reduced plant growth) even in limed soils and also noted that liming reduced the correlation between DTPA extractable Cd and Cd uptake by wheat grain. Apparently, liming of contaminated soils can increase plant growth and obscure the relationship between increased plant growth and increased metal uptake. Liming also reduced correlation between DTPA extractable heavy metals and plant uptake of heavy metals.

In conclusion, the plant bioassay procedure was implemented using metal-contaminated mining wastes from old mining sites. The procedure was shown to be appropriate for evaluating contaminant mobility. Resulting plant uptake data can be used to link the Welsh agronomic and WES *C. esculentus* data bases.

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Environmental Effects of Dredging Technical Notes



SYNTHESIS OF LEACHING RESEARCH AND WORKSHOP RESULTS

PURPOSE: This technical note briefly describes the results of recent studies conducted to evaluate leachate quality for dredged material in confined disposal facilities (CDFs). Directions for future research from a workshop on development of leach tests for contaminated dredged material conducted in Baton Rouge, LA, on June 23-24, 1988 are also provided.

BACKGROUND: Contaminated dredged material is sometimes placed in confined disposal facilities where potential for the movement of contaminants by leachate into groundwater and surrounding surface water is an important environmental concern. There is presently no routinely applied laboratory testing protocol to predict leachate quality and quantity from confined dredged material disposal facilities. In 1984, the Corps of Engineers initiated confined disposal facility leachate investigations by developing a theoretical framework for prediction of leachate quality based on mass transport theory. A preliminary laboratory program including batch and column leach tests was designed on the basis of the theoretical analysis and a literature review. Batch tests provide a quick, relatively easy method for determining the distribution of contaminants between dredged material and leachate. Column tests more closely approximate field conditions in a confined disposal facility, but require more time and equipment than batch tests. The approach recommended for application to dredged material used an operationally defined equilibrium distribution (partitioning) coefficient to relate aqueous phase concentration to solid phase concentration. Reviews and comments on the proposed approach were received from a technical working group assembled at the US Army Engineer Waterways Experiment Station (WES) in 1984.

The approach recommended for application to dredged material was used in studies at Indiana Harbor, IN; Everett Harbor, WA; and New Bedford Harbor, MA. Results of these studies provided site-specific information for use in management-level site selection treatment and control technology assessment for dredged material. Results of these studies were also evaluated in 1988 at a workshop in Baton Rouge, LA, hosted by Louisiana State University. The workshop provided outside critical review of past studies and direction for future research in this area.

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Introduction

At present, there is no routinely applied laboratory testing protocol capable of predicting leachate quality from confined dredged material disposal sites. Testing procedures to predict leachate quality are, therefore, needed in order to fully evaluate the confined disposal alternative for dredged material. If leachate quality and quantity can be predicted, the potential impacts of contaminated dredged material disposal in a confined disposal facility (CDF) can be determined, thus allowing the most cost-effective site design to be used.

Experimental procedures for predicting leachate quality have been used to evaluate the potential impacts of confined disposal of dredged material from Indiana Harbor, IN; Everett Harbor, WA; and New Bedford Harbor, MA (Environmental Laboratory 1987, Palermo et al. in publication, Myers and Brannon in publication). These procedures were based on theoretical analysis and a literature review as well as reviews and comments by a working group of experts held at the US Army Engineer Waterways Experiment Station (WES) in 1984 (Hill, Myers, and Brannon 1988). Results of laboratory studies conducted to date are briefly summarized in this technical note. Also included are directions for future research, which were developed at a workshop held at Louisiana State University in 1988; the proceedings of the workshop are available from WES upon request.

Methods

Batch tests (shake tests) were conducted to investigate contaminant release properties of sediment under anaerobic (oxygen free) and aerobic conditions. Batch testing procedures applied to dredged material included kinetic tests, liquid-solid ratio testing, and sequential batch testing. Kinetic batch tests determine the shaking time necessary to achieve steady state (i.e., no detectable change in leachate concentrations). Liquid-solid ratio batch testing is conducted to find the optimum sediment-water ratio for

use in batch testing. Sequential batch testing is used to determine the distribution of contaminants between sediment and leachate. Such testing is conducted by shaking sediment and water until steady-state leachate concentrations are reached, separating the sediment and water, adding fresh water to the solids, and continuing the shake tests. The leachate removed at each step of the procedure is chemically analyzed.

Continuous flow column leaching tests were conducted in divided-flow stainless steel permeameters designed to minimize wall effects and provide for pressurized operation (Figure 1). The applied pressure (maximum of 25 psi) forced water through the sediment at rates sufficient to allow sample collection in a reasonable period of time.

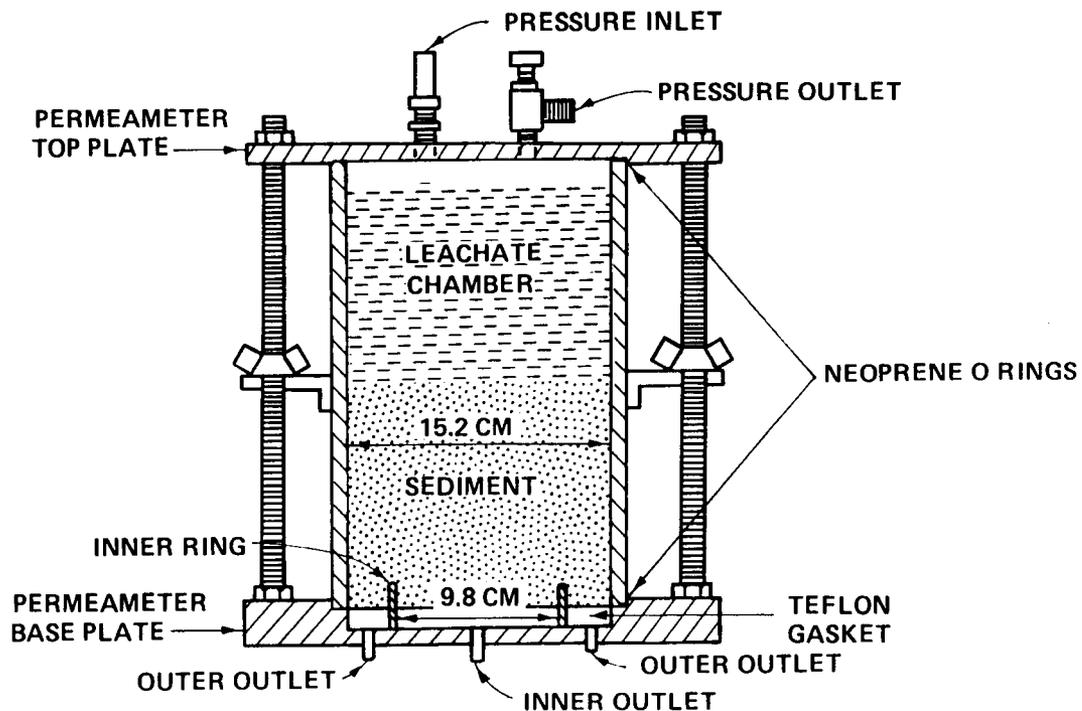


Figure 1. Divided-flow permeameter

Results of column and batch leaching tests were compared by integrating batch leach tests and column leach tests with a mass transport equation to predict permeameter leachate quality as a function of volume throughout (time). The approach used is outlined in Figure 2.

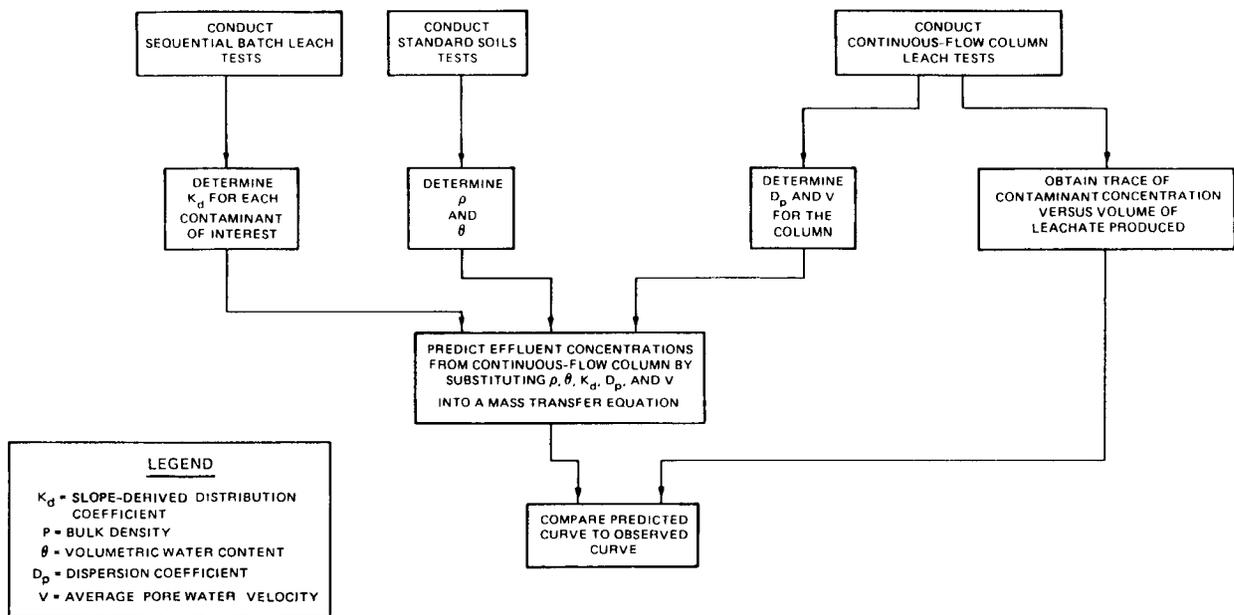


Figure 2. Schematic diagram of integrated approach for examining the source term

Results and Discussion

Summary of previous leach testing

Batch testing of Indiana Harbor sediment was difficult because of the oil and grease content of the sediment. Despite the difficulties, anaerobic sequential batch tests for metals produced well-defined desorption isotherms. Aerobic sequential batch tests for metals produced ill-defined clusters. An example for zinc and cadmium is presented in Figure 3.

Polychlorinated biphenyl (PCB) desorption isotherms for Indiana Harbor sediment were characterized by clustering of data. Cluster analysis allowed single-point distribution coefficients to be calculated.

The integrated approach for comparing column and batch test results (Figure 2) was applied to the Indiana Harbor data. PCB results are presented in Figure 4 for two conditions--contaminant leaching governed by equilibrium-controlled, linear desorption (coefficients determined during sequential batch leaching), and no desorption (distribution coefficients of zero). Prediction of PCB elution from columns was within an order of magnitude of that achieved in the tests and was conservative; i.e., predicted concentrations were generally higher than concentrations observed during column testing.

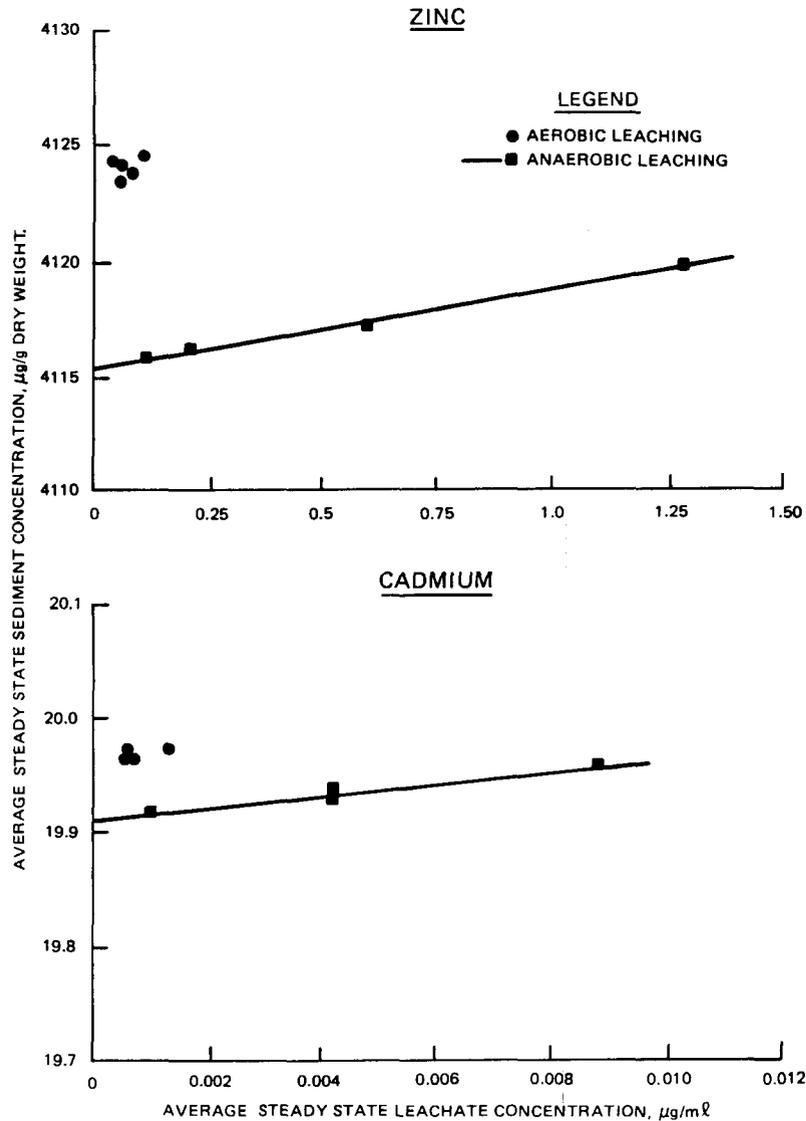


Figure 3. Desorption isotherms for zinc and cadmium in Indiana Harbor sediment

Everett Harbor leaching results differed sharply from those observed for Indiana Harbor. Everett Harbor sediment contaminant concentrations were much lower than those observed in Indiana Harbor, especially for organic contaminants, and Everett Harbor sediment was from a brackish, rather than a fresh-water environment. The sediment developed a low pH (4.3) when allowed to oxidize, resulting in mobilization of metals from aerobic sediment during sequential batch leaching. Release of metals during anaerobic batch testing did not follow the classical desorption behavior which was observed for metals in anaerobic Indiana Harbor sediment. Copper desorption from anaerobic Everett Harbor sediment is illustrated in Figure 5.

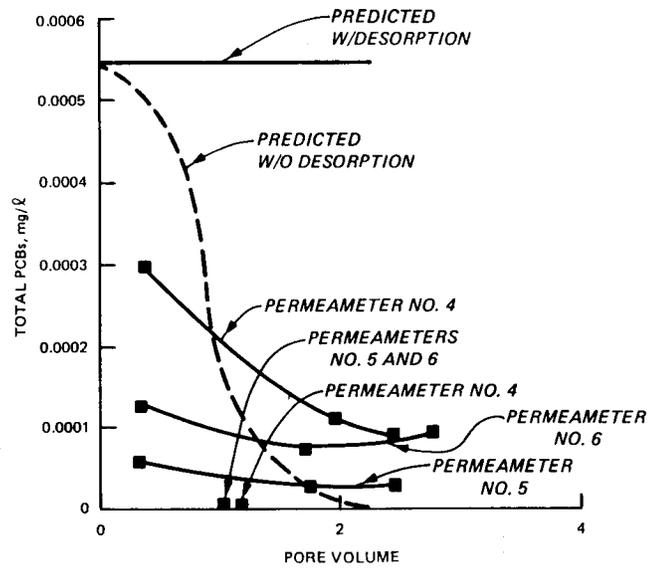


Figure 4. Total PCB concentrations in anaerobic permeameter leachate

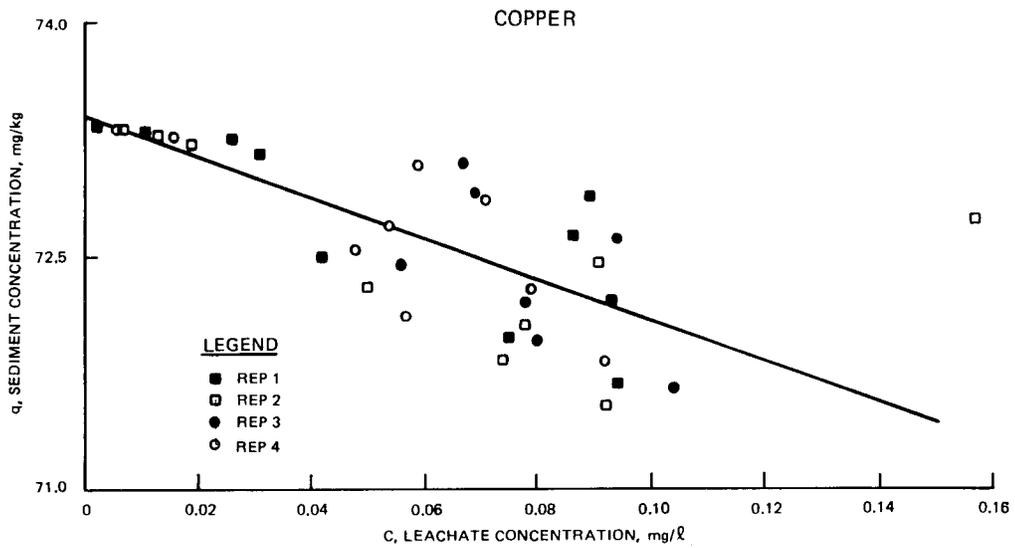


Figure 5. Copper desorption isotherm for anaerobic Everett Harbor sediment

Because the mass transport equation used to implement the integrated approach requires constant distribution coefficients, it was not possible to predict permeameter leachate concentrations using the approach applied to the Indiana Harbor batch and permeameter data. A simplified method that related pore volumes in the sequential batch tests to pore volumes in the permeameter tests was therefore used and gave good qualitative agreement for some, but not all metals tested. A problem was encountered with aerobic sediment during permeameter testing. When aerobic Everett Harbor sediment was placed in a column and flooded, sufficient oxygen demand remained to rapidly deplete all oxygen and return the sediment to an anaerobic condition. Therefore, the column test did not simulate leaching under aerobic conditions.

The New Bedford Harbor site sediments differed from previous sediments tested in that it contained 2,167 mg/kg of total PCB, which is orders of magnitude higher in concentration than observed for Indiana Harbor and Everett Harbor sediments. Many metals in New Bedford Harbor sediment were higher than 1,000 mg/kg, much higher than metal levels observed in Everett Harbor sediment.

The shape of desorption isotherms for metals in New Bedford Harbor sediment was similar to the example given in Figure 4 for Everett Harbor sediment. Aerobic New Bedford Harbor sediment developed a low pH (2.1), resulting in releases of some metals during aerobic batch leaching.

Leaching of anaerobic New Bedford Harbor sediment with distilled water resulted in development of reverse slope isotherms which in some cases turned back toward the sorbed concentration (vertical) axis. The isotherm is illustrated in Figure 6 for total PCB. Further leaching and analysis of leachate showed that as the conductivity in the distilled water leachate decreased, colloidal organic matter and microorganisms containing adsorbed PCB were destabilized, resulting in PCB mobilization in colloidal or microparticulate form.

Significantly lower concentrations of PCBs and some metals were observed in column leachate compared to batch leachate. The reasons for these significant differences are presently unexplained.

As was the case with Everett Harbor, the integrated approach could not be used with New Bedford Harbor sediment because of the type of desorption isotherms obtained. However, simulation of PCB elution during nonconstant partitioning by coupling PCB concentrations to conductivity in the column

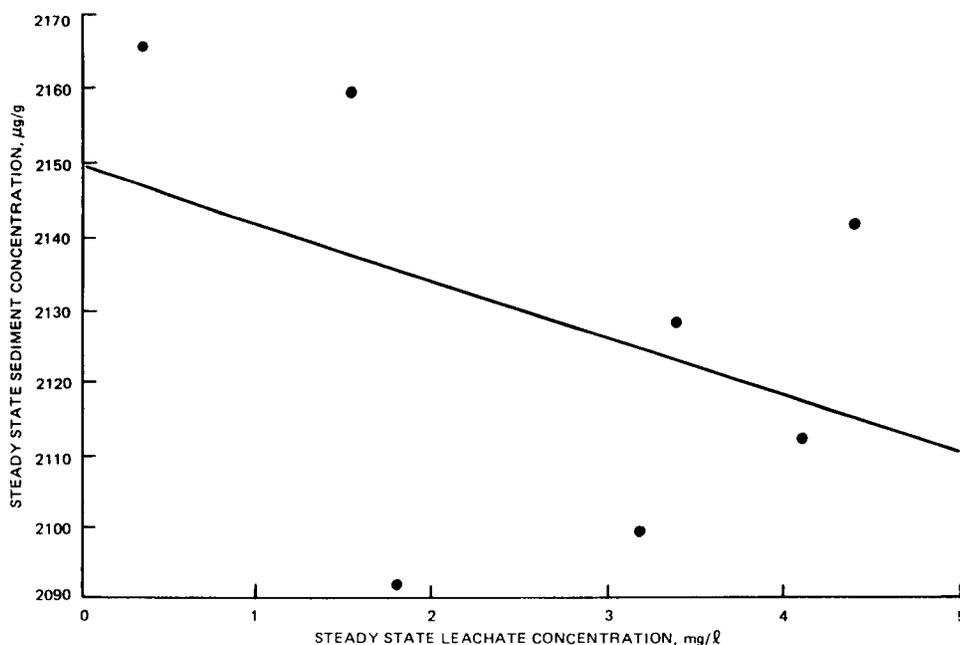


Figure 6. Total PCB desorption isotherm for New Bedford Harbor sediment distilled-water sequential batch leach test

leachate resulted in qualitative agreement in elution trends for predicted and observed PCB elution curves.

Louisiana State University Workshop

Results of the three studies previously summarized were discussed in detail at a workshop on development of leach tests for contaminated dredged material, conducted June 23-24, 1988, in Baton Rouge, LA. The workshop was hosted by the Louisiana Water Resources Institute, the Hazardous Waste Research Center, and the Center for Wetland Resources, all of Louisiana State University. The workshop was organized to gather prominent researchers in the area of contaminant mobility in dredged material for review and evaluation of available leach data on dredged material. Workshop panelists thought that work conducted to date was good and that the work generally validated the basic approaches suggested by the 1984 working group. However, the consensus was that much research remains to be done before a leachate test protocol will be ready for routine use. The following research directions were developed during workshop discussions:

- Redesigning of the column leach tests to include thin-layer columns and improved leachate collection systems.

- Reevaluation of the aerobic column test.
- Investigation of the impact of colloidal systems on interactions between solid and liquid phases.
- Determination of the role of key parameters such as ionic strength, pH, and contaminant-sediment association on leachate results.
- Investigation of desorption kinetics.
- Investigation of techniques for accelerated sediment oxidation.
- Development of a more comprehensive mass transport model for comparing batch and column test results and verification of the model structure.
- Verification of test protocols in a field situation, preferably at a national multiagency research site.

Future Plans

In the leachate studies conducted to date, each of the sediments tested behaved in a unique manner. Future study will build on the lessons learned in these projects and the research directions identified in the workshop. During the upcoming fiscal year, research will be initiated on basic research needs such as the impact of colloidal systems on interactions between solid and liquid phases, the role of parameters such as ionic strength and pH on leachate quality, an in-depth investigation of desorption kinetics, and design of thin-layer columns and improved leachate collection systems for columns. Research in future years will be a continuation of these efforts as well as reevaluation of the aerobic column tests, investigation of techniques for accelerated sediment oxidation, and refinement of the mass transport model for comparing batch and column test results. Verification of testing protocols developed will then be conducted and predictive techniques for assessing leachate impacts from confined disposal facilities will be finalized.

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Environmental Effects of Dredging Technical Notes



CONFINED DISPOSAL GUIDANCE FOR SMALL HYDRAULIC MAINTENANCE DREDGING PROJECTS--DESIGN PROCEDURES

PURPOSE: This note presents a simplified procedure for design of small confined disposal facilities. Applications of this procedure will be presented in a future technical note. The design approach is the same as presented in "Confined Disposal of Dredged Material," Engineer Manual (EM) 1110-2-5027 (Headquarters, US Army Corps of Engineers 1987), except that no settling tests are required. The guidance is limited to the design of areas to be used only for small one-time disposal operations. Typically, the areas are less than 10 acres in size and the disposal takes less than 20 days. This procedure does not require laboratory settling tests because the time and expense of these tests are generally not warranted for the small quantity of sediment being disposed. However, there may still be circumstances where better estimates of storage requirements and effluent quality are needed. In those cases the design procedures and settling tests presented in EM 1110-2-5027 are recommended. This technical note is not intended for use in designing larger disposal areas because the procedure may yield too large and costly a design. This design procedure is necessarily conservative to ensure adequate storage capacity and acceptable effluent suspended solids concentrations since settling data specific to the material being disposed are not used.

BACKGROUND: The US Army Corps of Engineers dredges over 482 million cu yd of sediment annually from the nation's rivers, harbors, and ship channels in response to its mission of maintaining navigable waterways. Approximately 75 percent of this material is placed in confined upland disposal sites. Therefore, the Dredged Material Research Program (DMRP), the Long-Term Effects of Dredging Operations (LEDO) Program, and the Field Verification Program (FVP) have examined settling characteristics, storage requirements, and effluent quality for a large number of upland disposal sites (Averett, Palermo, and Wade 1988) and developed procedures and guidelines for the design, operation, and management of confined disposal areas (Headquarters, US Army Corps of Engineers 1987) to meet required effluent standards and provide adequate storage volume. These procedures require sediment and water sampling, laboratory sediment characterization, and settling tests and therefore are too costly or time-consuming for small dredging projects. Consequently, a simplified design alternative, presented in this technical note, was developed using a collection of settling data from 20 series of tests on sediments from 13 different locations in place of site-specific settling data.

Confined disposal design consists of six principal parts:

1. Collection of project data.
2. Sediment characterization.
3. Design for initial storage.
4. Design for clarification (if zone settling occurs).
5. Design for effluent quality (suspended solids concentration).
6. Weir design.

The simplified design procedure presented here uses nomographs in place of settling tests for parts 3, 4, and 5.

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Nomograph Development

Nomographs were developed for sedimentation design using data from 20 series of column settling test data conducted by the US Army Engineer Waterways Experiment Station on sediments from 13 locations. These tests were conducted and the results analyzed in accordance with the procedures outlined in Engineer Manual (EM) 1110-2-5027. Table 1 lists the sediment sites, sedimentation description, and tests performed on these materials which provided the data used in the development of the nomographs.

The nomographs were developed using a least-squares regression analysis package to establish the best-fit relationship for settling characteristics of each material. Each data set was then given equal weight in regressing the best fits to prepare the average fit used in the nomographs. The conservative fit presented in the nomographs is based on the 95-percent confidence limit about the average fit. In the nomograph for flocculent settling of the slurry (for circumstances where zone settling does not occur) the worst-case data set was substituted for the confidence limit because this limit fell greatly outside the range of the data.

Design Procedure

The approach and nomenclature used in this design procedure parallel the design procedures used in Chapter 4 of EM 1110-2-5027. However, the laboratory testing, data analysis, and calculations used in the EM design procedures

Table 1
Sediments Evaluated by Settling Column Tests

Site	Salinity ppt	Type of Settling Tested		
		Zone	Compression	Flocculent
Ashtabula Harbor (1984)	<1.0	X	X	X*
Black Rock Harbor (1982)	24.4	X	X	X*
Everett Bay (1985)	>3.0	X		X*
Hart-Miller Island (1984)	7.5		X	X*
Indiana Harbor (1979)	<1.0	X		
Indiana Harbor (1984)	<1.0		X	X**
Kings Bay (1983)	24.0		X	
Little Lake (1981)	12.5	X	X	
Mobile Harbor (1978)	17.0	X		
Mobile Harbor, sta 28 (1983)	14.0		X	X*
Mobile Harbor--Composite (1983)	15.0			X*
Norfolk Harbor-1B (1980)	15.0		X	
Norfolk Harbor-16B (1980)	15.0	X	X	
Norfolk-55 Channel (1981)	20.0	X		
Port Bienville (1981)	13.0	X	X	
Savannah Harbor (1981)	25.0	X	X	
Savannah Harbor (1983)	<1.0			X*
Yazoo River (1978)	<1.0			X**
Yazoo River (1980)	<1.0			X**
Yellow Creek (1982)	<1.0			X**

* Flocculent settling test was performed on supernatant following zone settling of the slurry.

** Flocculent settling test was performed on sediment slurry.

are replaced by nomographs. A reading of this Engineer Manual during use of this technical note may provide a better understanding of confined dredged material disposal.

Data requirements

The following data are required to use this design procedure. The data are available from field investigations, laboratory testing on sediment characterization, project-specific operational constraints and experience in dredging and disposal activities. Estimates are often available from past experience.

1. In situ sediment volume.

2. Physical characteristics of sediment.
 - a. In situ sediment concentration, void ratio or water content.
 - b. Specific gravity of sediment solids.
 - c. Degree of saturation (100 percent for maintenance dredging).
 - d. Fraction of volume that is coarse-grained.
 - e. Slurry settling behavior (zone settling or flocculent settling).
3. Disposal data.
 - a. Dredge pipeline size or discharge flow rate.
 - b. Dredging schedule and operating hours.
 - c. Influent solids concentration.
 - d. Desired effluent suspended solids concentration.
 - e. Maximum allowable dike height.
 - f. Freeboard height.

Design for initial storage (compression settling)

Step 1--compute or estimate disposal duration. This duration can be estimated from past experience or calculated using production rates, dredging schedules, operating hours, and downtime estimates. The project length is equal to the downtime plus the volume of in situ sediment divided by the dredge production rate and the fraction of time that the dredge is producing.

Alternatively, the project length (PL) can be computed as follows:

$$PL = [V/(\bar{Q} \times 3,200)] + \text{downtime} \quad (1)$$

where V = volume of dredged material being disposed, cu yd

$$= V_i \times C_i/C_o \quad (2)$$

V_i = volume of in situ sediment to be dredged, cu yd

C_o = solids concentration of influent dredged material, g/l

C_i = solids concentration of in situ sediment, g/l; typically, ranges from 600 to 1,300 g/l

$$= [G_s \times Y_w / (e_i + 1)] \quad (3a)$$

$$= 100,000 / [(100/G_s) + w_i] \quad (3b)$$

G_s = specific gravity of the sediment solids

γ_w = specific weight of water, 1,000 g/l

e_i = void ratio of in situ sediment

w_i = water content of in situ sediment, percent

and where \bar{Q} = daily average flow rate, cfs
= $(v_o \times A_o \times T_o / 24)$ (4)

v_o = pipeline velocity of influent dredged material, fps;
typically about 15 fps

A_o = cross-sectional area of influent pipe, sq ft

T_o = hours of active disposal per day

Downtime is the estimate of the number of days that the dredge will not operate during the disposal period; it includes downtime for repairs, weather, holidays, and other scheduled off-days.

Step 2--determine site constraints. Upon determining the project duration, the initial storage volume requirement can be determined from the nomograph in Figure 1. However, the dimensions of the disposal facility cannot be assigned until constraints on the dike height or disposal area are determined. Commonly, the maximum allowable dike height is constrained by foundation conditions which limit the loads placed on the dikes without special construction practices. The disposal area is also commonly constrained by the available area.

If the maximum dike height is known, the maximum depth of initial storage is computed as follows:

$$H_{dm} = H_{dk} - H_{pd} - H_{fb} \quad (5)$$

where H_{dm} = maximum height of dredged material storage, ft

H_{dk} = maximum allowable dike height, ft

H_{pd} = average depth of ponded water, ft; generally, 2 ft

H_{fb} = height of freeboard, ft; generally, 1 to 2 ft for small sites

Step 3--use initial storage nomograph. Use the initial storage nomograph given in Figure 1 to estimate the initial storage volume requirement given the project length in days and the in situ sediment volume in thousands of cubic yards. Enter the nomograph at the value for the project duration on the length of project axis. Proceed vertically to the first turning line representing the average case (Point A on the inset in Figure 1) and then to the second turning line (Point A' for the conservative case). These turning lines represent statistical fits of the ratio of the concentration of in situ sediment to the concentration of settled dredged material or ratio of the volume of settled dredged material to the in situ volume of sediment dredged as a function of the project duration. Draw horizontal lines through these points of intersections (Points A and A') from the initial storage ratio axis (Points B and B') to the line representing the in situ volume of sediment to be dredged (Points C and C'). Then continue both lines downward to the storage volume axis to obtain a range of storage volume in acre-feet (between Points D and D') for design consideration. The precision of these values can be improved by multiplying the in situ sediment volume by the initial storage ratios obtained at the intersections of the horizontal lines and the upper vertical axis (Points B and B'), remembering that 1,000 cu yd equals 0.62 acre-ft.

The larger value for storage volume should be used if the sediment has a high solids concentration or is expected based on past experience to settle and consolidate slowly. If the sediment concentration is low or consolidates rapidly, use the lower storage volume determined from the averaging of sediments' compression settling properties. In selecting the value for use, it is important to consider the likely impacts of and solutions for underestimating or overestimating the storage volume. Underestimating can cause a reduction in depth available for ponding and freeboard, impair effluent quality, reduce the quantity of material that can be dredged, and reduce the dredge production rate to maintain acceptable effluent quality and to permit additional

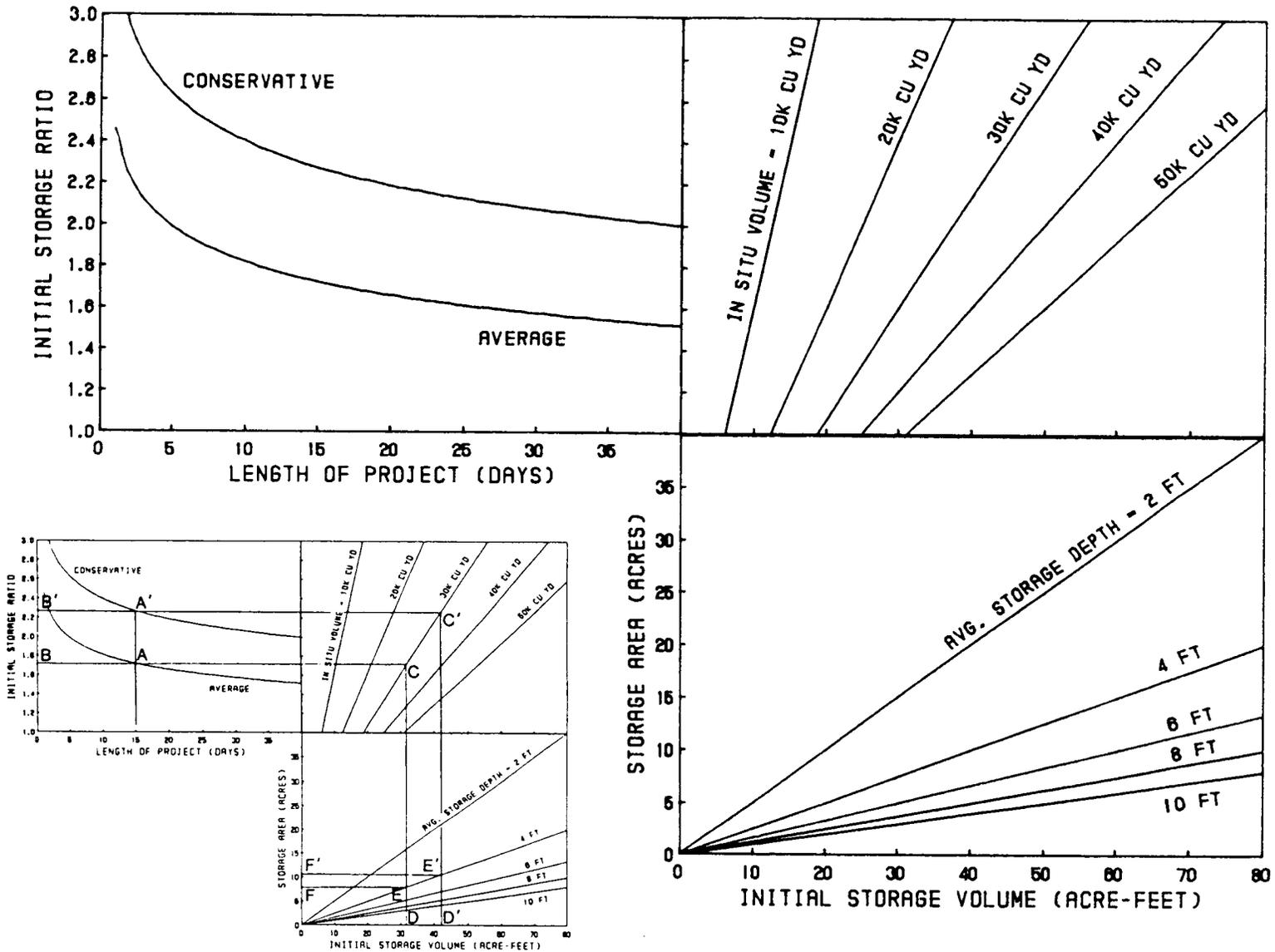


Figure 1. Nomograph to perform initial storage design of confined disposal facilities for small dredging projects using statistical fits of a compression settling data base

consolidation. Overestimating the initial storage volume unnecessarily increases the size and cost of the disposal facility, requiring more land or dike volume.

In addition to required storage volume, the nomograph can also be used to determine either the minimum area required for storage or the depth of initial storage. If the maximum allowable storage depth in feet is known from step 2 above, enter the nomograph at the value of the required initial storage volume (e.g., Points D and D') and move vertically to intersect with the line for the maximum allowable storage depth (e.g., Points E and E'). Then, draw a horizontal line to the area axis and read the value of the minimum required surface area in acres (e.g., Points F and F'). For more precision, this area could be determined by dividing the storage volume by the maximum storage depth after performing the appropriate unit conversions. Similarly, if the surface area is known, the storage depth can be computed by dividing the storage volume by the surface area after performing unit conversions. The storage depth can be read from the nomograph by drawing a horizontal line at the value of the surface area in acres (e.g., Points F and F') and a vertical line at the value of the initial storage volume in thousands of cubic yards (e.g., Points D and D') and then estimating the storage depth in feet at the point of intersection of these two lines (e.g., Points E and E').

Design for clarification (zone settling)

Slurries of most sediments undergo zone settling, particularly those slurries having a salinity greater than 3 ppt or a clay content less than 5 percent. Flocculent settling has been observed for only a few freshwater maintenance projects where the influent slurry concentrations of fine-grained solids were low (less than 80 g/l). The salinity, grain size distribution, and past experience can normally be used to determine whether zone settling occurs; however, if uncertainty exists, a pilot column settling test can be performed on the simulated influent slurry in a 4-l graduated cylinder to determine the settling behavior. The procedures for this determination are given in EM 1110-2-5027.

If zone settling occurs, sufficient surface area must be provided for clarification so that supernatant will be generated as rapidly as water is discharged from the disposal facility over a weir. This procedure does not determine the quality of the supernatant. Quality or suspended solids concentration is a function of residence time, not surface area. If zone

settling does not occur, then the design of the disposal facility is based on just initial storage (compression settling) and effluent quality (flocculent settling).

Step 1--selection of design data. Use of the nomograph requires knowledge of the concentration of fine-grained solids in the influent, and the average flow rate or surface area of the disposal facility. The influent solids concentration is obtained as discussed above in step 1 for initial storage design or computed in Equations 3a and 3b. The average flow rate is needed if the minimum surface area is to be computed. If the mean residence time of the disposal facility is expected to be less than half of the number of hours of active disposal per day, the average flow rate is equal to dredge discharge rate (pipeline velocity times the cross-sectional area of the pipeline). If the mean residence time is expected to be greater than half of the operating hours per day, the average flow rate should be computed by Equation 4 as described in Step 1 for initial storage design. If the surface area is known and accepted as a given, the nomograph can be used to determine the maximum allowable average flow rate.

Step 2--use clarification nomograph. The clarification nomograph given in Figure 2 is typically used to estimate the minimum surface area in acres required for clarification by zone settling given the influent solids concentration in grams per litre and the average flow rate in cubic feet per second. The procedures are illustrated in the inset on Figure 2. Start by entering the nomograph at the value of the influent solids concentration in grams per litre on the left side of the bottom axis. Proceed vertically up to the first turning line representing the average case (Point A on the inset in Figure 2) and then to the second turning line (Point A' for the conservative case). These turning lines correspond to the statistical fits of the inverse of the zone settling velocity data as a function of influent solids concentration. Draw horizontal lines from the points of intersections (Points A and A') to the line representing the average flow rate in cubic feet per second (Points B and B'). Then continue both lines downward to the surface area axis to obtain a range of surface area in acres (between Points C and C') for design consideration. The nomograph assumes a hydraulic efficiency of 0.44.

The larger surface area should be used if the sediment is known to settle slowly. Materials with high clay fractions and high plasticity indices tend to settle slower. Underestimating the required surface area reduces the

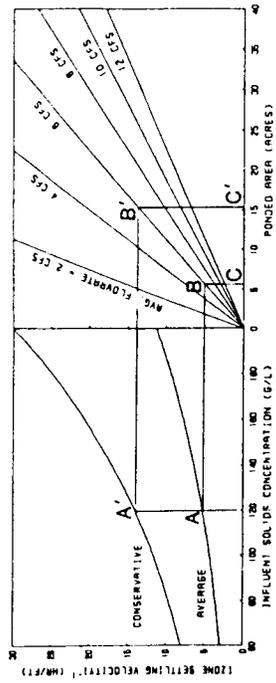
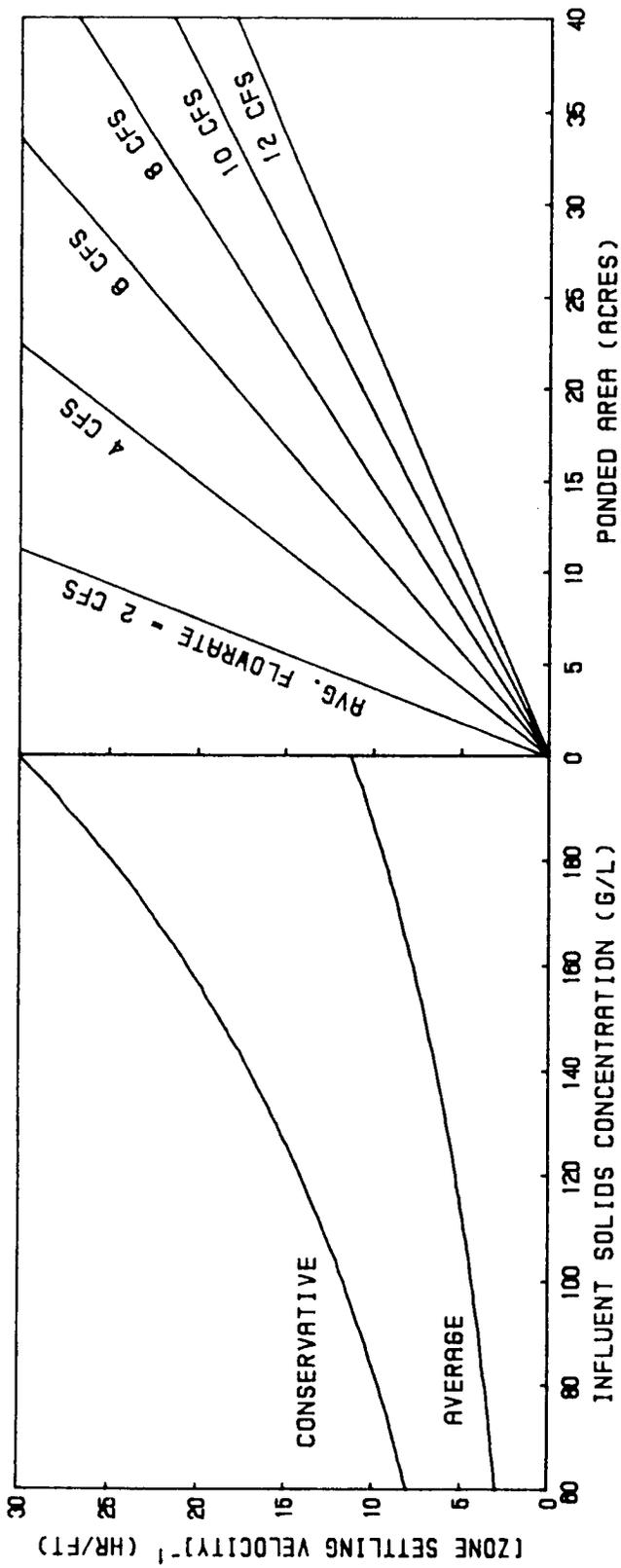


Figure 2. Nomograph to perform clarification (zone settling) design of confined disposal facilities for small dredging projects using statistical fits of a zone settling data base

allowable production rate, forcing the dredge to operate intermittently to lower the flow rate and permit clarification. Overestimating the required surface area for clarification increases the size and cost of the disposal facility.

Alternatively, the nomograph can be used to determine the maximum allowable flow rate for clarification given the surface area and the influent solids concentration. This procedure determines a range of maximum allowable flow rates for design consideration just as the above procedure yields a range of minimum surface areas. Start by drawing vertical lines at the value of the influent solids concentration in grams per litre and the value of the surface area in acres. Then draw horizontal lines at the intersections of the vertical line from the influent solids concentration with the lines for the average and conservative cases (Points A and A'). The points where these horizontal lines intersect the vertical line from the surface area axis define the range of maximum design flow rates in cubic feet per second. The lower flow rate should be used for slow settling sediments.

Design for effluent quality (flocculent settling)

Flocculent settling occurs under two different conditions--in some freshwater slurries with high clay content and in supernatants generated by zone settling of slurries. These two conditions are treated separately and a nomograph was developed for each--one for supernatants and one for slurries. However, both nomographs are identical in form and use. The nomographs assume that the depth of ponding is 2 ft. For other ponded depths the surface area axis must be adjusted by the multiplying the scale values by 2 and dividing the products by the actual ponded depth in feet. This adjustment is only approximate but should be adequate considering that the overall design approach is based on general settling trends instead of site-specific settling data. The nomographs also assume a hydraulic efficiency correction factor of 2.25 (a hydraulic efficiency of 0.44).

The development of the effluent quality nomographs assumed that the effluent quality is achieved solely by sedimentation. As can be seen in these nomographs in Figures 3 and 4, there is a practical limit to the effluent solids concentration that can be achieved solely by gravity settling, approximately 50 mg/l for slurries that settle by zone settling and 2 g/l for slurries that settle by flocculent settling. Better effluent quality can be achieved using chemical clarification. However, this additional treatment is

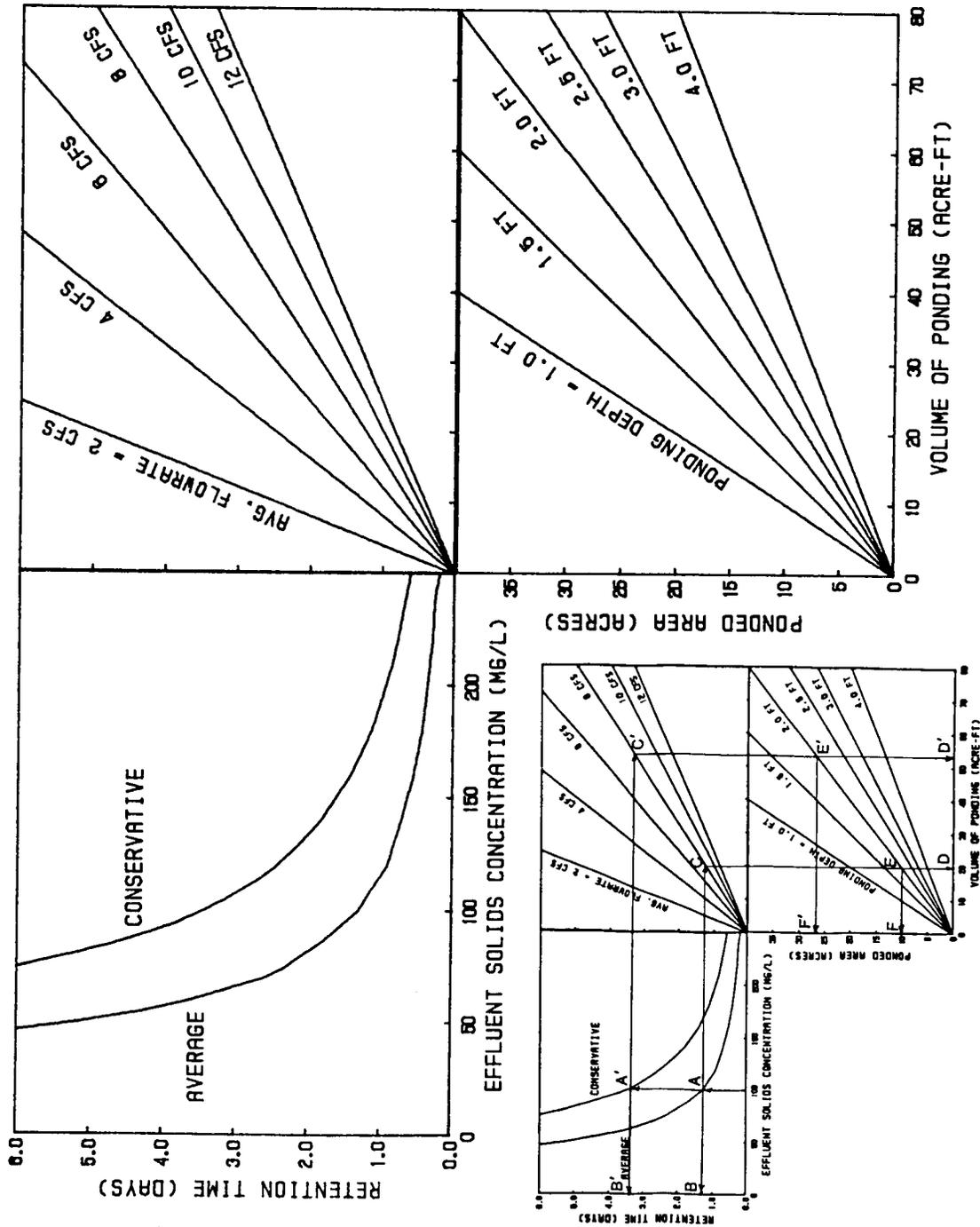


Figure 3. Effluent quality design nomograph developed for confined disposal facilities at small dredging projects using statistical fits of a flocculent settling data base for supernatants of dredged material slurries that settle by zone settling

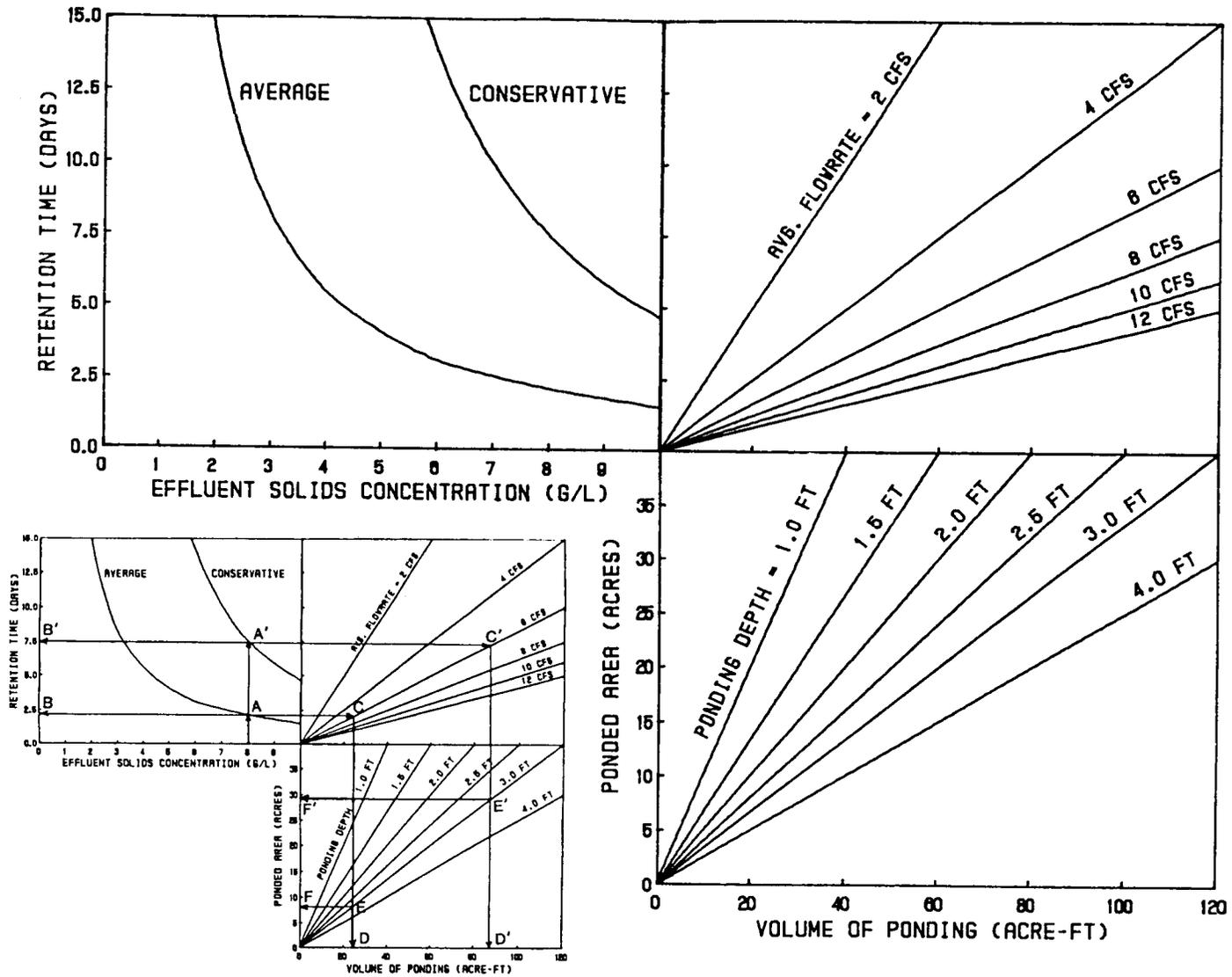


Figure 4. Effluent quality design nomograph developed for confined disposal facilities at small dredging projects using statistical fits of a flocculent settling data base for dredged material slurries that settle by flocculent settling

necessary only when the desired effluent solids concentration cannot be practically achieved considering the size of the available disposal area and the average flow rate or dredge production rate.

Step 1--selection of design data. The nomographs shown in Figures 3 and 4 can be used three ways. Typically, they would be used to estimate the minimum required surface area given the desired effluent solids concentration and the average flow rate. The selection of an average flow rate is the same as described above in step 1 for clarification design. However, the nomographs can also be used to estimate the effluent solids concentration given the surface area and average flow rate or the maximum allowable flow rate given the desired effluent solids concentration and surface area.

Step 2--use effluent quality nomograph (flocculent settling). To determine the minimum surface area, in acres, required to achieve the desired effluent quality, enter the effluent quality nomograph at the value of the desired effluent quality (in milligrams per litre on Figure 3 and in grams per litre on Figure 4) on the left side of the bottom axis. Proceed vertically up to the first turning line, representing the average case (Point A on the inset in Figures 3 and 4), and then to the second turning line (Point A' for the conservative case). These turning lines represent statistical fits of required retention time as a function of the desired effluent suspended solids concentration. Draw horizontal lines from the retention time axis (Points B and B') through these points of intersections (Points A and A') to the line representing the average flow rate in cubic feet per second (Points C and C'). The values where the horizontal lines meet the retention time axis define the design range of retention times that should be provided by ponding. Then continue both lines downward to the volume of ponding axis to obtain a range of volumes in acre-feet (between Points D and D') for design consideration. To determine the minimum required ponded area, draw horizontal lines from the points where the vertical lines for volume determination (Lines C-D and C'-D') intersect the line of the desired ponded depth (at Points E and E'), typically 2 ft, to the surface area axis. The points where the lines meet the area axis (Points F and F') define the range of minimum required surface area for achieving the desired effluent quality using the desired ponding depth.

The larger volume or area should be used if achieving the desired effluent quality is critical or if it is known from past experience with dredged material in the project area that long residence times are required to achieve

the desired effluent quality. To determine the maximum likely effluent quality when designing for average conditions, draw a vertical line downward from the point where the horizontal line for the average design conditions (the line connecting Points B and C) crosses the turning line for conservative design conditions. Then read the value where the vertical line meets the effluent solids concentration axis. As can be seen, underestimating the required surface area results in higher effluent suspended solids concentration. Overestimating the required surface area can result in higher disposal facility costs.

The nomographs can also be used to estimate the likely and maximum likely average effluent solids concentration for a disposal operation where the surface area in acres and the average flow rate in cubic feet per second are known. To determine the effluent quality, enter the nomograph at the value of the surface area in acres on the vertical axis of the lower right side of the nomograph (such as Point F). Proceed horizontally over to the line corresponding to the desired ponding depth (such as Point E). Then move vertically up to the line corresponding to the average flow rate in cubic feet per second (such as Point C). From this point of intersection draw a horizontal line to intersect the average and conservative turning lines on the left side of nomograph. At these intersection points on the turning lines, draw vertical lines downward to the effluent solids concentration axis and read the values of the likely and maximum likely average effluent solids concentration.

The maximum allowable average flow rate can also be estimated for a disposal operation where the surface area in acres and the desired effluent solids concentration are known. For these circumstances, enter the nomograph at the value of the surface area in acres on the vertical axis of the lower right side of the nomograph (such as Point D). Proceed horizontally over to the line corresponding to the desired ponding depth (such as Point E). Then move vertically up through the entire right side of the nomograph. Then, draw a vertical line up to the turning lines for the average and conservative design conditions from the value of the desired effluent solids concentration on the horizontal axis of the left side of the nomograph. Then, starting at the intersections of the vertical line and the two turning lines (Points A and A' on the inset), draw two horizontal lines to intersect with the vertical line drawn on the right side of the nomograph. The points of intersection on

this vertical line define a range of likely maximum allowable average flow rates in cubic feet per second. Overestimating the allowable flow rate results in higher effluent solids concentrations, while underestimating the allowable flow rate may unnecessarily restrict the dredging production rate.

Determination of disposal area geometry

In the three previous sections, procedures were presented to determine the minimum area required for initial storage, the minimum surface area required for clarification by zone settling, and the minimum surface area required for effluent quality when the size of the disposal facility was unknown. Ideally, all three of these area requirements should be equal to achieve the least costly facility because this would prevent the design from having greater volume for storage or effluent quality than is needed or used. In addition, facilities with smaller areas and higher dike heights are generally more economical and desirable.

Since the sizing of a disposal facility for initial storage and effluent quality is based on volume instead of area, the design procedures used a ponding depth and an estimate of the available depth for storage based on the maximum allowable dike height. Maximizing the storage depth minimizes the area required for storage; similarly, maximizing the ponding depth minimizes the surface area required for effluent quality. Since these depths are constrained by the maximum allowable dike height, trade-offs between storage depth and ponding depth can be made to more closely equate the area required for these design procedures. The minimum area required for clarification can be decreased only by decreasing the average flow rate or adding flocculents to the influent to increase the settling rate. Decreasing the average flow rate also proportionately decreases the surface area required for effluent quality and slightly decreases the area required for initial storage.

Surface area. The surface area of the disposal facility must be equal to or greater than the largest of the three minimum surface areas determined in the above procedures. If the minimum area for initial storage is much greater than the other two values, investigate the possibility of increasing the storage depth by increasing the maximum allowable dike height or decreasing the ponding depth or freeboard. Then repeat the initial storage analysis and if the ponding depth was decreased, perform the effluent quality analysis again. If the minimum area for clarification by zone settling is much greater than the other two values, consider decreasing the average flow rate or dredge

production rate (dredge size), particularly if this area is larger than the available site. After decreasing the flow rate, repeat the entire design procedure. If the minimum area for effluent quality is much greater than the other two values, examine the possibility of increasing the ponding depth by increasing the maximum allowable dike height or decreasing the storage depth or freeboard. Then repeat the effluent quality analysis and, if the storage depth was decreased, perform the initial storage design again.

After settling on a design area, compare this area with the size of the available sites. If the design area exceeds the available areas, consider a smaller flow rate or higher dikes. Also consider chemical clarification when the design is controlled by the clarification or effluent quality.

Dike height and storage depth. The height of dredged material at the conclusion of the disposal operation is computed by dividing the initial storage volume in thousands of cubic yards determined in Figure 1 by the surface area in acres. This quotient is then multiplied by 0.62 to convert the result to the height of stored material in feet.

To compute the dike height, add the ponding depth and freeboard depth to the height of stored dredged material. The required ponding depth can be computed if effluent quality requirements did not control the design. The required ponding depth is computed by dividing the volume of ponding in acre-feet determined in Figure 3 or 4 by the surface area in acres. The result will be the ponded depth in feet, but the design depth normally should not be less than 2 ft except when required by design constraints. Similarly, the freeboard normally should not be less than 2 ft except when required by design constraints.

Weir design

The effective weir length required to prevent resuspension at the weir can be determined using the nomographs in Figures 5 and 6. If the slurry settles by zone settling, use the nomograph in Figure 5; if the slurry undergoes flocculent settling, use Figure 6. A discussion of these settling processes is presented above in the design section for clarification (zone settling). To use the nomograph, enter the nomograph at the value of the average flow rate in cubic feet per second on the horizontal axis. Then, proceed vertically to the line corresponding to the design depth of ponding. At the point of intersection, draw a horizontal line to the vertical axis and read the value of the required effective weir length.

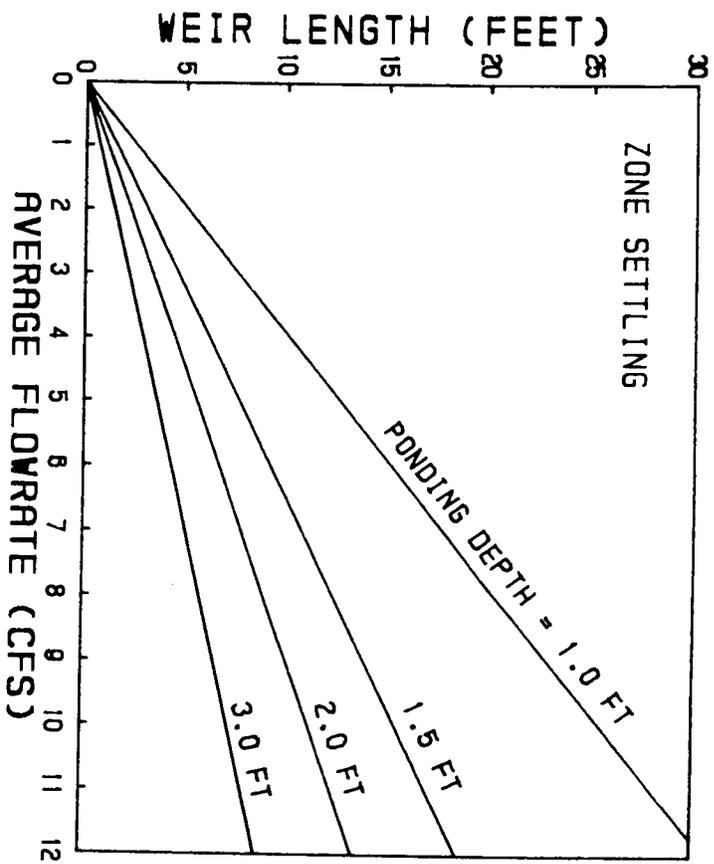


Figure 5. Weir design nomograph for confined disposal facilities receiving dredged material that settles by zone settling

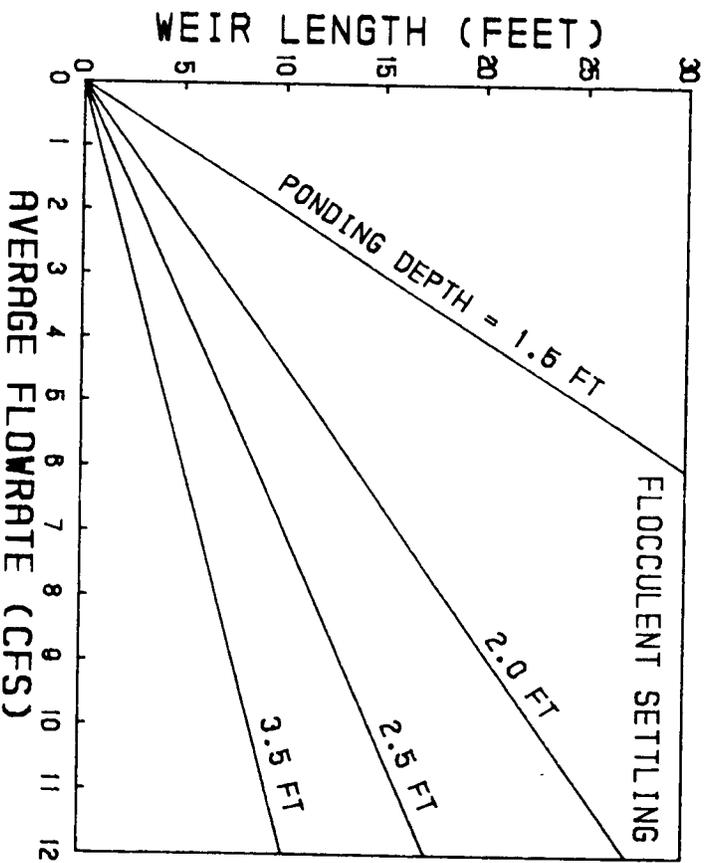


Figure 6. Weir design nomograph for confined disposal facilities receiving dredged material that settles by flocculent settling



Environmental Effects of Dredging Technical Notes



ROLE OF CONTAMINANT UPTAKE IN THE POTENTIAL USE OF *PHRAGMITES AUSTRALIS* (CAV.) TRIN. ON CONFINED DISPOSAL FACILITIES

PURPOSE: *Phragmites australis* (Cav.) Trin., common reed, is a plant species that is common to fresh- and brackish-water marshes of the world. *P. australis* has been recommended as one plant species that could survive and grow after being completely buried during dredged material disposal (Lee et al. 1976). *P. australis* can also serve as a physical barrier, because of its strong stems, to dredged material flow during hydraulic disposal. Decreasing dredged material flow helps to increase consolidation of hydraulically dredged material (Lee et al. 1976). *P. australis* is a plant species recommended for habitat development on dredged material disposal sites (Hunt et al. 1978). Plant establishment on marsh creation projects using uncontaminated dredged material poses little threat of increasing environmental cycling of contaminants. However, plant establishment or natural invasion of plants on contaminated dredged material has the potential for increased environmental cycling (mobility) of contaminants. Therefore, a literature review was conducted to determine contaminant uptake by *P. australis* since many dredged material disposal sites support lush stands of *P. australis* and contaminant uptake by this species was unknown.

BACKGROUND: Site management to favor colonization by desirable plant species can be used to minimize adverse environmental effects of contaminated dredged material. A desirable plant species is a species that minimizes contaminant uptake and subsequent environmental cycling (mobility) while providing dewatering and increased particle settling of the dredged material, as well as providing wildlife habitat. Two characteristics that a desirable plant species should have include a shallow rooting depth if a "clean cap" is used over contaminated dredged material and restricted uptake and translocation of contaminants. *Phragmites australis* may not be one of the desirable species due to its deep rooting behavior; also, virtually nothing is known about its contaminant uptake.

ADDITIONAL INFORMATION: This technical note is a summary of a contract report prepared under the Toxic Substances Bioaccumulation by Plants work unit in the Long-Term Effects of Dredging Operations Program. Dr. M. van der Werff of Vrije University, Amsterdam, The Netherlands, conducted the study. This note was written by Dr. Bobby L. Folsom, Jr., Environmental Laboratory, and Dr. M. van der Werff. For additional information, contact Dr. Folsom, (601) 634-3720, or the manager of the Environmental Effects of Dredging Programs, Dr. Robert M. Engler, (601) 634-3624.

The common reed, *Phragmites australis* (Cav.) Trin., is a halophytic grass having a worldwide distribution. It generally inhabits wetlands, particularly in disturbed environments, and often comprises the sole or dominant plant species. The wide distribution, the ability to withstand extreme environmental conditions (e.g., deep burial, anaerobiosis, and salinity flux) and its aggressive growth make this plant important in the overall management of dredged material disposal sites.

The survival and reproductive strategies of *P. australis* make it one of the first colonizers in newly reclaimed wetlands such as dredged material disposal sites or lakes drained for agricultural uses. Despite its aggressive growth habit, *P. australis* does not normally invade established wetlands and does not generally displace other wetland plant species. Deep root and rhizome formation are important morphological characteristics of *P. australis* that could result in increased contaminant mobility through plant uptake and may preclude its use.

Many studies on the nutritional status of *P. australis* have been conducted during the past 20 to 30 years, but only a few have studied contaminant uptake. Most of the literature on contaminant uptake by *P. australis* has been concerned with trace metals essential for plant nutrition, especially copper, iron, manganese, and zinc. *P. australis* plays an important role in the cycling of nutrients in lakes (Wetzel and Allen 1972, Schroder 1973, Banoub 1975, Mason and Bryant 1975). However, very little is known about the role of *P. australis* with respect to heavy metal cycling (Schierup and Larson 1981). Schierup and Larsen (1981) investigated *P. australis* cycling of zinc, copper, lead, and cadmium in two Danish lakes--one polluted and one unpolluted. They found that uptake of these heavy metals by *P. australis* was greater in the unpolluted lake population than in the polluted lake population. Schierup and Larsen (1981) indicated that the difference in uptake was dependent on edaphic factors rather than on the amount of heavy metals present in the sediment. Two of the edaphic factors thought to influence heavy metal availability, sediment pH, and sediment oxidation-reduction (redox) status were sufficiently different between the lakes to explain the difference in uptake (i.e., uptake increased as redox increased or pH decreased). Auclair (1979) also found that tissue concentrations of several emergent hydrophytes (of which *P. australis* is one) were dependent on edaphic factors and indicated plant growth affected both nutrient and heavy metal tissue concentrations as well. A study of heavy

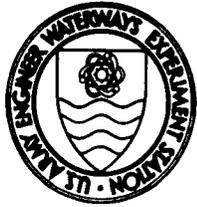
metal uptake by marsh plants in Lake St. Clair (Mudroch and Capobianco 1978) revealed that increased plant growth during the growing season resulted in increased heavy metal concentrations in several plant species. Mudroch and Capobianco (1978) showed that plant concentrations of nickel, chromium, and copper increased during vegetative growth of *Typha latifolia*; cadmium and zinc increased during vegetative growth of *Myriophyllum heterophyllum*; cobalt and lead increased during vegetative growth of *Chara* spp.

Increased heavy metal uptake resulting from increased plant biomass production appears to be real and may significantly contribute to heavy metal cycling by marsh plants, especially *P. australis*. Various investigators have shown that *P. australis* has a great potential for increased biomass production through increased nutrient uptake from nutrient-enriched sediments (Wile, Palmeteer, and Miller 1981, Pratt and Andrews 1981, Bjork 1967). Ulrich and Burton (1985) found that *P. australis* responded to nitrogen and phosphorus but not to potassium. They determined that both biomass production and the concentration of nitrogen and phosphorus in the plant tissue increased with increasing availability of nitrogen and of phosphorus in the sediment. In a study on seasonal effects of heavy metal concentrations in *P. australis*, Larsen and Schierup (1981) showed that plant concentrations of zinc and copper increased as plant biomass increased. The implications of this behavior are significant. If edaphic factors of a polluted lake become equal to those of a nonpolluted lake, then there is greater potential for increased contaminant uptake due to increased plant biomass production. Most contaminated dredged material contains elevated quantities of nitrogen and phosphorus and is capable of high plant biomass production. Increased plant biomass production from *P. australis* (or other plant species) growing on contaminated dredged material may result in increased contaminant cycling into the food web. Enhanced biomass production/contaminant cycling combined with factors known to increase contaminant availability (e.g., oxidized sediment redox conditions, oxidation of organic matter, and low pH) may result in significant contaminant cycling (mobility). *P. australis* cannot be recommended as a desirable plant species until the relationship between increased plant growth and increased contaminant uptake can be determined.

The relationship between increased plant biomass production (growth) and increased contaminant uptake is important and needs to be addressed. Understanding this relationship may prove to be a key factor in predicting environmental cycling of contaminants by plants grown in contaminated dredged material. The work unit, Toxic Substances Bioaccumulation by Plants, in the Long-Term Effects of Dredging Operations Program is an ongoing work unit that could address the relationship between increased plant growth and increased contaminant uptake.

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Environmental Effects of Dredging Technical Notes



PCDDF89--UPDATED COMPUTER MODEL TO EVALUATE CONSOLIDATION/DESICCATION OF SOFT SOILS

PURPOSE: This technical note describes a modified and updated version of the computer program Primary Consolidation and Desiccation of Dredged Fill (PCDDF). PCDDF was developed under the Dredging Operations Technical Support Program for use in evaluating the long-term storage capacity of confined dredged material disposal areas. The program accounts for both the consolidation and desiccation of compressible materials and has recently been modified to more accurately simulate layered field conditions which often exist in disposal sites. The modified computer program is called PCDDF89.

BACKGROUND: As a part of the planning and management activities associated with dredging of the Nation's navigable waterways, evaluations are periodically conducted to assess the disposal site capacity needs for storing dredged sediments. Such evaluations help identify shortfalls (both short-term and long-term) in existing containment area storage capacity; they may also be used to evaluate potential new disposal sites.

Storage capacity evaluations require quantification of the amount and rate of both primary consolidation and desiccation which will occur in the site of interest. A computer program was developed to predict surface settlement as a result of these two phenomenon (Cargill 1985). This program incorporates a finite (large) strain theory of consolidation and an empirical desiccation model. The original program was capable of accounting for placement of multiple lifts of dredged material at various points in time as well as for the consolidation and desiccation of the entire deposit. However, the original model could only handle one dredged material type and one foundation soil type.

With increased emphasis on the long-term management of dredged material disposal and the required development of long-term disposal plans (greater than 10 years), the need to accurately predict dredged material containment area site capacity has also increased. To assist Corps of Engineers elements in these planning efforts, PCDDF has been modified to account for multiple material types in both the dredged material and the foundation soils.

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Original Program

PCDDF simulates the filling and subsequent settlement due to consolidation and desiccation of multiple lifts of dredged material within a confined disposal facility; it also accounts for consolidation of a compressible foundation layer. The consolidation process is modeled by the finite strain theory of consolidation which accounts for the large deformations and nonlinear soil properties inherent in the very soft soils commonly encountered during maintenance dredging (Gibson, England, and Hussey 1967; Cargill 1985). The desiccation process is modeled using an empirical description of the water balance in the uppermost dredged material lift. The surcharge which results from the desiccated crust is accounted for in consolidation computations for the underlying lifts.

PCDDF uses an explicit finite difference solution at successive time steps for modeling the one-dimensional consolidation process, and it makes monthly adjustments in the top boundary condition and boundary location in accordance with the amount of consolidation and desiccation which have occurred. In addition to material settlement, which is calculated from the void ratio-permeability relationship, the program also calculates the stresses and pore pressures throughout the material deposit using the void ratio-effective stress relationship. Any sequence of varying dredged material disposal volumes as well as consolidation in an underlying foundation material can be considered. The original PCDDF model was limited to analysis of only one dredged material type, i.e., dredged material with one compressibility and one permeability relationship, although placement of numerous lifts of this material can be simulated; it can analyze only one compressible foundation soil layer.

The accuracy of the original PCDDF to simulate the settlement of dredged material due to consolidation and desiccation has been verified for a number of sites (Cargill 1985; Poindexter 1988). At all of these sites, predictions of surface elevation versus time were made and were compared to measured field data. Generally very favorable results were obtained. However, innovative approaches were sometimes necessary to bypass the limitation of one material type. For

example, sometimes samples of different materials to be placed into one disposal site would be combined before laboratory testing to provide "average" compressibility and permeability data. When one layer was significantly thicker than any others, the properties of the thick layer would often be assigned to the entire material thickness. In some cases when multiple thick compressible layers required analysis, superposition of settlement results for the various layers was used (Poindexter 1988).

Modifications

PCDDF has recently been modified by Stark (in preparation) to execute faster and to account for different types of foundation and dredged fill materials. PCDDF uses seven different interpolation routines to calculate various soil properties, such as stresses and pore pressures, at specified times. In a typical problem involving the behavior of a single layer of dredged fill, PCDDF will make 90,000 to 100,000 interpolations over 15 time steps. As a result, the interpolation routines had to be optimized before the multi-layer option could be effectively implemented. A "history-dependent" interpolation scheme was chosen so the interpolations were not required to start at the beginning of the soil property distribution, but at the point of the previous interpolation. The use of the history-dependent interpolation scheme resulted in a 20 to 25 percent increase in the execution speed of PCDDF.

PCDDF was also modified to allow the analysis of 10 different foundation layers and 25 different dredged fill materials. The same input is required for each material type as was required for the single-layer problem. In fact, the existing single-layer data files can be used in the new version of PCDDF by adding one parameter to the data file which indicates whether the problem is single- or multi-layer. If the parameter indicates single layer, the program will use the existing input and produce the same output as the older version of PCDDF but 20 to 25 percent faster. The multi-layer output has the same format as the original single-layer output except that the different material properties and the final void ratios, stresses, and pore pressures will be printed with a corresponding material identification number.

The ability to model the various types of foundation and dredged fill materials results in better predictions of the long-term capacity of confined

dredged disposal areas. The increased speed of PCDDF89 will also make the periodic capacity evaluations of the areas a more manageable task.

Other Applications

Although PCDDF was originally developed to assess settlement of very soft layers of dredged material in confined disposal facilities, it is also applicable to other compressible soil deposits. The finite strain consolidation theory used in PCDDF89 is applicable to soils ranging in compressibility from soft to firm and can be used for a variety of consolidation analyses including conventional one-dimensional analyses.

PCDDF can also properly be used to analyze soils located either above or below the water table. Since the program uses the principle of effective stress, it will accurately analyze subaqueous soil deposits such as in-situ bottom soils and dredged material deposits. Although PCDDF is a one-dimensional program, it has been used successfully to analyze subaqueous mounds of dredged material with side slopes of approximately 1.5 to 5H:100V (Poindexter 1988).

Availability

PCDDF89 will execute on any IBM-compatible microcomputer containing 640 kilobytes of random access memory. It is highly recommended, but not required, that the computer have a math coprocessor chip and a hard disk. The data can be entered into the program interactively or through a data file. The program's output can be stored in a file, sent to a printer, or displayed on the screen. A comprehensive user's guide which accompanies the program describes in detail the mathematical model and the various input and output options. PCDDF89 will be incorporated into the Automated Dredging and Disposal Alternatives Management System (ADDAMS) in the near future (Schroeder 1988). At present, the old version is available under ADDAMS.

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Environmental Effects of Dredging Technical Notes



FACTORS AFFECTING LEACHATE QUALITY

PURPOSE: This technical note describes factors affecting leachate quality for dredged material in confined disposal facilities (CDFs). Factors evaluated include desorption kinetics, sediment concentration, and association of PCBs with soluble and colloidal organic matter.

BACKGROUND: Contaminated dredged material is often placed in confined disposal facilities where movement of contaminants by leachate is an important environmental concern. No routinely applied laboratory testing protocol to predict leachate quality and quantity from confined dredged material disposal facilities is currently available. In 1984, the US Army Corps of Engineers (USACE) initiated confined disposal facility leachate investigations by developing a theoretical framework for prediction of leachate quality based on mass transport theory. The theoretical framework included both batch and column testing. Batch testing provides a quick, relatively easy method for determining the distribution of contaminants between dredged material and leachate, while column testing more closely approximates contaminant losses under field conditions in a CDF. Operationally defined equilibrium distribution (partitioning) coefficients were derived from batch tests to relate aqueous phase concentration to solid phase concentration. Distribution coefficients derived from batch testing could then be used in conjunction with column operating parameters and mass transport theory to compare predicted results with those observed from column leaching experiments.

The approach recommended for application to dredged material was used in studies at Indiana Harbor, IN; Everett Harbor, WA; and New Bedford Harbor, MA. Results of these studies were evaluated in 1988 at a workshop hosted by Louisiana State University in Baton Rouge. Among the recommendations of the workshop was investigation of desorption kinetics and the impact of colloidal organic matter on interactions between solid and liquid phases. Results of those investigations for PCBs are reported in this Technical Note.

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Introduction

At present, no laboratory testing protocol capable of routinely predicting leachate quality from confined dredged material disposal sites is available. Testing procedures to predict leachate quality are, therefore, needed in order to fully evaluate contaminant mobility for the confined disposal alternative for dredged material. If leachate quality and quantity can be predicted, the potential impacts of contaminated dredged material disposal in a confined disposal facility (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, IN; Everett Harbor, WA; and New Bedford Harbor, MA (Environmental Laboratory 1987, Palermo et al. 1988, Myers and Brannon 1989). Results of these laboratory studies, summarized previously in Technical Note EEDP-02-7, were reviewed at a workshop hosted by Louisiana State University in Baton Rouge, LA. Participants concluded that work conducted to date is good and generally validates the basic approaches taken, but that much research remains to be conducted before a leachate test protocol will be ready for routine use.

This Technical Note reports on results of investigations conducted on desorption kinetics of polychlorinated biphenyls (PCBs), the impact of colloidal microparticulates and soluble organic matter on interactions between solid and liquid phases, and the comparability of methodologies using sequential and single-point desorption batch tests.

Methods

Desorption kinetics

Desorption kinetics were determined for a saline sediment from Oakland Harbor and a freshwater sediment from the Chicago River. Sediments were treated to a level of $1 \mu\text{g } 2,2',5,5' [^{14}\text{C}] \text{tetrachlorobiphenyl (PCB-52) / g dry weight sediment}$. A 4:1 water-sediment ratio was used in the testing. As appropriate desorption times were reached, tubes were centrifuged and 1 ml of the solution was counted by liquid scintillation (LS). A subsample passed through a C-18 Sep-Pak cartridge (Waters Associates, Milford, MA) that traps free PCB and passes organically complexed PCB (Landrum et al. 1984) was also counted.

The procedure in the preceding paragraph was repeated with Oakland Harbor, CA, sediment at 20 ppm PCB-52 and desorption times of 1 hr, 2 hr, 6 hr, 24 hr, 7 days, and 30 days.

Water-sediment ratio

Sediments from Oakland Harbor, CA, Baltimore Harbor, MD, and the Chicago River, IL, were loaded with 20 ppm of PCB-52 at water-sediment ratios of 2:1, 4:1, 25:1, 50:1, and 100:1 and leached for 24 hr. Sediments from Oakland and Baltimore Harbors were leached with saline water (25 ppt); sediment from the Chicago River was leached with distilled-deionized water.

Sequential desorption

Sediments used in the water-sediment ratio batch testing were also subjected to sequential desorption following loading with 20 ppm PCB-52. A 4:1 water-sediment ratio and a shaking time of 24 hr were used in seven sequential cycles of the batch leach tests, details of which are described by Myers and Brannon (1988). The two sediments from saline environments (Oakland and Baltimore Harbor) were leached with distilled-deionized water in one set of tests and with saline (25 ppt) water in another set of tests.

Data analysis

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

Results and Discussion

Desorption kinetics data for Oakland Harbor and Chicago River sediments with an initial PCB-52 level of 1 μg [^{14}C]PCB-52/g dry weight showed that steady-state conditions were attained within 2 hr. This experiment was repeated at higher [^{14}C]PCB-52 loading (20 $\mu\text{g}/\text{g}$ dry weight) with Oakland Harbor sediment in order to examine the contribution of complexed PCB on PCB desorption kinetics.

Results of this experiment (Figure 1) paralleled those observed in the first experiment and showed that steady-state PCB-52 concentrations were rapidly attained in the leachate, essentially reaching steady-state at the first sampling time (1 hr). Organic and complexed PCB-52 constituted from 4.8 to 9.6 percent of the total PCB-52 in solution and did not change appreciably over time. These results demonstrated that the majority of the PCB-52 was present in uncomplexed form and that complexed PCB-52 did not appreciably change the concentration of

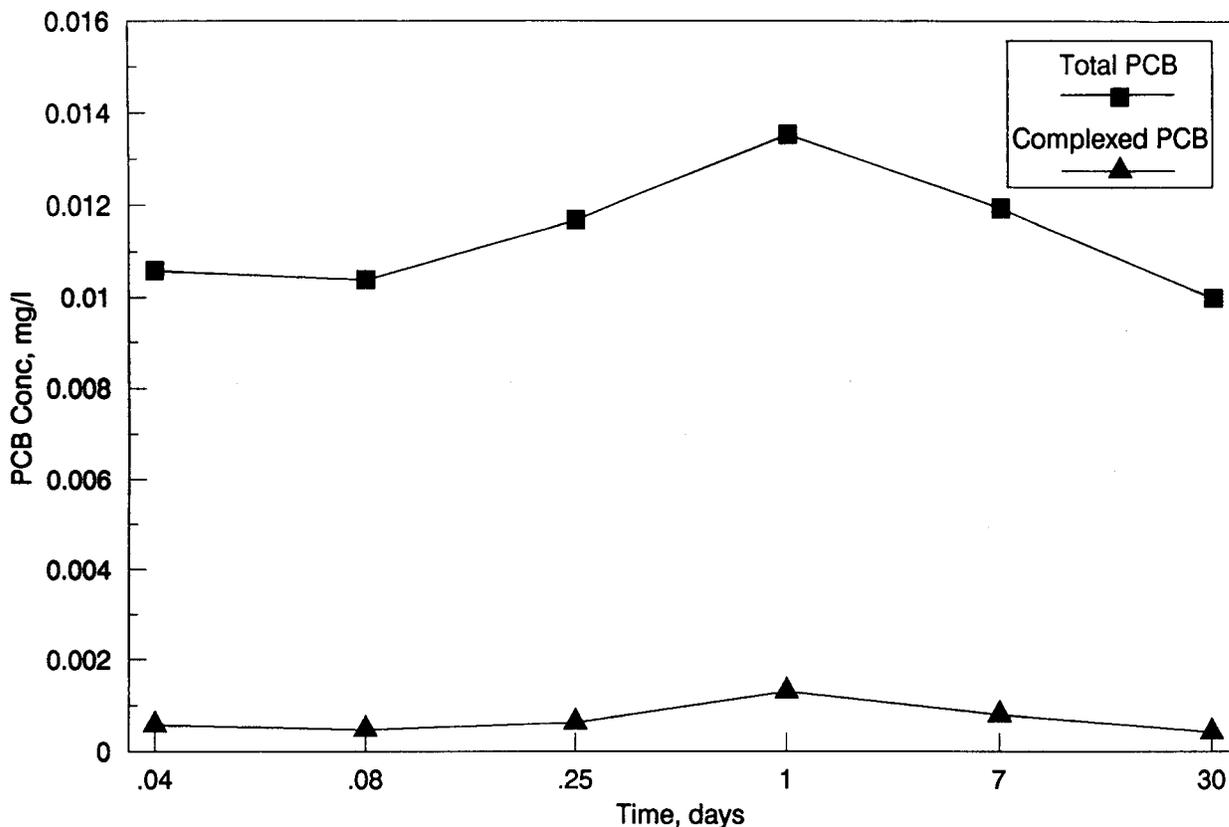


Figure 1. Desorption kinetics for PCB-52 in leachate from Oakland Harbor sediment amended with 20 $\mu\text{g C}^{14}\text{PCB-52/g}$ dry weight sediment

PCB-52 in the leachate as the time of shaking increased. The rapid attainment of steady-state conditions by PCB-52 in this study supports the findings of previous desorption kinetics studies (Environmental Laboratory 1987, Palermo et al. 1988, Myers and Brannon 1989), which showed that 24 hr was sufficient to attain steady-state conditions in leachate from dredged material for hydrophobic organic contaminants such as PCBs. Results from this study indicate that for PCB-52, desorption from sediment to water will not appreciably change over one month.

Desorption results from the sediment-water ratio batch testing showed that sediment concentration exerted a pronounced effect on distribution coefficients (K_d s) derived from a single desorption step (Figure 2). These findings agree with those of other (Voice, Rice, and Weber 1983; Gschwend and Wu 1985; DiToro et al. 1982; O'Connor and Connolly 1980) who reported a pronounced effect of solids on contaminant partitioning, although they did not examine solids concentrations at the high levels reported in this study.

Concentrations of total and complexed PCB-52 in leachate at each sediment concentration are presented in Figure 3. These results suggest that the PCB-52

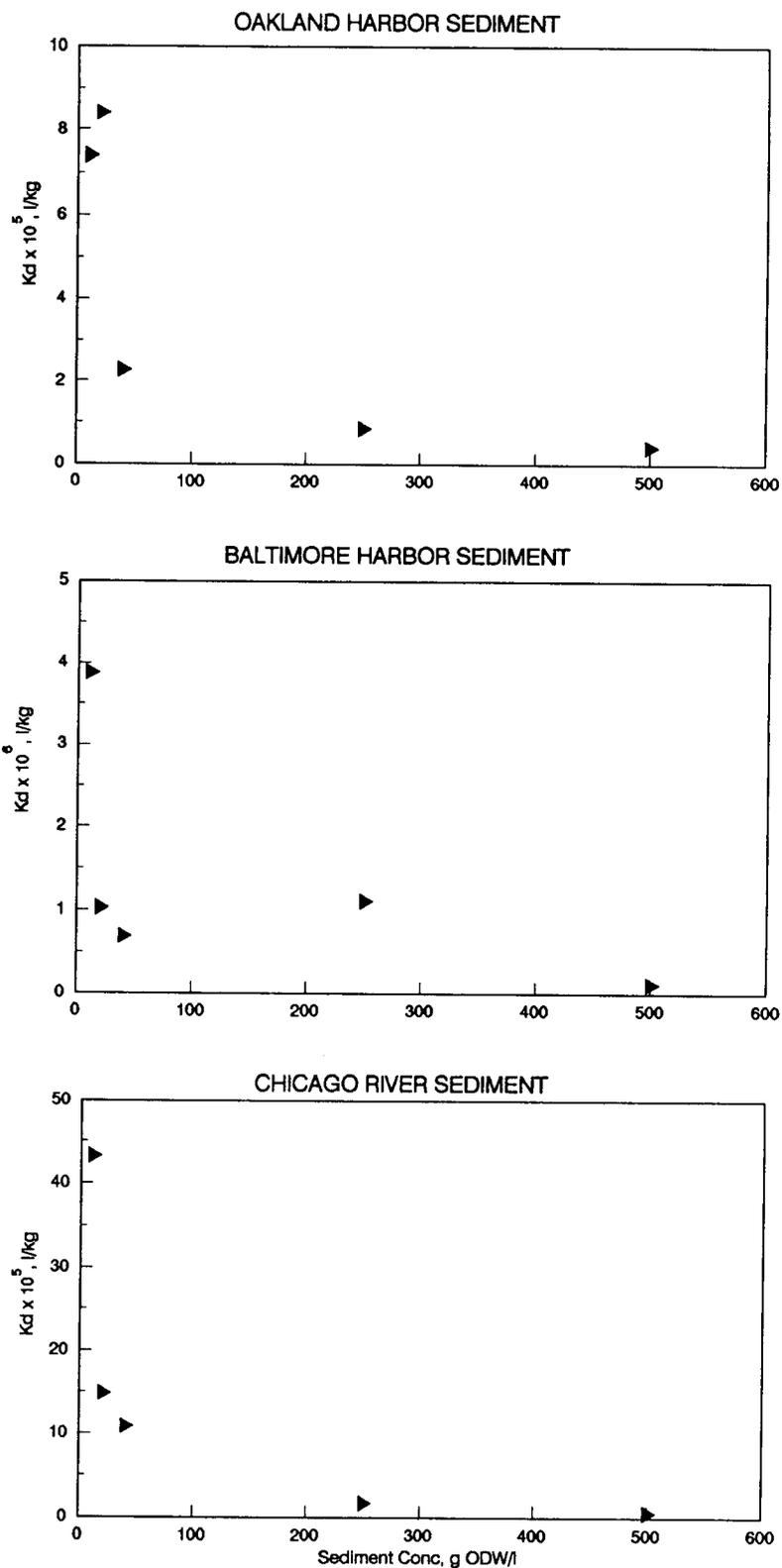


Figure 2. Single-step desorption distribution coefficients at varying sediment concentrations from sediments amended with $20 \mu\text{g C}^{14}\text{PCB-52/g}$ dry weight sediment

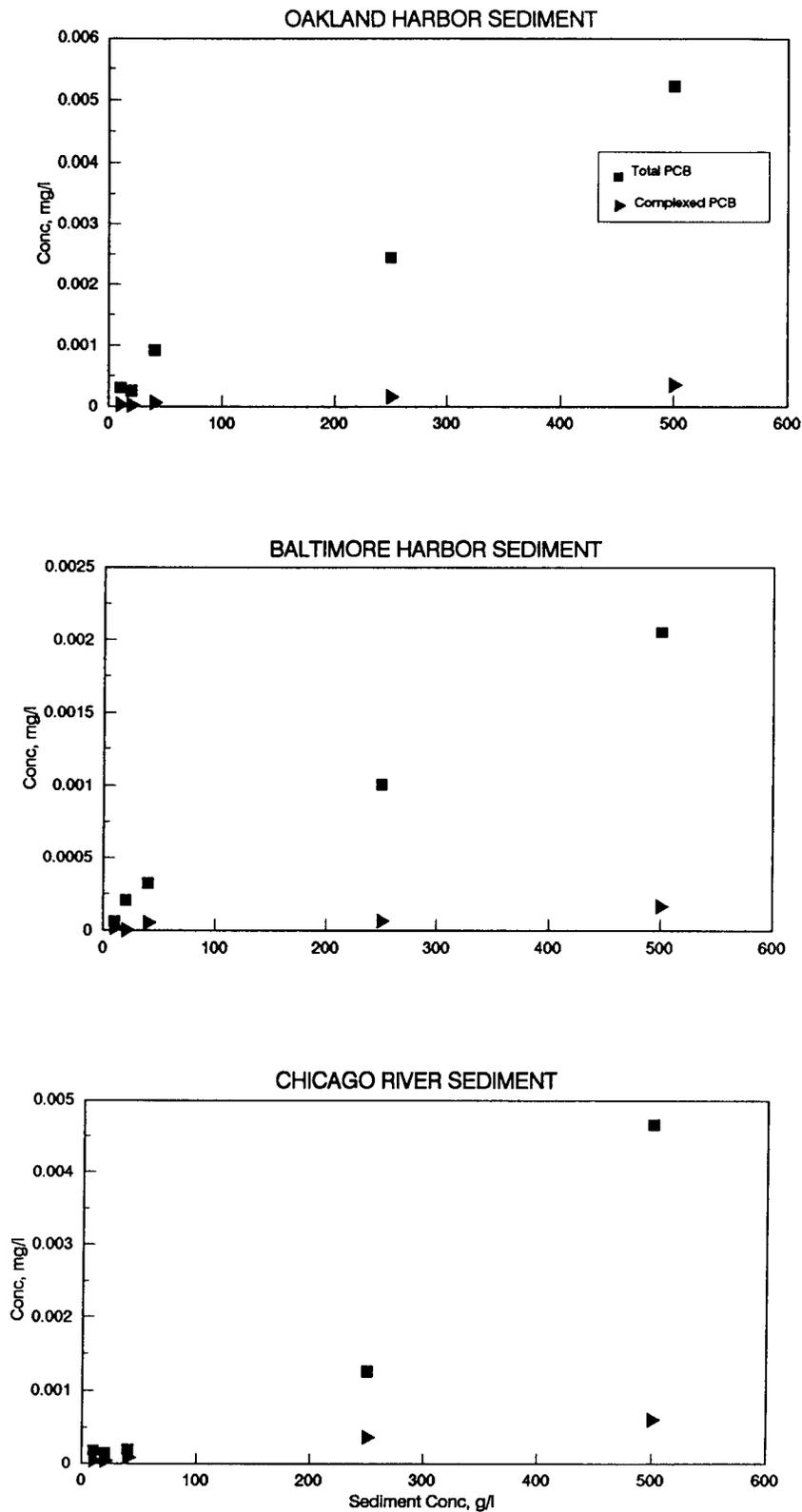


Figure 3. Total and complexed C^{14} PCB-52 leachate concentrations as a function of sediment concentration (sediments amended with $20 \mu\text{g } C^{14}$ PCB-52/g dry weight sediment)

in solution, which includes particulate matter smaller than $0.01 \mu\text{m}$, is free and uncomplexed at higher sediment concentrations, e.g., 250 and 500 g/l. Although the amount of complexed PCB-52 does increase slightly with increasing sediment concentration, free PCB-52 constitutes most of the total leachate PCB-52. The implication of these results for leachate testing is that desorption isotherms obtained by conducting batch tests with varying sediment-water ratios will not yield a useable K_d . The isotherms resulting from such data exhibit a negative slope (the slope of the line is K_d). Negative K_d s cannot be used in mass transport equations.

Sequential desorption testing indicated that pronounced differences existed between the behavior of PCB-52 in leachate from freshwater and saline sediments. In saline sediments leached with fresh water, the fraction of complexed PCB-52 in leachate increased as leaching proceeded, peaked at the third leach cycle, and then decreased (Figure 4). This is possibly due to release of dissolved organic carbon from sediment as salinity decreased in the leachate (Myers and Brannon 1988) during sequential leaching of saline sediment with freshwater. This mechanism is supported by results for freshwater Chicago River sediment leached with freshwater. For Chicago River sediment, the fraction of complexed PCB-52 decreased as leaching proceeded, a phenomenon that was also observed when sediments from saline areas were leached with saline water. The fraction of complexed PCB-52 peaked at less than 0.35 (35 percent of total leachate PCB-52) in saline sediments leached with freshwater.

Sequential batch testing results indicate that complexed and free PCB-52 are both important components of leachate for saline sediments leached with freshwater. Instead of decreasing as leaching proceeds as predicted by theory, leachate PCB-52 concentrations increase and then decrease in saline sediments leached with freshwater. Peak concentrations of leachate PCB-52 in saline sediments leached with freshwater were almost double the peak concentrations reached when saline sediments were leached with saline water. In saline sediments leached with saline water almost all PCB-52 released was free (>95 percent) following the initial leach cycle.

Results of sediment ratio and sequential batch testing from PCB-52 indicate that sediment concentration and release of both complexed and free PCB-52 during leaching are important factors affecting leach test results. The use of saline water or freshwater also exerts a pronounced effect on sequential batch leaching results, producing a peak in the middle of the leach cycle instead of steadily

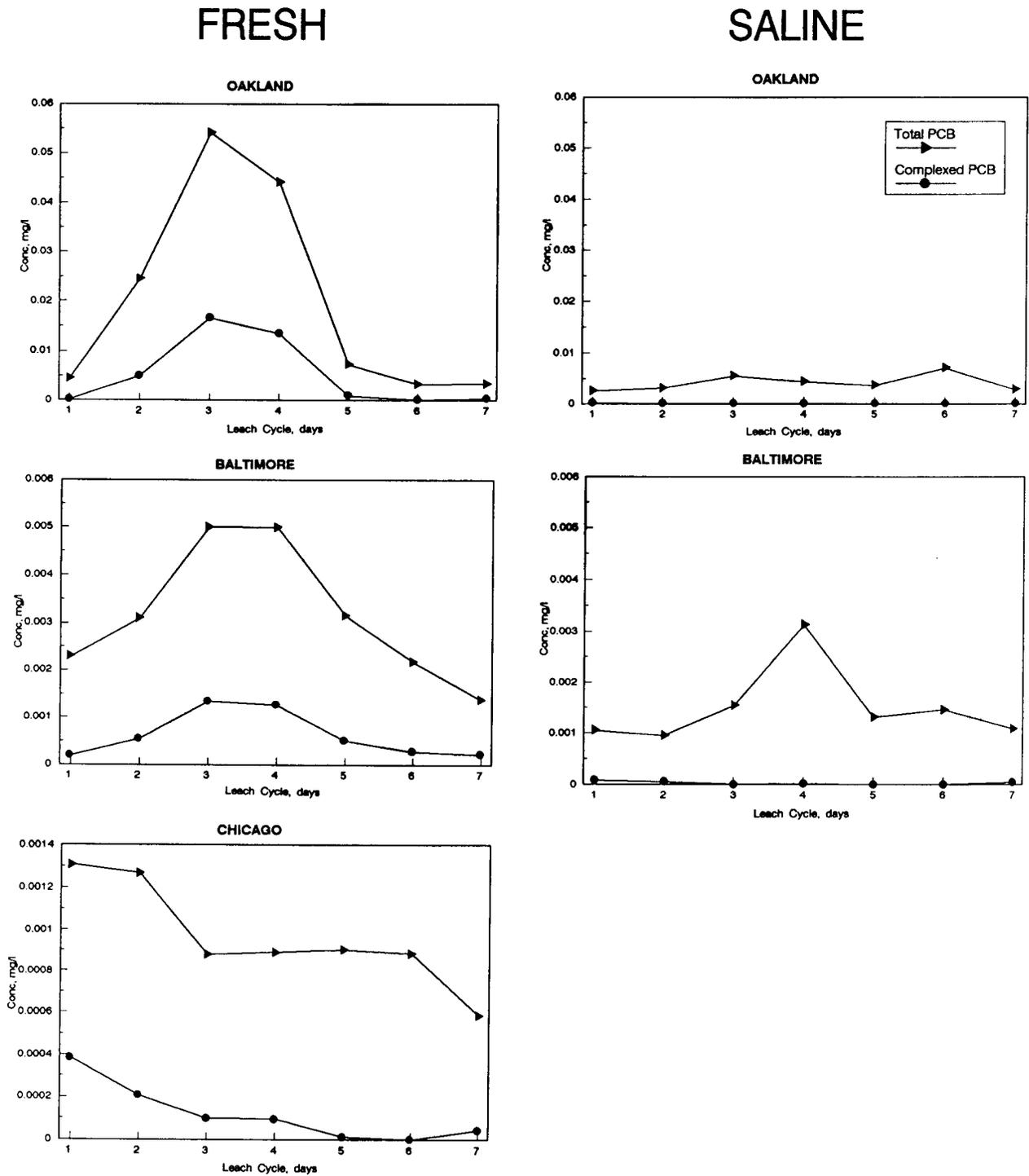


Figure 4. Concentration of total and complexed $C^{14}PCB-52$ in sequential batch leachate from sediments amended with $20 \mu g C^{14}PCB-52/g$ dry weight sediment and leached with fresh and saline water

decreasing leachate concentrations. This behavior by free and complexed PCB in sequential leachate from saline sediments is complex. Therefore, development of distribution coefficients for describing leaching of hydrophobic organic compounds from saline sediment with freshwater is difficult, but possible.

Desorption batch testing results with varying sediment concentrations indicate that for PCB-52, sediment concentration should be kept as high as possible to closely simulate the sediment concentrations found in deposited sediments. Batch tests that involve a series of tests using varying sediment concentrations will not provide distribution coefficients for predicting the desorption of PCB-52 at the high sediment concentrations found in confined disposal facilities.

The studies reported here provide a basis for evaluating the application of batch test procedures for determining PCB losses from dredged material in CDFs. The expanded understanding of mechanisms by which PCBs partition between water and sediment at high solids concentrations contributes significantly to development of appropriate test procedures for hydrophobic organic compounds.

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Environmental Effects of Dredging Technical Notes



PCB Volatilization from Dredged Material, Indiana Harbor, Indiana

Purpose

This note summarizes the theory and application of a model to predict the mass loss of polychlorinated biphenyls (PCBs) from dredged material through volatilization. A comparison to other contaminant pathways is presented for both in-lake and upland disposal.

Background

Contaminated sediments placed in a confined disposal facility (CDF) provide the potential for volatile organic chemicals (VOCs) to be released through volatilization. Theoretical models have been developed to describe the physical and chemical processes involved in transferring the VOC from the solid or liquid phase to the air (Thibodeaux 1989). To date, PCBs have been the VOC of concern; however, the theory presented is applicable to other VOCs including polycyclic aromatic hydrocarbons (PAHs). The documentation provided is not sufficient to fully understand the development of the models described in this note. The user should refer to the original reports, for complete understanding of model development and limitations.

Additional Information

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Introduction

Volatilization is the process whereby a compound passes into the air from a solid or liquid surface. The degree of volatilization can be generally related to Henry's constant of the compound: a compound with a high Henry's constant has a higher volatilization potential than one with a low Henry's constant.

The model presented in this note provides an estimate of the mass of polychlorinated biphenyls (PCBs) lost from an in-lake and an upland confined disposal facility (CDF). PCB was the only compound considered due to its regulatory significance and to simplify development of the models. It is anticipated that other semi-volatile and volatile compounds such as polycyclic aromatic hydrocarbons (PAHs) will be modeled in the future for sediments contaminated with these substances.

Chemical equilibrium principles are used in this note to determine the transfer of the volatile organic chemicals (VOCs) between various phases. In the case of VOCs associated with sediment, three phases of matter are involved. These are the solid particles which constitute the sediment and include both organic matter and mineral matter comprising the particles. The two other primary phases include air and water. With respect to dredging, VOCs can enter the air from either the water or sediment surfaces. For volatilization to occur from the water surface, the VOC must first desorb from the suspended solids phase and diffuse through the water before being emitted into the air.

Model Purpose

PCB volatilization models developed by Thibodeaux (1987) were adopted by the Chicago District to local conditions as part of the preparation of the Draft Environmental Impact Statement (DEIS) for Indiana Harbor and Canal Maintenance Dredging and Disposal Activities, Lake County, Indiana. The models estimate the mass flux of PCBs from a proposed CDF by volatilization from dredged material. Two scenarios were considered: the first assumes that the dredged materials are placed in an in-lake CDF, while the second assumes placement in an upland CDF.

Volatilization is complicated and can involve a number of transfer pathways. In order to quantify volatilization of contaminants to air, the major sources, pathways, and external parameters which affect the transfer must be addressed. Lab and field verification of critical transfer coefficients are lacking, and hence a complete quantification of PCB volatilization for all activities associated with a dredging operation is impossible. Therefore, the models were used as an indication of the relative significance of volatilization when compared to other loss pathways (such as leachate, seepage, plant, and animal uptake) for various operational schemes. In this manner, potential PCB mass flux for different placement options can be estimated and viable options can be evaluated against each other and the no action plan.

Model Assumptions

Theoretical chemodynamic models for organic pollutants in dredged material have been developed to estimate potential emission rates of PCBs to the air (Thibodeaux 1989). Although these models have not been verified experimentally for dredged material, studies of pesticide volatilization from soils, VOC emissions during refinery waste landfarming, and VOC emissions from hazardous waste lagoons indicate that theoretical chemodynamic models, when properly formulated, provide realistic estimates of VOC volatilization (Thibodeaux and Hwang 1982; Thibodeaux and Becker 1982; Thibodeaux, Parker, and Heck 1984; and Ek-lund, Nelson, and Wetherhold 1987). It should be noted that input to the model is highly dependent on the physical aspects of a particular CDF, the placement method, and the amount of time for a particular filling operation, as well as the lifetime of the CDF.

The equation used to calculate flux from exposed sediments describes chemical movement in the unsaturated pore spaces near the exposed surface. Sediments are initially in a semisaturated state, but surface layers soon will approximate the unsaturated situation. This initial transient state is not accounted for by the model. Also, wetting and drying cycles generated by rainfall were not considered.

The major emission locales for a CDF and its inherent operations are dredging and transporting, submerged sediments (ponded zone), exposed sediments void of vegetation, and sediments with vegetative cover.

Because of complexities involved and the lack of sufficient theory, this evaluation considers only the submerged sediments and the exposed sediments void of vegetation locales as emission sources for PCB flux.

Model Formulation

Submerged Dredged Material (Pond Volatilization) Algorithms

The pathway for volatilization in the case of submerged dredged material involves desorption from the suspended solids phase, diffusion through the water, and transport through the air-water interface. Assuming a constant suspended solids concentration, the steady-state flux of an organic chemical through the air-water interface is given by the following equation:*

* Environmental Laboratory. 1988 (20 July). Information on the Volatilization of Organic Pollutants from Dredged Material, Memorandum, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

$$n_a = {}^1K'_{A2} \left(\frac{W_A}{K_d + 1/\rho_{32}} - \rho_{A2}^{**} \right) \left(\frac{1}{1,000} \right) \quad (1)$$

where

n_A = flux of A through air-water interface, mg A/cm² hr

A = organic chemical of interest

${}^1K'_{A2}$ = overall liquid phase mass transfer coefficient, cm/hr

W_A = concentration of A in the original bed sediment, mg/kg

K_d = sediment-water distribution coefficient for A, L/kg

ρ_{32} = concentration of suspended solids, kg/L

ρ_{A2}^{**} = hypothetical concentration in water for air side concentration of A, mg/L

With respect to the overall liquid-phase mass transfer coefficient, when the emission rate is liquid-phase resistance controlled, as it is for hydrophobic organics, ${}^1K'_{A2}$ depends on wind speed and molecular diffusivity of A in water, and can be estimated using the following equation (Lunney, Springer, and Thibodeaux 1985):

$${}^1K'_{A2} = 19.6V_x^{2.23}D_{A2}^{2/3} \quad (2)$$

where

V_x = wind speed, mph

D_{A2} = molecular diffusivity of A in water, cm²/sec

If the diffusivity of A in water is not known, it can be estimated using the following equation (Thibodeaux 1979):

$$D_{A2} = D_{B2} [M_B/M_A]^{0.6} \quad (3)$$

where

D_{B2} = molecular diffusivity of B in water, cm²/sec

B = model organic chemical of known molecular diffusivity

M_B = molecular weight of B

M_A = molecular weight of A

The quantity $W_A/(K_d + 1/\rho_{32})$ is the dissolved concentration of A in the pond water and can be thought of as the dissolved concentration of A at the air-water interface. The difference between it and ρ_{A2}^{**} is the driving force which causes the flux of A into the air.

The value of ρ_{A2}^{**} is derived from the existing concentration of A in the air. This value is very small compared to the water concentration and therefore, if assumed to be zero, would have little effect on the driving force. This is a conservative assumption that maximizes volatilization.

Equilibrium partitioning uses the relative chemical solubilities of hydrophobic organic compounds (like PCBs) in sediment and water to estimate the concentrations of the compound in these two media at equilibrium. PCBs are poorly soluble in water and have a high affinity for sediments, particularly those with much organic matter. The ratio of PCB concentrations in sediment and water at equilibrium is referred to as K_d . This partitioning coefficient (K_d) can be calculated from chemical properties of the contaminant (PCB) and information about the total organic content (TOC) of the sediment or through a number of laboratory procedures. The K_d for PCBs in the Indiana Harbor sediments was determined through sequential batch leach testing and column leach testing by the US Army Engineer Waterways Experiment Station (WES) as 256,000 L/kg (Environmental Laboratory 1987).

Equation 1 is applicable as long as the suspended solids concentration is not reduced to identically zero. In a CDF, the suspended solids concentration usually decreases when filling operations are discontinued, but never goes to zero because of resuspension. When the suspended solids concentration is very low and cannot be reliably estimated, flux may be better estimated using the following equation (Thibodeaux 1979):

$$N_A = {}^1K'_{A2} (\rho_{A2} - \rho_{A2}^{**}) \quad (4)$$

where

ρ_{A2} = bulk liquid dissolved concentration of A , g/cm³

ρ_{A2}^{**} = hypothetical concentration in water for air side concentration of A , g/cm³

Exposed Dredged Material Algorithms

The volatilization pathway for exposed dredged material incorporates a number of steps. Although sediments are placed in a semisaturated state, water and VOCs become quickly depleted from the surface layer, and continuing losses come from the pore spaces within the dredged material beneath the surface. At this point VOC emission is dredged material-side vapor phase diffusion controlled. The emission pathway involves desorption from particle surfaces into

a water film surrounding the particles, diffusion through the water film, desorption from the water film into the pore gas, and diffusion through the pore gas prior to emerging into the atmosphere. This last step is apparently the limiting step in soil systems (Dupont 1986), and this condition is thought to apply to the top layers of dredged material in a CDF (Thibodeaux 1989). Ficks second law, with an effective diffusivity that accounts for tortuosity of the diffusion path and other factors that affect diffusion, is an appropriate mathematical model. Because of the depth of the dredged material and the relatively flat surface, a semi-infinite solution to Ficks second law can be applied without serious error. (The semi-infinite solution is conservative; that is, flux is maximized). The instantaneous flux is given by*

$$n_{A,t} = \left[\frac{D_{A3} \left(E_1 + \frac{K_d \rho_B}{H} \right)}{\pi t} \right]^{1/2} \left[\frac{W_A H}{1,000 K_d} - \rho_{A1i} \right] \quad (5)$$

where

- $n_{A,t}$ = instantaneous flux of A through dredged material-air interface at time t , mg A/cm²/sec
- D_{A3} = effective diffusivity, cm²/sec
- E_1 = air filled porosity, dimensionless
- ρ_B = bulk density of dredged material, kg/L
- H = Henry's law constant, dimensionless
- t = time since initial exposure, sec
- ρ_{A1i} = background concentration in air at dredged material surface, usually assumed to be zero, mg/cm³

The average flux over a given time t is given by

$$\bar{n}_A = \frac{\int_0^t n_A dt}{\int_0^t dt} \quad (6)$$

It can be shown that

$$\bar{n}_A = 2n_{A,t} \quad (7)$$

The above equation is an idealized diffusion transport model that describes chemical movement in the unsaturated pore spaces near the surface of exposed

The above equation is an idealized diffusion transport model that describes chemical movement in the unsaturated pore spaces near the surface of exposed dredged material. It does not account for the development of cracks as the dredged material dewateres by evaporative drying.

Effective diffusivity is a constant diffusion coefficient that characterizes the movement of chemical A as a vapor within the porous solid. It is one parameter for which there is no information available. To calculate the flux, it is therefore necessary to estimate D_{A3} . As an approximation, tortuosity can be accounted for using the equation below (Thibodeaux 1987):

$$D_{A3} = \frac{D_{A1} [E_1^{10/3}]}{E^2} \quad (8)$$

where

D_{A1} = molecular diffusivity of chemical A in air, cm^2/sec

E = total porosity, dimensionless

Henry's law constant (H) applies for dilute solutions of chemicals in air and water. It is an equilibrium partition coefficient for chemical A between the air and water phase. Henry's law constant can be estimated using the equation below (Dilling 1977):

$$H = 16.04 \left[\frac{P_A^o M_A}{T \rho_{A2}^*} \right] \quad (9)$$

where

P_A^o = vapor pressure of A as pure solute, mm Hg

ρ_{A2}^* = solubility of A in pure water, mg/L

T = temperature, deg K

The background concentration ρ_{A1i} in air has an analogous meaning to ρ_{A2}^{**} and also is assumed to be zero. This is a conservative assumption that maximizes volatilization.

Results

Table 1 shows the maximum annual simulated PCB loss for three contaminant transfer pathways. The data presented in the table represent loss of PCB occurring in the first year after disposal of the highest contaminated sediment. Table 2 shows the input parameters used to estimate PCB volatile losses. Estimated PCB

volatilization losses from an upland CDF were considerably higher than estimated losses from an in-lake CDF. This is because over the filling life of the CDF, the exposed surface area in an in-lake CDF is much lower than for an upland CDF. During most of the filling, the dredged material is placed and remains submerged.

Table 1
Estimated (Worst Case) Annual PCB Loss (lb)

In-lake CDF			Upland CDF		
Seepage*	Leachate**	Volatile	Seepage*	Leachate**	Volatile
0.0001	0.001	2	0.0001	0.001	8

* Mass of PCB loss estimated through dike wall or CDF bottom.

** Mass of PCB loss estimated to be collected and treated as leachate.

Interpretation of Results

The results indicate that volatilization of VOCs is a significant contaminant transfer pathway. Also, PCB mass flux is less when the sediments are maintained in a submerged state because of the hydrophobic nature of PCBs. The flux is highly dependent on two factors—the exposure time of the sediments and the surface area of the sediments. The exposure time for submerged sediments encompasses the entire time a pond is in contact with PCB-contaminated sediments. However, the rate of volatilization is directly related to the concentration of dissolved PCBs in the pond, which is derived from the mass fraction of PCBs in the sediments. The rate of volatilization changes over time, since the pond-dissolved concentration of PCBs varies over time with the highest rate during an active filling operation. The surface area is that area of the pond which is in direct contact with the air and is dependent on the volume of dredged material being placed and the volume of material already placed within the CDF.

The exposure time for exposed sediments encompasses the time in which unsaturated sediments are in direct contact with the air, while the surface area is that area which is in direct contact at any given time.

Table 2
Input Parameters for PCB Volatilization Models

<u>Parameter</u>	<u>Description</u>	<u>Value</u>
<u>Assumed Values</u>		
K_d	Sediment-water distribution coefficient	256,000 L/kg
W_A	PCB sediment concentration	
	1. Backlog sediment (zone 1)	38 mg/kg
	2. Backlog sediment (zone 2)	6 mg/kg
ρ_{32}	3. Long-term maintenance sediment	2 mg/kg
	Suspended solids concentration	
	1. Within 100-ft radius of disposal	100 mg/L
ρ_{A2}	2. Away from disposal area	10-50 mg/L
	Dissolved PCB concentration	5-60 ng/L
M_A	Composite molecular weight of PCB	300
ρ_B	Bulk density of sediment	1.2 mg/kg
D_{A2}	Molecular diffusivity of PCB in water	4.2E-06 cm ² /sec
D_{A1}	Molecular diffusivity of PCB in air	0.049 cm ² /sec
P_A^o	Vapor pressure of PCB as pure solute	4.94E-04 mm Hg*
ρ_{A2}^*	Solubility of PCB in pure water	0.054 mg/L*
E	Total porosity	0.70
E_1	Air filled porosity	0.30
V_x	Mean wind velocity	8-12 mph
<u>Calculated Values</u>		
$1'_{KA2}$	Mean overall liquid phase mass transfer coefficient	0.78 cm/hr
D_{A3}	Mean effective diffusivity	1.63E-03 cm ² /sec
H	Mean Henry's law constant	0.156

* Value used for Aroclor 1248.

Laboratory analysis has recently been completed by WES on New Bedford Harbor sediments in order to determine the volatile emission rates of PCBs from freshly placed drying sediments.* This experiment was conducted under laminar conditions, excluding the effects of wind. Laminar flow represents an overall simplified condition but does support the analyses presented in this note.

In summary the approach taken in model formulation was conservative in nature in that it simulated a worst-case scenario. For instance, the exposed sediments were assumed to be completely void of vegetation throughout the life of the CDF. However, from past experience a vegetative cover will form over the exposed sediments over time. No quantitative theory predicts the effects of vegetation on flux, but it is anticipated that the vegetation cover would reduce the flux rate. Also, the surface area of exposed sediments was simulated as a layer covering the entire cell (only for upland CDFs). Realistically, the deposited sediments would flow outward, but probably not far enough to cover the entire cell of an upland CDF. Finally, the suspended and dissolved solids concentrations in the ponded areas were based on conservative estimates. For the reasons stated above, the actual PCB mass flux from a CDF could be substantially lower than what is predicted by the model simulation.

Conclusions

Theoretical models must be tested against and adjusted to both laboratory and field data prior to their acceptance and widespread use as predictive tools. Preliminary model calculations can be made for the submerged sediment locale and the exposed sediment locale void of vegetation. However, some aspects are based on very simple equations and further development is needed. Laboratory and field testing must be performed to build a higher degree of confidence in the predictive capability of the PCB volatilization models. A substantial amount of work in laboratory/field testing and verification needs to be completed before any conclusive results can be made on PCB flux simulation from an active CDF.

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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

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- μm 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,

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 freshwater 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

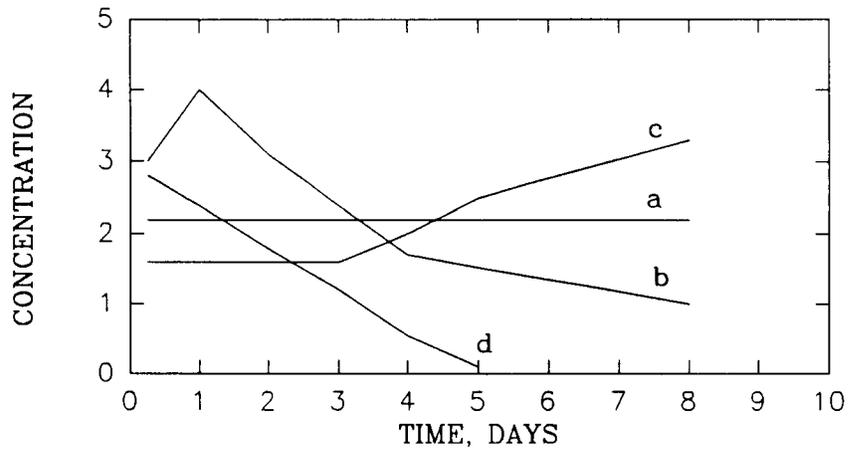
Results of batch testing with freshwater and saline sediments have shown that time of sediment-water contact, sediment salinity, and sediment oxidation status affect leaching of metals. Results of this study indicate that a 24-hr shaking time should continue to be used in sequential batch tests for metals. 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.

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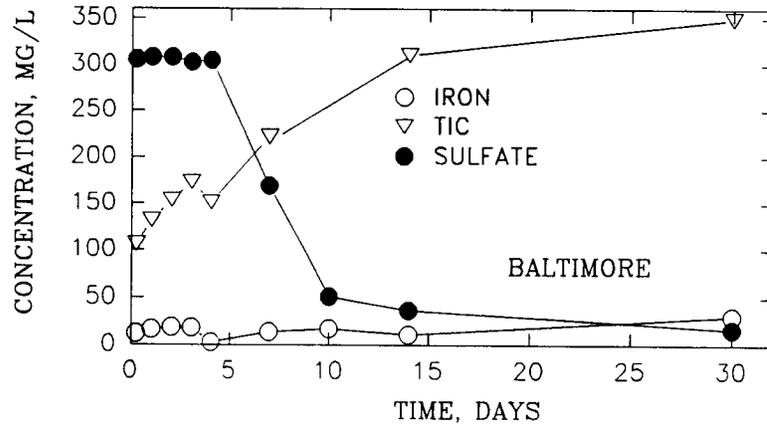
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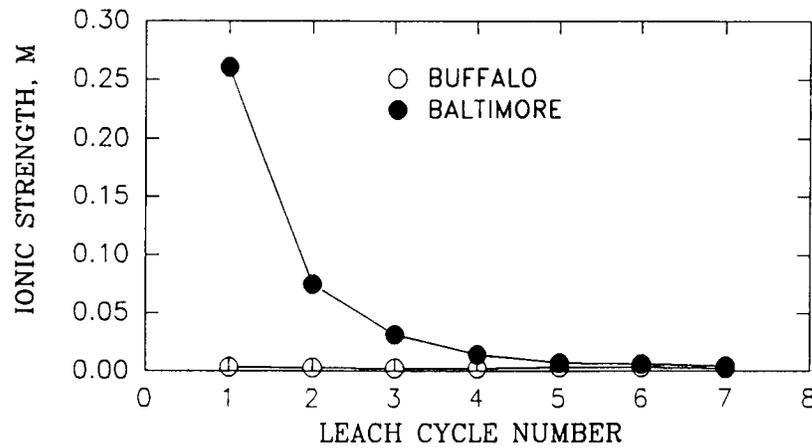
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a. Typical types of concentration curves observed during kinetic batch testing of dredged materials; concentration values are relative and show increasing and decreasing concentrations only

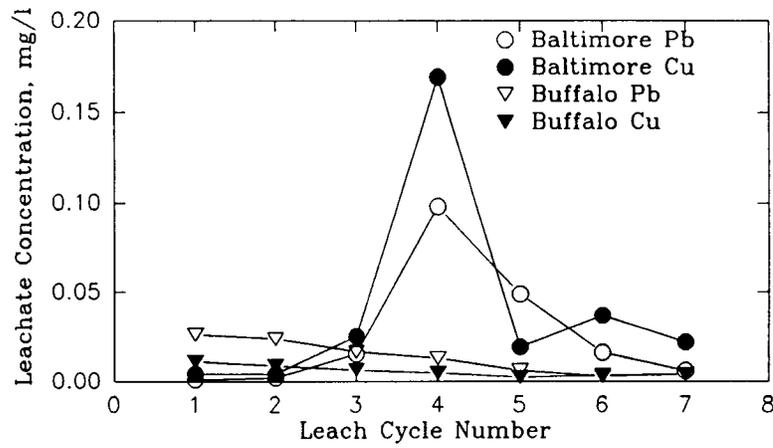


b. Changes in Baltimore Harbor leachate as a function of sediment-water contact time during batch leaching

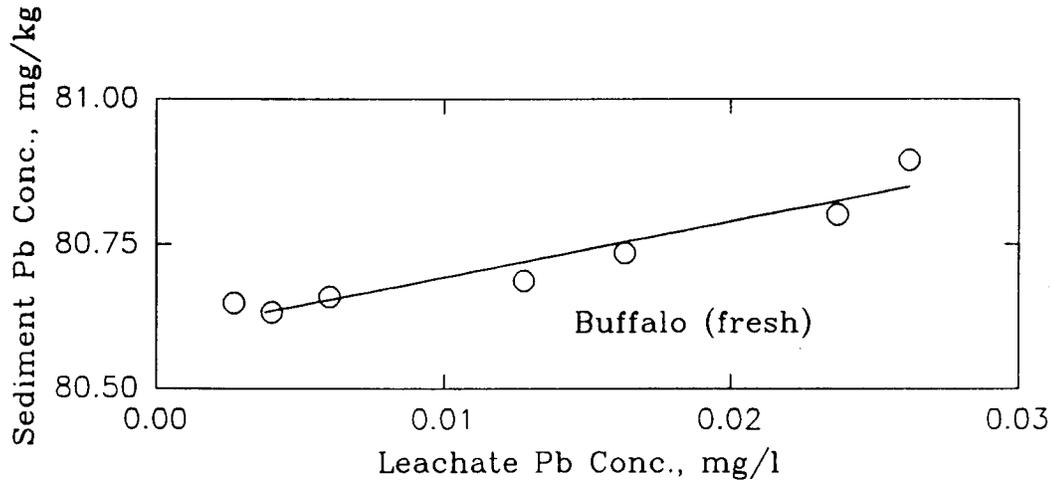


c. Ionic strength changes during sequential batch leaching of saline Baltimore Harbor sediment and freshwater Buffalo River sediment

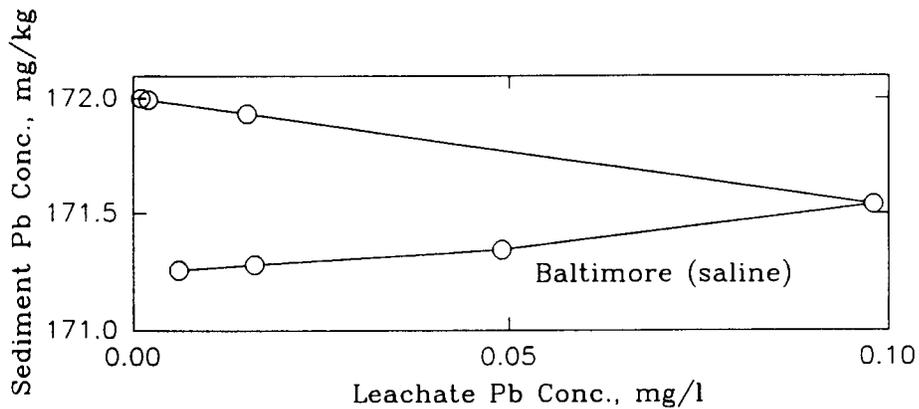
Figure 1. Sediment-water time of contact test results



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

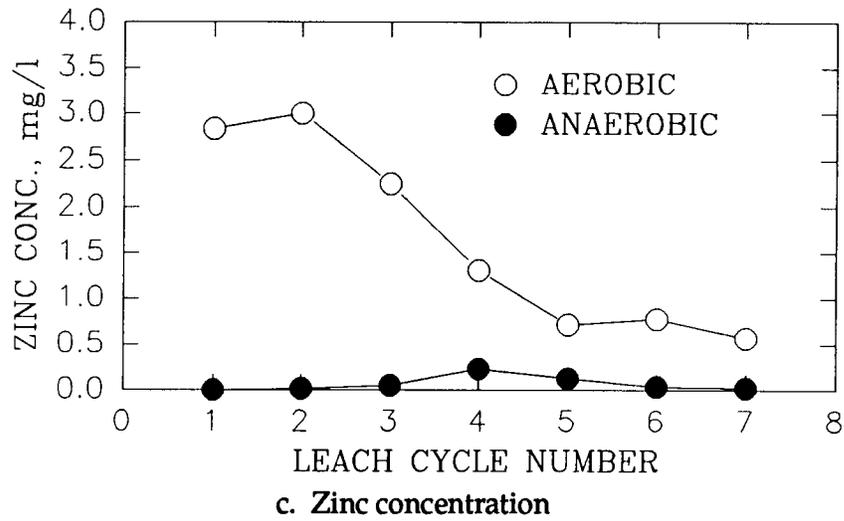
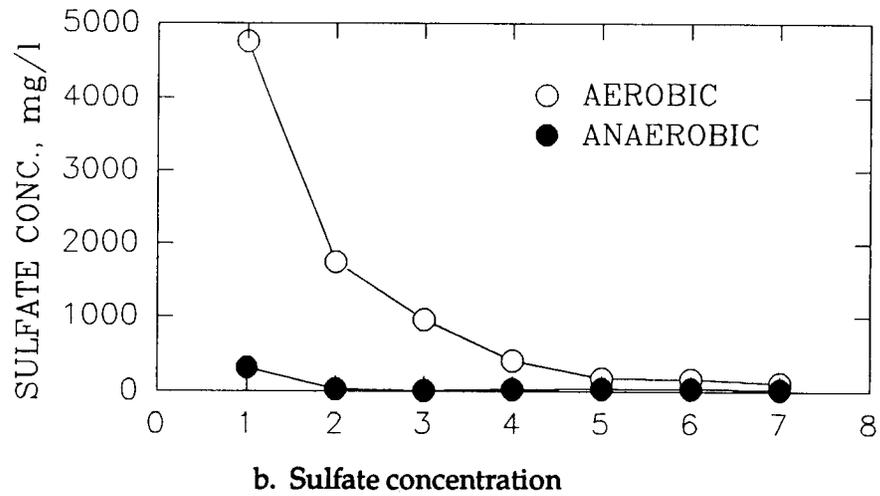
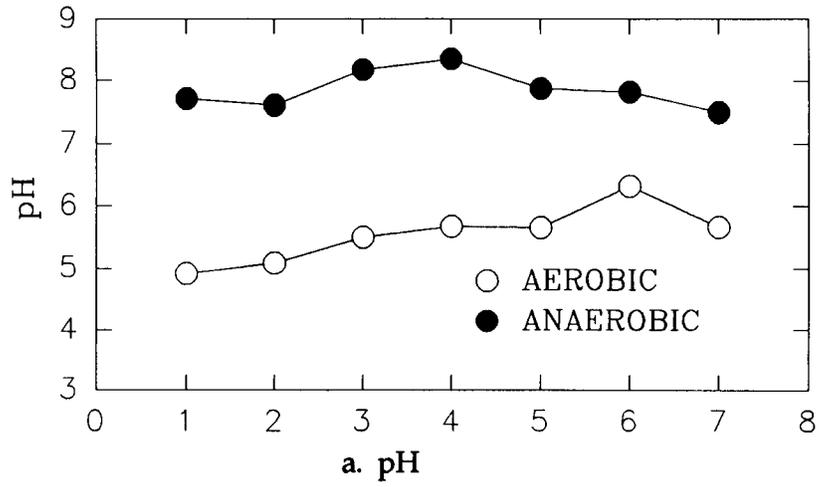


Figure 3. Relationship between oxidation state in Baltimore Harbor sediment and leachate



Environmental Effects of Dredging Technical Notes



Long-term Evaluation of Plants and Animals Colonizing Contaminated Estuarine Dredged Material Placed in an Upland Environment

Purpose

This technical note summarizes data collected between 1983 and 1989 that relate to plant and animal communities colonizing the upland disposal site of the US Army Corps of Engineers/Environmental Protection Agency Field Verification Program (FVP). The management of contaminated dredged material and the mobility of contaminants from the dredged material into plants and animals are also described. This site will be evaluated through September 1995 under the Long-Term Effects of Dredging (LEDO) Program.

Background

Long-term evaluation of ecosystems developing on dredged material has been accomplished on some of the marsh creation sites established during the Dredged Material Research Program (DMRP). These sites were not classified as contaminated and their evaluations did not consider contaminant mobility. Contaminated dredged material has been evaluated only on a short-term basis, such as laboratory tests before dredging and disposal operations and during the operational phases of some confined disposal facilities (CDFs). Monitoring is normally conducted during the operational phase of a dredging/disposal project and perhaps during the first year after completion of the dredging/disposal activity. Changes in contaminant mobility may occur over the long-term, but no long-term evaluation data are available to document such changes.

Additional Information

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Introduction

Contaminated sediment was dredged from Black Rock Harbor, Connecticut, in October 1983 and placed in aquatic, upland, and wetland environments as part of the US Army Corps of Engineers/Environmental Protection Agency Field Verification Program (FVP), 1981-1986 (Peddicord 1988). Upland tests (plant and earthworm bioassays) were conducted on the sediment before dredging to evaluate potential contaminant mobility under the upland disposal alternative. Laboratory test results were subsequently field verified at the field test site at "Tongue Point," Bridgeport, Connecticut. The results of the upland disposal portion of the FVP and the changes occurring since the completion of the FVP for the upland disposal environment are summarized herein. This technical note emphasizes the contaminant mobility of heavy metals. Contaminant mobility and the progressive development of the upland ecosystem at this site will be evaluated until September 1995.

Site History

Before construction, the field site was used as an open dump. The debris consisted mainly of urban building rubble (bricks, cement, and rebar). Both upland and wetland ecosystems were present as were assortments of flora and fauna characteristic of each. During the initial field survey conducted in July 1983, plants were collected along four transects that included both upland and wetland areas. *Phragmites australis* (common reed), *Solanum dulcamara* (nightshade), *Robinia pseudoacacia* (black locust), and *Populus deltoides* (cottonwood) were collected and the tissues analyzed for metals (Brandon and others, in preparation). Both plant species and the general rubble constituents were typical of the urban neighborhood adjacent to "Tongue Point." The field survey described the abundance and diversity of the animal species on site. These included rats, insects, snakes, and several species of birds.*

Construction

All grading and dike construction were performed with conventional equipment. Total surface area was approximately 2,600 m². A weir with adjustable

* Lance L. Stewart, Douglas Moffat, Kurt Buchholz, and Michael Coon. 1983. "Field Work Report," unpublished report, Marine Sciences Institute/Sea Grant Advisory program, University of Connecticut, Groton, CT.

risers was installed to control overflow. Peddicord (1988) provides additional information on site design and preconstruction evaluations. Folsom and others (1988) provide further discussion of upland construction.

Physicochemical Changes in Dredged Material

Placement of Black Rock Harbor sediment in an upland disposal environment resulted in pronounced changes in the contaminated sediment. Following upland disposal, the dredged material dried and oxidized. Salinity dropped from a high of 29 to <1 ppt. The pH of the dredged material dropped from 7.6 in 1983 to 3.2 by the end of the FVP in 1986. This substantial decrease in dredged material pH was presumably a result of the decomposition of organic matter, the oxidation of sulfide, limited pH buffering capacity in Black Rock Harbor sediment, low percent CaCO₃ equivalent, and the acid rainfall of pH 4.0-4.5 at the field site location (Skogerboe and others 1987). This substantial decrease in the pH of the dredged material enhanced the solubility and availability of the toxic metals: zinc, cadmium, copper, nickel, chromium, and lead (Folsom and others 1988). After placement in an upland environment, control plots of unamended dredged material have been barren of vegetation from 1985 through 1989 even after repeated attempts to establish acid-tolerant, salt-tolerant, and metal-tolerant plant species (Brandon and others, in preparation).

Plants

The FVP laboratory test predicted that *Spartina alterniflora* would not grow in unamended dredged material in the field. This was field verified as no *S. alterniflora* plants survived in the unamended dredged material. The lab test also predicted plant species might grow in amended material. *Sporobolus virginicus* survived in amended material in the lab as well as the field (Folsom and others 1988).

Sediment CaCO₃ content was as low as 1.0 percent. Limited buffering of sediment pH occurred and the pH dropped from 7.6 to 3.2. Lime was added to neutralize the acids generated upon drying and oxidation of the dredged material. Manure was added to replace the organic matter oxidized, increase surface metal adsorption, immobilize metals released when organic bound metals were oxidized, and ameliorate the toxic effects of excess salinity. Before planting, a layer of sand and limestone gravel was used to provide a nontoxic microhabitat and a substrate for seed germination. Coarse limestone gravel was placed on the surface to neutralize acid rainfall that might impact the plot and also provide release of acid-neutralizing material over the longer term. The site was partitioned into plots with each amendment being randomly assigned to four plots. The lime and lime + manure amendments were surface broadcast, and then a surface layer of sand and limestone gravel was placed over the lime and manure (Brandon and others, in preparation).

Amendments of lime, lime + manure, lime + sand + gravel, and lime + manure + sand + gravel resulted in vegetation becoming established on the dredged material. Of the plant species seeded on the field plots, only *Agrostis alba* (redtop) became permanently established. *Phragmites australis* had extended its rhizomes

from the upland containment facility dike of construction rubble onto some of the plots. Other plant species observed on the plots in 1989 are typical Eurasian species and urban weeds that probably originated from seed sources in the Bridgeport area.

In 1985, the best vegetative establishment was observed on the lime + manure + sand + gravel amended plots. These plots were 97 percent covered with vegetation in 1989. Apparently, the sand and gravel cover allowed rainfall to soak the surface-applied lime and manure into the surface of the dredged material, enhancing plant growth and establishment. The lime and lime + manure plots showed 51 and 28 percent cover, respectively, in 1989. However, subplots receiving an additional application of 56 metric tons/hectare (mt/ha) of lime and rototilling resulted in a soil pH of 4.4 and 4.1 and produced 96 and 99 percent vegetative cover, respectively, in 1989.

Contamination of Plants

The chemical analyses of *Agrostis alba* tissues are presented in Table 1. Lee and others (1991) compiled plant tissue information from a number of sources to indicate demonstrated effects of contaminants on plants. When these data are used as guidance, *Agrostis alba* leaf tissue contents of zinc are within the normal range of 15-150 µg/g found in agricultural crops. Plant cadmium concentrations are equal to or slightly above the normal range and substantially below the critical content level of 8 µg/g. Copper concentrations appear to be either in the normal range or slightly elevated above phytotoxic levels of 25-40 µg/g. However, there was considerable variability in the analyses of the elevated samples. Nickel concentrations were equal to or slightly above the critical content level of 11 µg/g. Chromium concentrations were above normal (1 µg/g) in 1988, and three of the four amendments showed tissue content above phytotoxic levels of 20 µg/g in 1989. Lead concentrations were equal to or slightly above the normal range of 2-5 µg/g. The only mercury reference tissue concentration available was 1.0 µg/g in wheat kernels as an action level for human foodstuff. Mercury contents of *A. alba* were approximately one tenth this action level and therefore should not be of concern (Brandon and others, in preparation).

Animals

The upland animal bioassay predicted that earthworms would not survive in this dredged material under oxidized conditions. Through 1986, earthworms could not survive on this dredged material (Folsom and others 1988). Presently, control plots devoid of vegetation contain few animals. In particular, no soft-bodied animals (slugs) were observed or collected from this environment. Those animals that were collected or observed were transient, foraging arthropod species. In contrast, establishment of vegetation on the amended dredged material enhanced the abundance and diversity of animals present. There were numerous species of macroinvertebrates associated with the plant cover and the leaf litter layer of the soil. The animals observed, while relatively abundant, provided too little biomass per species for chemical analysis. Consequently, no data are available to evaluate contaminant uptake (Brandon and others, in preparation).

Summary

Upland control plots of unamended dredged material were barren of vegetation from 1985 through 1989. Six years after placement in an upland disposal environment, unamended estuarine dredged material decreased in salinity to <1 ppt. However, soil pH remained extremely acidic at 3.4, keeping toxic metals soluble and available to plants that attempt to colonize the unamended dredged material. In contrast, amended dredged material became vegetated and soil and vegetation-dwelling macroinvertebrates have begun to colonize these plots, and food webs involving vertebrates have evolved.

In the upland disposal field site, there are developing plant and animal communities. The extent of the populations and the species compositions of the ecosystems may require management procedures if unanticipated routes of contaminant mobility develop. Continued evaluation will better define the extent and nature of contaminant mobility at the FVP site. This evaluation should include the contaminant mobility of organics into both plants and animals. The development of the upland ecosystem at this site will be evaluated through September 1995.

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Table 1

Tissue Contaminant Contents of *Agrostis alba* Plants Growing on the FVP Upland Disposal Site

Contaminant	1988	1989	From Lee and others (1991)		
	<u>Amended Lime</u>		<u>Normal</u>	<u>Critical</u>	<u>Phytotoxic</u>
	N=3	N=4			
Zn	85.4 (76.3)	138.7 (40.1)	15-150	200	500-1,500
Cd	1.1 (0.1)	1.5 (0.9)	0.1-1	8	5-700
Cu	15.0 (1.8)	92.2 (80.0)	3-20	20	25-40
Ni	13.4 (4.0)	11.9 (5.1)	0.1-5	11	500-1,000
Cr	6.7 (0.8)	26.5 (9.2)	0.1-1	--	20
Pb	3.1 (1.7)	6.2 (4.0)	2-5	--	--
Hg	0.1 (0.03)	0.1 (0.01)	--	--	--
<u>Amended Lime + Manure</u>					
	N=3	N=3			
Zn	105.0 (27.5)	124.9 (32.2)			
Cd	1.0 (0.3)	1.1 (0.8)			
Cu	21.6 (8.0)	15.3 (5.4)			
Ni	12.8 (4.0)	15.2 (4.4)			
Cr	11.2 (3.3)	10.6 (4.0)			
Pb	4.6 (1.4)	6.4 (3.7)			
Hg	0.1 (0.01)	0.05 (0.01)			
<u>Amended Lime + Sand + Gravel</u>					
	N=1	N=4			
Zn	110.1 (0.0)	128.5 (57.8)			
Cd	1.7 (0.0)	1.5 (0.8)			
Cu	23.6 (0.0)	101.0 (77.0)			
Ni	13.7 (0.0)	13.5 (5.3)			
Cr	11.1 (0.0)	34.8 (27.6)			
Pb	6.6 (0.0)	11.0 (7.9)			
Hg	0.2 (0.0)	0.07 (0.03)			
<u>Amended Lime + Manure + Sand + Gravel</u>					
	N=1	N=2			
Zn	111.0 (0.0)	1.5 (26.0)			
Cd	1.1 (0.0)	1.4 (0.06)			
Cu	140.9 (0.0)	79.9 (73.1)			
Ni	13.7 (0.0)	11.9 (1.4)			
Cr	24.4 (0.0)	36.0 (28.5)			
Pb	8.6 (0.0)	6.5 (6.6)			
Hg	0.1 (0.0)	0.1 (0.02)			

Notes: Measurements are given in micrograms per gram dry weight. N equals the number of samples collected and analyzed. Values given in parentheses are the standard deviations.



Environmental Effects of Dredging Technical Notes



Technical Considerations for Application of Leach Tests to Sediments and Dredged Material

Purpose

This note summarizes the characteristics of and differences among laboratory leach tests used for preproject evaluation of leachate quality in confined disposal facilities (CDFs) for dredged material. The guidance provided in this note is based on ongoing research conducted under the Long-Term Effects of Dredging Operations (LEDO) Program.

Background

Contaminated dredged material is sometimes placed in CDFs where the potential for movement of contaminants to groundwater and surrounding surface water by leaching is an important environmental concern. The US Army Corps of Engineers (USACE) has initiated a laboratory program of CDF leachate investigations by developing a theoretical framework for prediction of leachate quality based on contaminant transport theory. The laboratory tests and theoretical framework under development by the USACE provide estimates of leachate quality in CDFs as elution histories related to the amount of water percolating through dredged material. The US Environmental Protection Agency (EPA) Toxicity Characteristic Leach Procedure (TCLP) is also sometimes used to provide predictions of dredged material leachate quality. The USACE leachate tests under development and the TCLP are reviewed in this technical note.

Additional Information

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Need for Predictive Techniques

When contaminated dredged material is placed in a confined disposal facility (CDF), contaminants may be transported to site boundaries by leachate generation and seepage. Subsurface seepage through foundation soils and dikes may then reach adjacent surface water and groundwater and act as a source of contamination (Figure 1). Section 404 of the Clean Water Act of 1972, as amended, the National Environmental Policy Act of 1969, and the US Army Corps of Engineers (USACE) management strategy for dredged material disposal (Francingues and others 1985) require evaluation of the confined disposal alternative for dredged material to include groundwater impacts. The information for preproject evaluation of leachate impacts on groundwater resources will necessarily come from some type of laboratory leach test(s) conducted on sediments before dredging and disposal. Thus, leach tests and predictive techniques that use leach data are needed to establish sound engineering and environmental data for the selection, design, operation, and management of CDFs.

USACE Approach to Leachate Quality Prediction

In the USACE leachate research, theoretical contaminant transport equations are being used to determine what type of information laboratory leach tests should provide. The basic equations are shown in Figure 2. Equations 1 and 2 in the figure couple porous media fluid mechanics (convection and dispersion) with chemistry (interphase transfer of contaminants from sediment solids to pore water). Since most of the contaminants in dredged material are adsorbed to sediment solids, leaching in a CDF is defined as interphase transfer of contaminant mass from sediment solids to pore water. The leach tests under development by the USACE focus on quantitation and mathematical description of contaminant

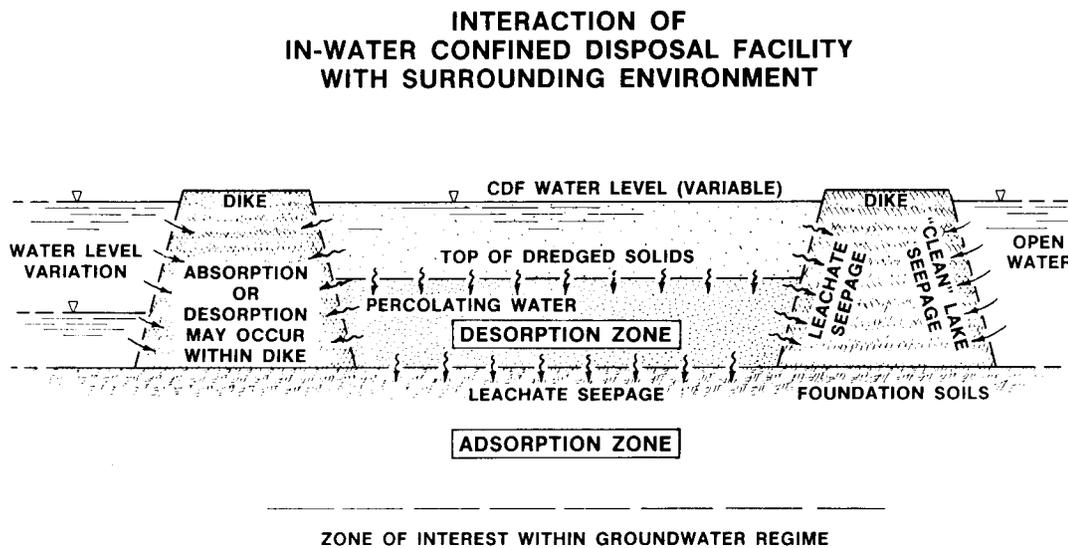


Figure 1. Contaminant migration pathway: leachate seepage

transfer from dredged material solids to pore water. Figure 3 illustrates the important processes and factors affecting leachate quality in dredged material. As shown in Figure 3, interphase transfer during dredged material leaching is a complicated interaction of many elementary processes and factors affecting these processes.

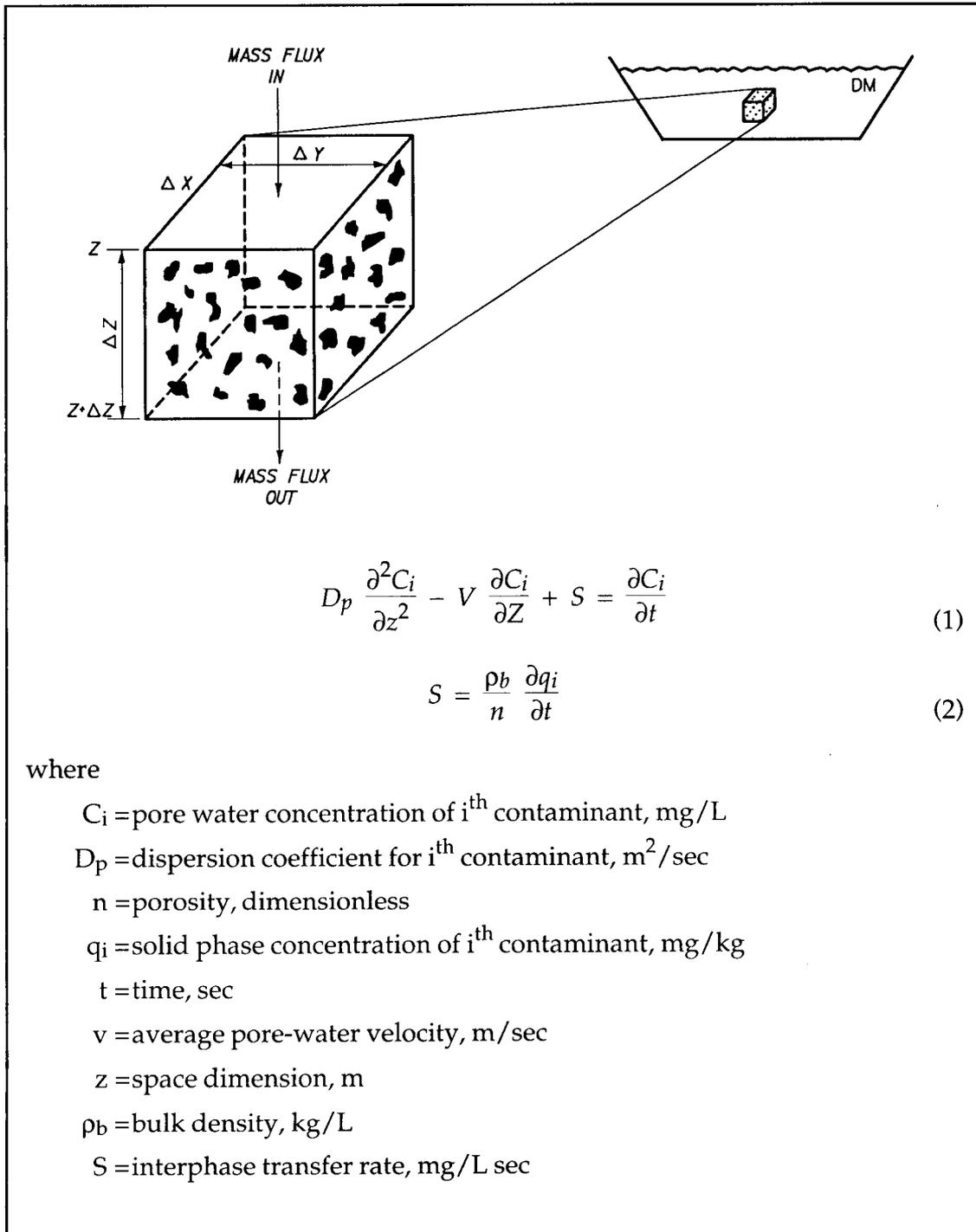


Figure 2. Mathematical model of dredged material leaching

Factors Affecting Leachate Quality

Site-specific Factors

Contaminant mobilization in dredged material is regulated to a large extent by the physicochemical environment of the dredged material disposal site (Gambrell, Khalid, and Patrick 1978). The important site-specific physicochemical parameters for dredged material are oxidation-reduction potential (redox), pH, and ionic strength. Redox and pH determine the speciation and solubility of many chemical constituents, especially metals. Ionic strength affects the solubility of metals and organics, speciation of metals, and the stability of the sediment colloidal system (Stumm and Morgan 1981, Brannon and others 1991). Each of these factors should be considered in development and application of leach tests.

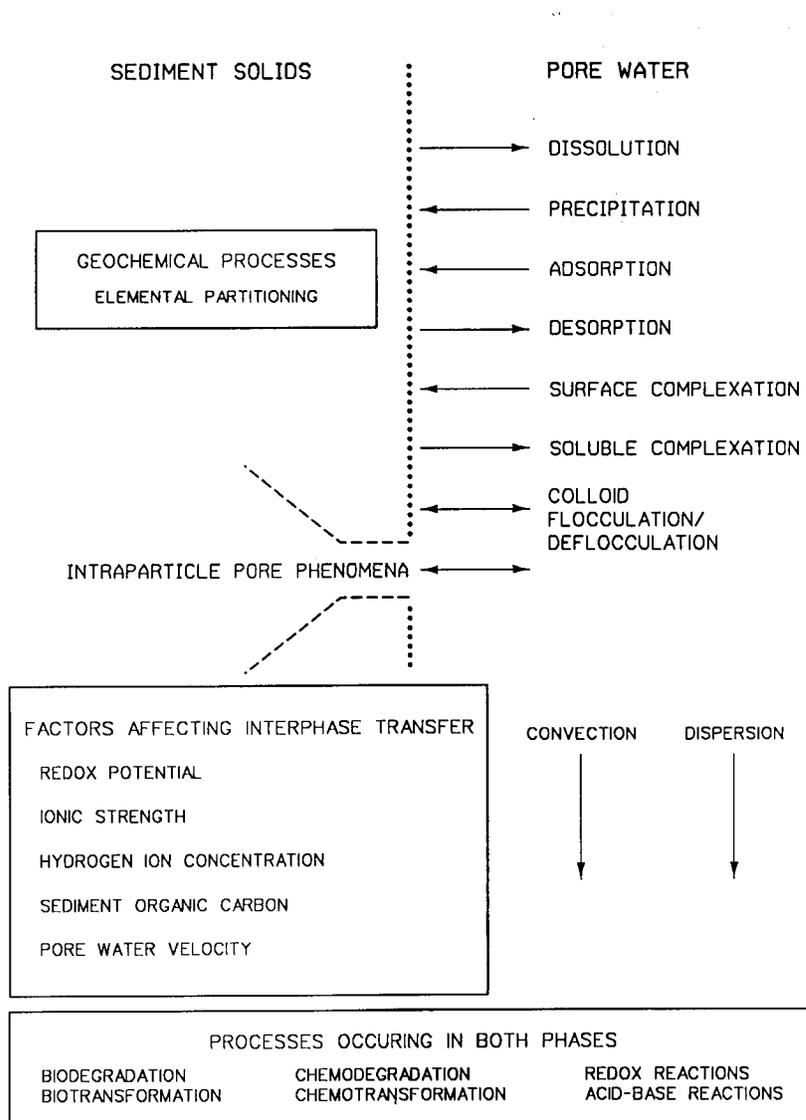


Figure 3. Interphase transfer processes and factors affecting interphase transfer processes

Test-specific Factors

In leach tests, liquid-solids ratio, contact time, and shear at the particle-water interface are test-specific parameters that affect leachate contaminant concentrations. The liquid-solids ratio is the ratio of the mass of water to the mass of dry solids; contact time in a batch leach test refers to the lapse time between introduction and removal of water. Contact time in a column leach test refers to the time required for elution of one pore volume. For a wide range of contaminants, the distribution of contaminant between solid and aqueous phases has been shown to depend on the liquid/solids ratio (O'Connor and Connolly 1980, Voice, Rice, and Weber 1983, DiToro 1985, Gschwend and Wu 1985). Contact time also affects the amount of contaminant that is leached. Another parameter affecting leachate contaminant concentrations in leach tests is the shear at the particle-water interface. The slower the water velocity across particle surfaces, the thicker the film of immobile water that contaminants must diffuse through.

CDF Conditions

Typical fine-grained sediments are anoxic (reducing) and have a pH near neutrality. Dredging and disposal results in short-term perturbations of the sediment redox regime, but due to the high oxygen demand of most sediments, initial leaching in CDFs occurs under anaerobic conditions. If a CDF is not managed to remove ponded water, most of the dredged material will remain anaerobic. If the CDF is managed to remove ponded water, the upper layer of dredged material will gradually transition from an anaerobic to an aerobic condition. This transition is characterized by drying and cracking of the surface and development of an aerobic crust which may eventually be several feet thick. CDFs containing fine-grained dredged material, however, never completely drain, resulting in a saturated layer at the bottom where anaerobic conditions persist.

Thus, leaching in a CDF can occur under redox conditions ranging from mildly aerobic to strongly anaerobic. In anaerobic soils and sediments, pH is buffered near neutrality by the substances produced as a result of microbial utilization of iron and manganese as electron acceptors (Patrick and Mikkelsen 1971, Ponnamperuma 1972, and Brannon and others 1978). Thus, the leachate that seeps into foundation soils is anaerobic and near neutral in pH. The aerobic microbial metabolism in the unsaturated crust of a CDF often results in a lowering of pH. The amount that pH is lowered depends on sediment geochemistry. In low sulfur sediments that are high in carbonates, the condition of many freshwater sediments, pH under aerobic conditions may not differ significantly from that under anaerobic conditions. In estuarine sediments, oxidation of sulfide to sulfate can decrease pH by one to three pH units relative to the pH under anaerobic conditions. Thus, leachate that seeps from the crust may be acidic as well as aerobic, depending on sediment geochemistry. Contact of aerobic-acidic leachate with anaerobic sediment results in an anaerobic near-neutrality in pH leachate (Environmental Laboratory 1987). Thus, percolation of aerobic-acidic leachate from an unsaturated-aerobic crust into saturated-anaerobic layers beneath a crust does not

alter the redox or pH of leachate in dredged material beneath the crust. Leachate that seeps from the crust into confining dikes may, however, be aerobic and acidic.

Pore-water ionic strength depends on the salinity of the dredged material and is a function of the amount and salinity of water that infiltrates the dredged material. In general, the in situ ionic strength will persist for many years before all of the salt in estuarine dredged material is washed out. For freshwater dredged material, there is little change in ionic strength as the dredged material is leached by fresh water.

The liquid-solids ratio in a filled CDF is less than 1:1. During filling, the liquid-solids ratio in the dredged material depends on the type of dredging and disposal operation. For mechanical dredging and disposal, the liquid-solids ratio applicable to leachate generation does not differ significantly from 1:1 at any time during the filling process. During hydraulic dredging and disposal, the influent to the CDF will have a liquid-solids ratio of about 4:1. In the solids that settle and consolidate in the bottom of the CDF, the liquid-solids ratio will initially be about 4:1 or less and will decrease with time as solids consolidate. The CDF effluent associated with hydraulic filling will have a substantially higher liquid-solids ratio, but this liquid-solids ratio is not representative of the liquid-solids ratio in the dredged material that produces leachate.

The shear at particle surfaces associated with dredged material leaching in CDFs is very low because pore-water velocities are low. Pore-water velocities are low because the hydraulic conductivity of fine-grained dredged material is usually very low (10^{-8} to 10^{-5} cm/sec). Mass transfer limitations to the leaching of contaminants from dredged material under these conditions could be important.

Leach Test Comparisons

Table 1 lists test conditions for the Toxicity Characteristic Leach Procedure (TCLP) and two leach tests under development at the US Army Engineer Waterways Experiment Station (WES), a sequential batch leach test (SBLT) and a column leach test. Typical CDF conditions are also listed in Table 1 for reference. The TCLP and the leach tests under development at WES are discussed in more detail in the following sections.

TCLP

The TCLP was developed by the US Environmental Protection Agency (EPA) for determining if a nonlisted waste is a hazardous waste. The regulatory purpose of the TCLP is to identify wastes that although not specifically listed in 40 Code of Federal Regulations 261 as hazardous, pose substantial hazard when improperly managed. This test, developed to accomplish a specific regulatory purpose under the Resource Conservation and Recovery Act (RCRA) of 1976, as amended (USEPA 1990) is sometimes used to assess the leaching potential of Superfund sediments.

Table 1. Comparison of Leach Test Variables

	TCLP	WES-SBLT	WES-Column	CDF
pH	pH 4.9 or pH 2.9 fluid	neutral/self adjusting	neutral/self adjusting	neutral/self adjusting
ORP	no control	anaerobic/aerobic	anaerobic	anaerobic/aerobic
Liquid-Solids Ratio	20:1	4:1	< 1:1	< 1:1
Agitation	tumbler	tumbler	none	none
Long-Term Predictive Capability	none	implied from mass transport theory	implied from mass transport theory	self evident
Contact Time	18 hours	24 hours	weeks	years

The TCLP is a criteria-comparison type test in which results from a standardized leach procedure are compared with a specific set of criteria. The test is conducted in one of two modes (nonvolatiles or volatiles) and consists of several parts as outlined in Figure 4. Figure 4 applies to both the nonvolatiles TCLP and the volatiles TCLP. The double lines in Figure 4 indicate the path normally taken for sediments.

The pre-extraction part of the test involves removal of water by vacuum or pressure filtration, removal of particles larger than 9.5 mm, and selection of a leaching fluid. For the volatiles TCLP, dilute acetic acid adjusted to pH 4.93 (Fluid No. 1) is used as the leaching fluid. For the nonvolatiles TCLP, the acid neutralization capacity of the material to be leached is evaluated, and on the basis of this information either Fluid No. 1 or dilute acetic acid at pH 2.9 (Fluid No. 2) is used as the leaching fluid. The water removed by filtration is combined with the TCLP extract developed later in the test. The solids and leaching fluid are agitated at a liquid-solids ratio of 20:1 on a tumbler for 18 hours, and the fluid and solids are separated by filtration. The liquid obtained in the pre-extraction filtration is combined with the acetic acid extract and defined as the TCLP extract.

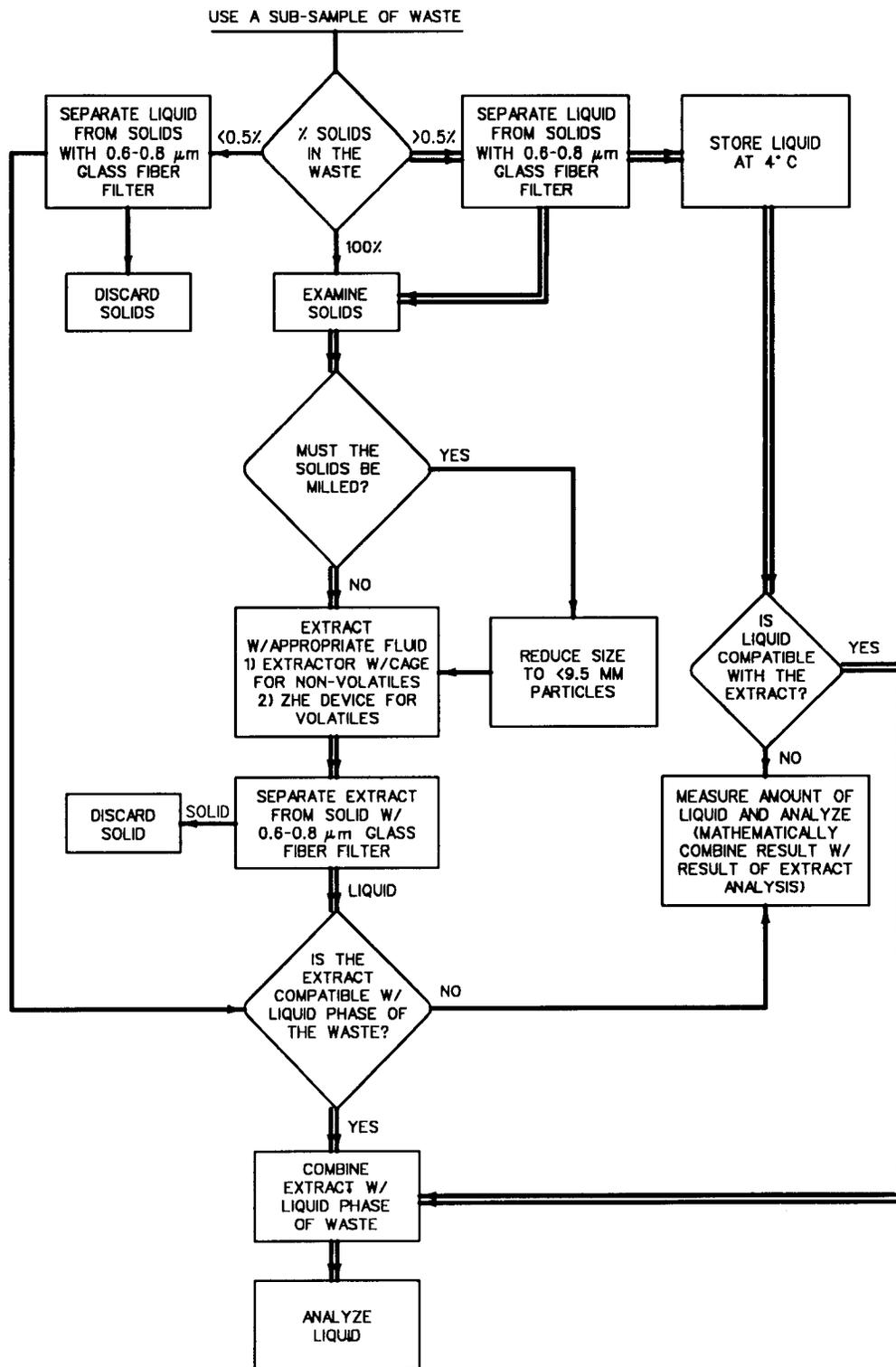


Figure 4. TCLP flowchart

WES-SBLT

In the WES-SBLT, sediment solids are challenged with successive aliquots of distilled-deionized water in an agitated system. After the aqueous and solid phases have reached steady-state, the phases are separated by centrifugation and filtration, and the leachate is analyzed for contaminants of concern. The solid phase is then reequilibrated with fresh distilled-deionized water, and the process of phase separation and leachate analysis is repeated. Each cycle in the WES-SBLT involves an equilibration step, a phase separation step, and a leachate analysis step (Figure 5). A table of solid phase and aqueous phase concentrations is developed from chemical analysis of the leachates, and these data are plotted to produce desorption isotherms. From the desorption isotherms, contaminant-specific equilibrium distribution coefficients, K_{ds} , are obtained.

Figure 6 shows cadmium and zinc desorption isotherms prepared from WES-SBLT tests conducted on sediment from Indiana Harbor, Indiana (Environmental Laboratory 1987). The isotherm slopes are the K_{ds} used to predict elution curves from column leach tests.

WES-SBLTs are conducted under nitrogen (anaerobically) to simulate the anaerobic conditions that prevail throughout most of a CDF and in the presence of air to simulate the aerobic condition of the surface crust that forms as a CDF dewateres. In anaerobic testing, the sediment as received is anaerobic, and all operations involving loading centrifuge bottles and filtration are conducted under a nitrogen atmosphere to avoid oxidation of iron, manganese, and sulfur. In the aerobic testing, sediment is aged six months in the presence of air. During the aging process, moist conditions are maintained by periodic additions of water, and the sediment is stirred manually on a daily basis. Testing has shown that the mobility of contaminants under anaerobic and aerobic conditions is substantially different (Environmental Laboratory 1987, Myers and Brannon 1988, and Palermo and others 1989). This is to be expected based on the environmental chemistry of iron and sulfur.

The pH level in the WES-SBLT depends on sediment biogeochemistry and leaching conditions (anaerobic or aerobic). The appropriate

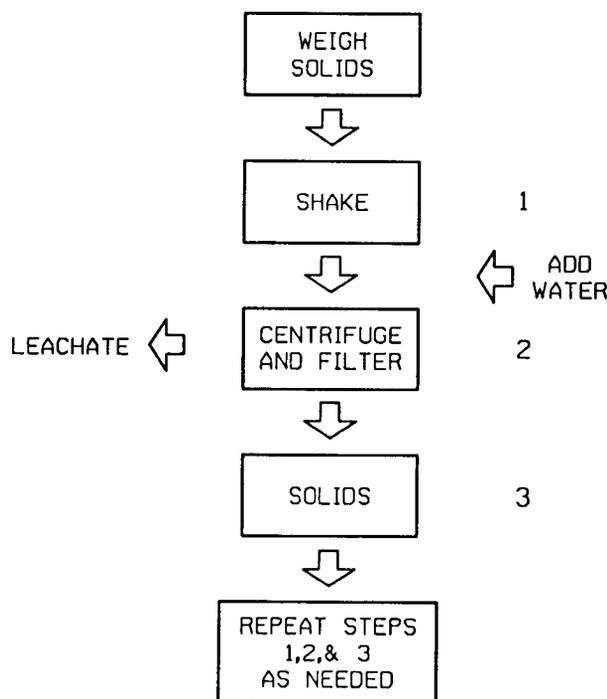


Figure 5. Schematic of WES-SBLT

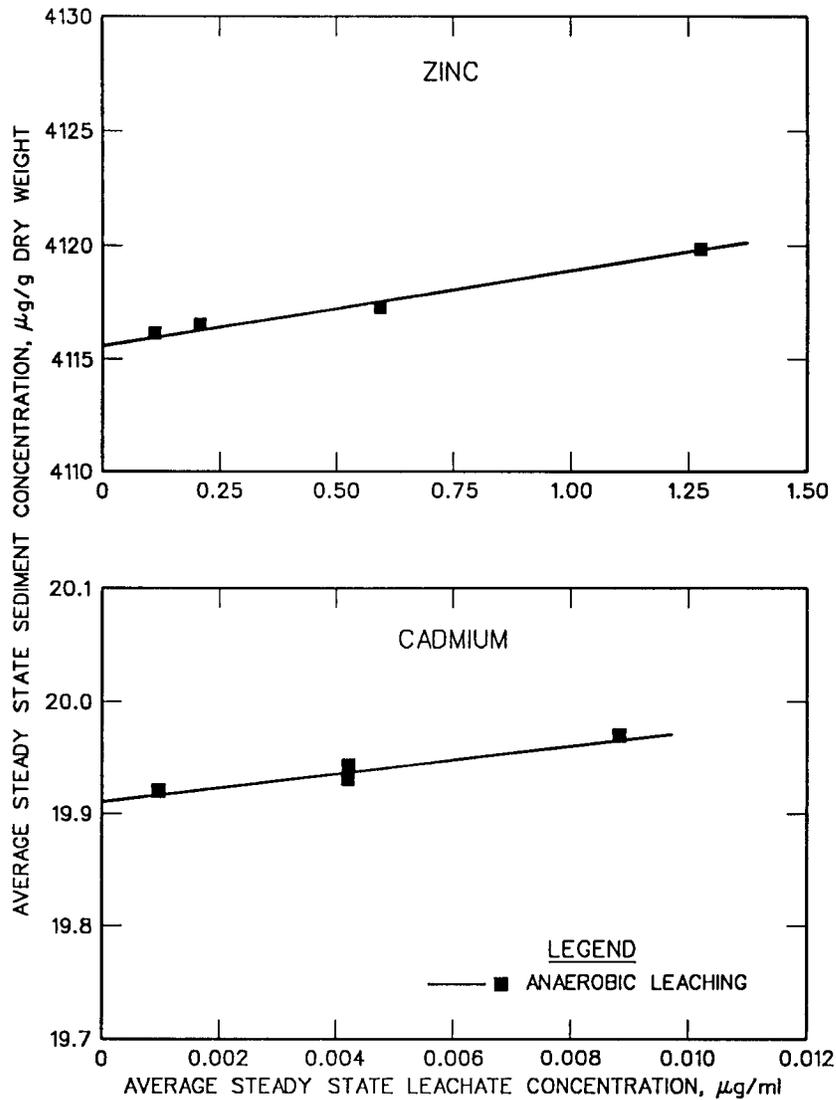


Figure 6. Desorption isotherms for zinc and cadmium in Indiana Harbor sediment (Environmental Laboratory 1987)

conditions for microbial adjustment of pH are maintained in the WES-SBLT by conducting the test as anaerobic or aerobic. Because there are no artificial adjustments of pH, the WES-SBLT allows the sediment biogeochemistry to adjust pH to values that are representative of field pH in anaerobic (saturated) and aerobic (unsaturated) zones.

The contact time for the WES-SBLT is still in a research and development stage. However, kinetic batch testing on three sediments has shown that a 24-hour shake time represents steady-state conditions for most contaminants (Environmental Laboratory 1987, Myers and Brannon 1988, and Palermo and others 1989). Investigation of desorption kinetics in additional sediments is ongoing.

As previously discussed, distribution coefficients determined at one liquid-solids ratio may not be appropriate at another if the liquid-solids ratios differ by orders of magnitude. Testing has shown that a 4:1 liquid-solids ratio is the lowest practical ratio for conducting batch leach tests with sediment (Environmental Laboratory 1987, Myers and Brannon 1988, and Palermo and others 1989). It is anticipated the final WES-SBLT recommended for adoption will include a liquid-solids ratio of 4:1.

WES-Column

Sequential batch leach tests, useful for determining the kinetics of desorption, equilibrium distribution coefficients, and long-term leaching characteristics, cannot simulate the advective-dispersive and other mass transfer effects occurring in a CDF. Column leach tests provide a laboratory-scale physical model of leaching in a CDF. The purpose of batch and column testing is to demonstrate that contaminant elution in a continuous flow system can be predicted using information from batch studies.

Elution histories predicted using batch-determined distribution coefficients have qualitatively agreed with observed column elution histories, but quantitatively the predicted and observed elution histories were not always in good agreement (Environmental Laboratory 1987, Myers and Brannon 1988, and Palermo and others 1989). A workshop organized to review the WES studies on sediment leaching identified problems with some of the column data and recommended redesign of the column leach apparatus (Louisiana Water Resources Research Institute 1990).

Figure 7 shows an improved column leaching apparatus for sediments and dredged material that replaces the columns used in previous studies (Myers, Tittlebaum, and Gambrell 1991). The new design overcomes some of the shortcomings of the column apparatus used previously. This design minimizes wall effects by having a large column diameter-to-particle diameter ratio, minimizes run time for obtaining elution curves by having a short column length, and provides sufficient sample volume for chemical analysis since the flow-through area is large. Columns based on the new design have been constructed and are being used in ongoing dredged material leaching studies.

Integrated Approach

This approach consists of using results from batch and column leach tests and Equations 1 and 2 from Figure 2 to verify the form of an assumed interphase transfer term. Application of the integrated approach is illustrated in Figure 8. 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 pore water has been adequately described. If not, other formulations for interphase transfer may be needed. Once interphase transfer has been adequately described, contaminant migration by leaching can be evaluated for the flow conditions that apply in the field.

As a single extraction, the TCLP does not provide information on the time-dependent characteristics of contaminant releases. In a CDF, leachate quality varies with time as infiltration percolates through the dredged material. The time dependency is not always one of decreasing contaminant concentration as percolating water removes contaminants. Studies have shown that when estuarine sediments are leached, changes in the pore-water ionic strength cause maximum concentrations of polychlorinated biphenyls to occur long after the initial pore volume of water has eluted (Myers and Brannon 1988).

WES-SBLT

The WES-SBLT provides quantitative information on the tendency to contaminants to move from dredged material solids to water under redox and pH conditions that are representative of CDFs. In addition, the WES-SBLT provides quantitative information on long-term elution trends. This type of information is needed to predict leachate quality in CDFs.

The desorption isotherm approach to interpreting WES-SBLT data assumes that the various processes responsible for interphase transfer can be represented by unique contaminant- and sediment-specific distribution coefficients for freshwater sediments and a set of contaminant- and sediment-specific distribution coefficients

INTERGRATED APPROACH FOR EXAMINING THE SOURCE TERM

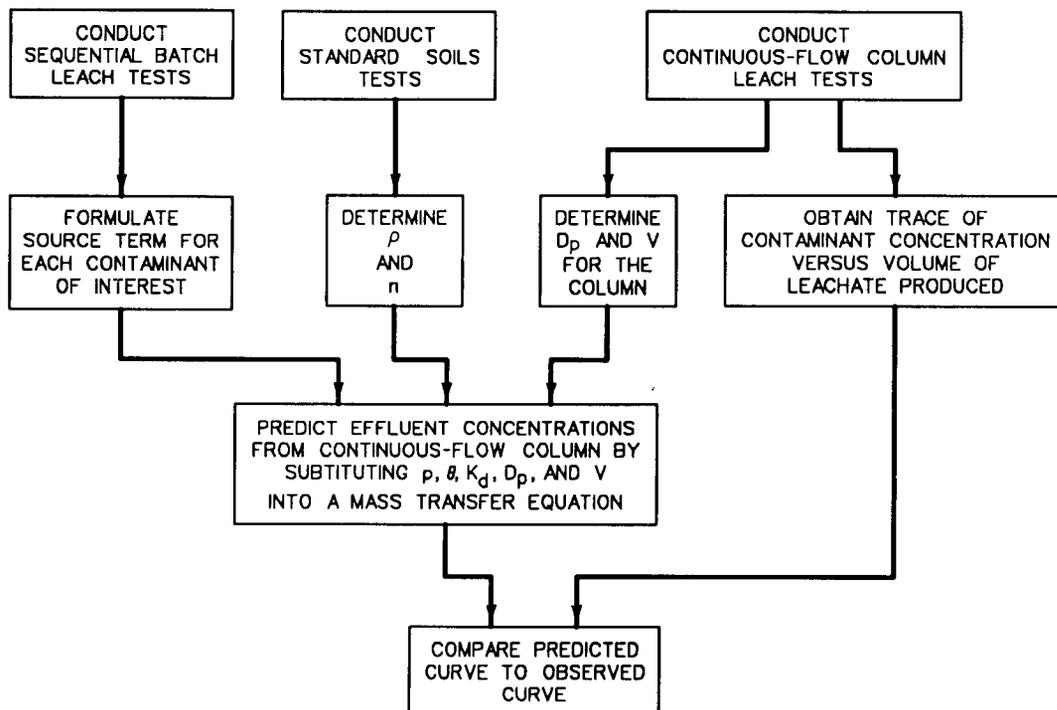


Figure 8. Schematic of integrated approach

for estuarine sediments. This approach seems to work, but has not been fully verified. Also, some aspects of the WES-SBLT, such as time required to reach steady-state leachate concentrations, are still under investigation.

Qualitative agreement between WES-SBLT elution trends and column elution trends has been obtained, but quantitative agreement is still lacking. In addition, there are no field data for verification of the WES-SBLT.

WES-Column

The WES-column leach test is less well-developed than the WES-SBLT, and additional work on column operation, sample collection and preservation, and mathematical modeling is needed before the integrated approach can be fully implemented. WES-column leach tests take several months to complete. Inspection and preservation of column leachates must be conducted on a daily basis for some contaminants. These requirements limit the usefulness of the WES-Column leach test beyond a research mode.

Summary

A thorough understanding of leachate generation in CDFs is necessary to judge the effectiveness of contaminant containment provided by these facilities. The integrated approach is being applied at the WES to provide the understanding needed for development of predictive techniques for leachate quality in CDFs.

Comparison of contaminant concentrations in the TCLP extract with concentration limits for the same is an approach best suited to regulation, not prediction. Although a waste may pass the TCLP, passing the TCLP provides no statutory release from liabilities associated with disposal (EPA 1990). The TCLP is best used as a hazardous waste regulatory tool, not a method for predicting contaminant mobility in dredged material.

When the objective is to predict leaching in a field setting, test conditions must be maintained that do not significantly alter chemical or physical parameters. Intentional adjustments in pH, redox, and ionic strength that yield artificial conditions should be avoided. For these reasons, the WES-SBLT is the most appropriate batch leach test available for developing the leach data needed for design of engineering controls. Until the WES-SBLT is fully developed, column leach testing and application of the integrated approach are recommended.

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Environmental Effects of Dredging Technical Notes



Influence of Sediment Properties on Bioaccumulation Potential of PCBs: Field Studies at the Calumet Confined Disposal Facility

Purpose

This technical note describes field testing conducted to examine the equilibrium partitioning of polychlorinated biphenyls (PCBs) between sediment and fish, changes in the partitioning over time, and the impact that depuration rates of PCBs can exert on apparent equilibrium observations.

Background

The US Environmental Protection Agency (EPA) is authorized to develop and implement sediment quality criteria (SQC) under Section 304(a) of the Clean Water Act. Under this authority, the EPA is proceeding with development of SQC for nonpolar organic compounds and metals. A major assumption in the current approach to SQC for nonpolar organic compounds such as PCBs is the existence of equilibrium in the sediment.

The US Army Corps of Engineers (USACE) is presently investigating the link between contaminant levels in sediment and sediment geochemistry, as well as the utility of equilibrium partitioning approaches for predicting contaminant levels in aquatic organisms in the field. Knowledge of these interactions will provide the USACE with a means of evaluating the adequacy of proposed SQC approaches for estimating the potential impacts of dredged material placement. The existence of steady-state (no measurable change over time) between sediments and organisms was investigated in the field at the Calumet confined disposal facility in the Chicago District.

Additional Information

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Introduction

The Calumet confined disposal facility (CDF) (Figure 1) is roughly triangular in shape, covers 43 acres, and was designed to hold 1.45 million cu yd of dredged material. The CDF was formed by a stone-filled dike with a core of prepared limestone. A synthetic membrane lines the entire interior face with a blanket of silty sand overlying the liner to create a barrier of low permeability (Dorkin and others 1988). Since its creation at the mouth of the Calumet River on the shore of Lake Michigan in 1983-1984, the CDF has received five separate lots of dredged material totalling approximately 300,000 cu yd. The most recent dredging operation included a large amount of debris (pilings, concrete, and rock) that was placed in area 5. Low levels of polychlorinated biphenyls (PCBs) have been reported and an endemic population of animals has developed inside the CDF (Dorkin and others 1988).

The Calumet CDF is relatively isolated from outside sources of water and contaminants because the sand and synthetic liner limits interchange between the CDF and Lake Michigan. The limited water interchange provides a good test of equilibrium partitioning between sediment and organisms in the field by localizing fish populations and providing consistent contaminant exposure conditions. The objective of this study was to determine whether steady-state conditions exist between sediment and organisms under optimum field conditions in the Calumet CDF and its immediate surroundings.

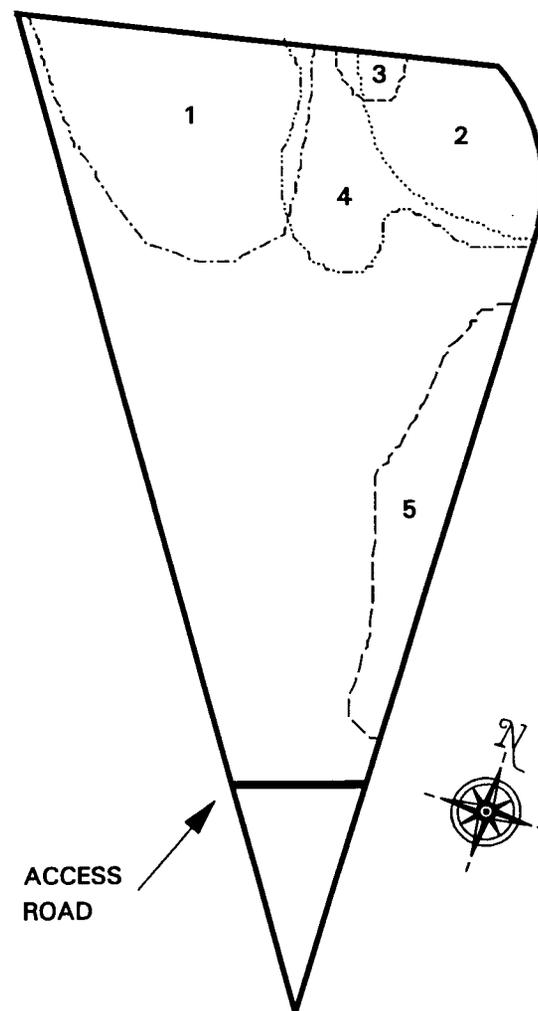


Figure 1. Calumet CDF and approximate location of the five disposal events

Materials and Methods

Thirty-six box cores in transects across the CDF were taken in early May and mid October 1990. At each sampling time, the top 2 cm of sediment were composited into 12 samples and analyzed for PCB, total organic carbon (TOC), humic and fulvic acid organic matter fractions, and grain size. The top 2 cm of sediment was analyzed to characterize the material most frequently contacted by bottom-dwelling organisms. Physical data (temperature, dissolved oxygen, light attenuation, and suspended sediments) were obtained in the water column.

Black bullhead (*Ameiurus* (= *Ictalurus*) *melas*) was collected on three occasions during the study (June 14, July 10, and July 28, 1990). This animal was selected because of its abundance in the CDF, its bottom foraging behavior, and its sufficient size (5-8 in.). Fish were stunned using standard fish-shocking techniques, netted, placed in buckets of water, and quickly transferred to a large (500-gal) tank for transport to the laboratory. The fish were treated for parasites by dipping in a weak formalin solution and placed into 4-ft-diameter circular tanks approximately 2 ft deep for depuration. The tanks were maintained in a flow-through mode at 25° C under natural daylight conditions. Commercial catfish chow was fed. Five fish (replicates) were removed from the aquaria and frozen at day 0, 2, 7, 14, 28, and 56. Animals were shipped to the WES where PCB concentrations and percent lipids were determined in standard fillets taken from the fish.

Results and Discussion

Existing data from the Calumet CDF and adjacent areas were reanalyzed (Dorkin and others 1988, Clarke, McFarland, and Dorkin 1988). Dorkin and others (1988) determined total PCB concentrations in many aquatic organisms including crayfish, alewife, yellow perch, bluntnose minnow, channel catfish, orangespot sunfish, green sunfish, gizzard shad, carp, goldfish, rainbow trout, brown trout, worms/leeches, and pumpkinseed. Not all organisms were found at every site investigated. Four sites were studied, including the pond inside the CDF, the area outside the CDF, in the Chicago River, and at the breakwater area near the CDF. The breakwater area is a high-energy environment, outside the CDF is intermediate, and inside the CDF is a pond with minimal interchanges with the outside water body.

Preference factors ((organism concentration ÷ decimal fraction lipids) ÷ (sediment concentration ÷ fraction TOC)) derived from the data in Clarke, McFarland, and Dorkin (1988) are presented in Figure 2 for crayfish, bullhead, and the mean of all other species. The mean of all other species was used because these fish are not associated with the sediment to the same extent as black bullhead and crayfish. Marked differences were observed in preference factors between sampling locations for crayfish, bullhead, and the mean of all other species. Results within a sampling location, however, were similar. Preference factors inside the CDF ranged from 3.44 for bullhead to 2.95 for all species, very close to the values reported for other laboratory and field situations (Brannon and others 1991a,b). Steady-state conditions between sediment and organism contamination appeared

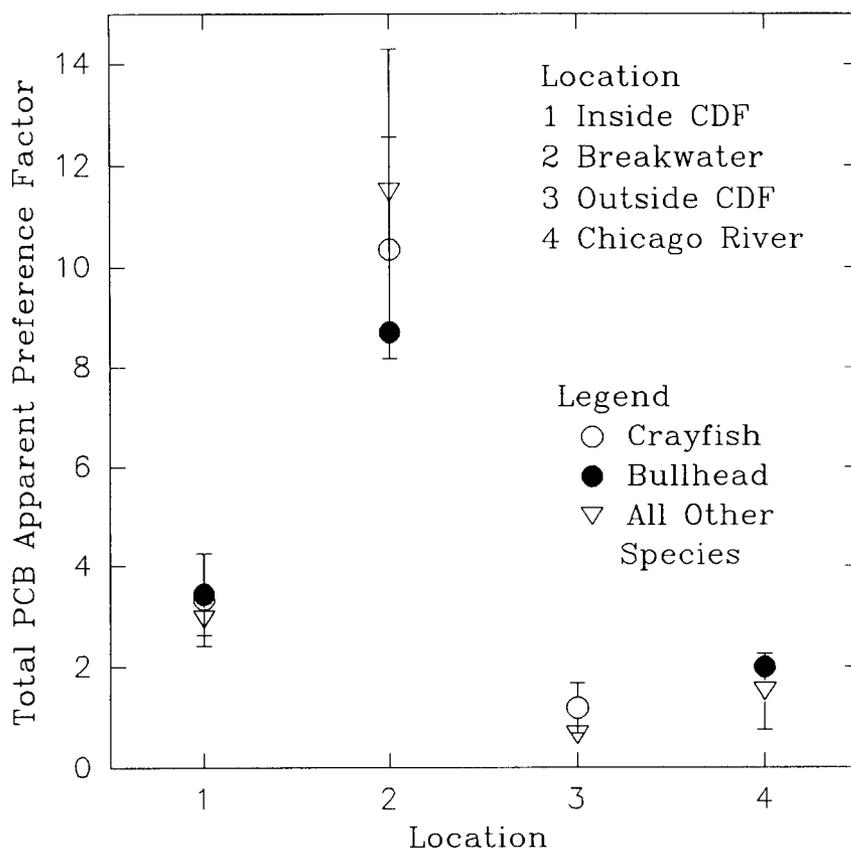


Figure 2. Apparent preference factors from the Calumet CDF and environs (Dorkin and others 1988, Clarke, McFarland, and Dorkin 1988)

to exist within the CDF for all organisms analyzed, including fish not thought to have direct contact with the sediment (Clarke, McFarland, and Dorkin 1988). Preference factors in organisms from the breakwater area were from two to three times higher than expected based on sediment PCB concentrations normalized to TOC; this indicated exposure to other sources (sediment or water) of PCB with higher bioaccumulation potential (Clarke, McFarland, and Dorkin 1988).

Preference factors within a location agreed closely in spite of differences in feeding (organism trophic level) and migratory habits of organisms, indicating that exposures were similar. Preference factors for organisms such as crayfish, closely identified with specific sediment locales, were much higher in the breakwater area than the range of 1.73 to 4.0 typically observed in laboratory and field studies (Brannon and others 1991b). PCB bioaccumulation outside the CDF, as indicated by preference factors, was lower than expected for all species tested (crayfish = 1.18 compared to 0.64 for all other species combined), indicating less exposure from the sediment or other sources. Deviations from the normal range of preference factors may indicate that steady-state conditions between sediment and organisms did not exist at the breakwater area or in other locales, even for crayfish.

These results imply that steady-state does not exist between sediment and aquatic organisms in relatively high-energy aquatic environments, even for organisms that are closely associated with the sediment. Application of equilibrium concepts in such areas may lead to incorrect sediment categorizations.

Field data collected in 1990 provide additional information on PCB partitioning between sediment and aquatic organisms. Concentrations of total PCBs, Aroclor 1254, and TOC in sediment from the Calumet CDF are presented in Table 1. Concentrations of total PCB and TOC are lower than the 1.1 mg/kg and 4.9 percent, respectively, reported by Dorkin and others (1988) for sediment inside the CDF.

Parameter	Value	
	Mean	Standard Error
Total PCB, $\mu\text{g/g}$	0.29	0.045
Aroclor 1254, $\mu\text{g/g}$	0.26	0.025
TOC, percent	2.85	0.17
Humic + fulvic, percent	0.32	0.014
Fraction Solids	0.445	0.006
Sand, percent	16.04	3.6
Silt, percent	58.96	2.56
Clay, percent	27.00	4.13

Preference factors normalized on both a TOC and humic + fulvic acid organic matter basis using the 1990 samplings (time 0 data) are presented in Figure 3 for total PCB and Aroclor 1254. Results show that no significant difference existed between preference factors at any of the sampling times. This result indicates that steady-state conditions between sediment and organism concentrations of PCB existed within the CDF. The TOC preference factor values did not significantly differ from the preference factor of 3.44 derived from the data of Dorkin and others (1988) for the black bullhead. These data indicate that preference factors between sediment and organisms within the CDF did not significantly change over either the short term (months and weeks) or long term (years). Preference factors computed using the humic + fulvic acid fraction, although exhibiting different absolute values, showed the same trends as those computed using TOC. There was no apparent improvement, however, over the use of TOC to normalize sediment PCB concentrations.

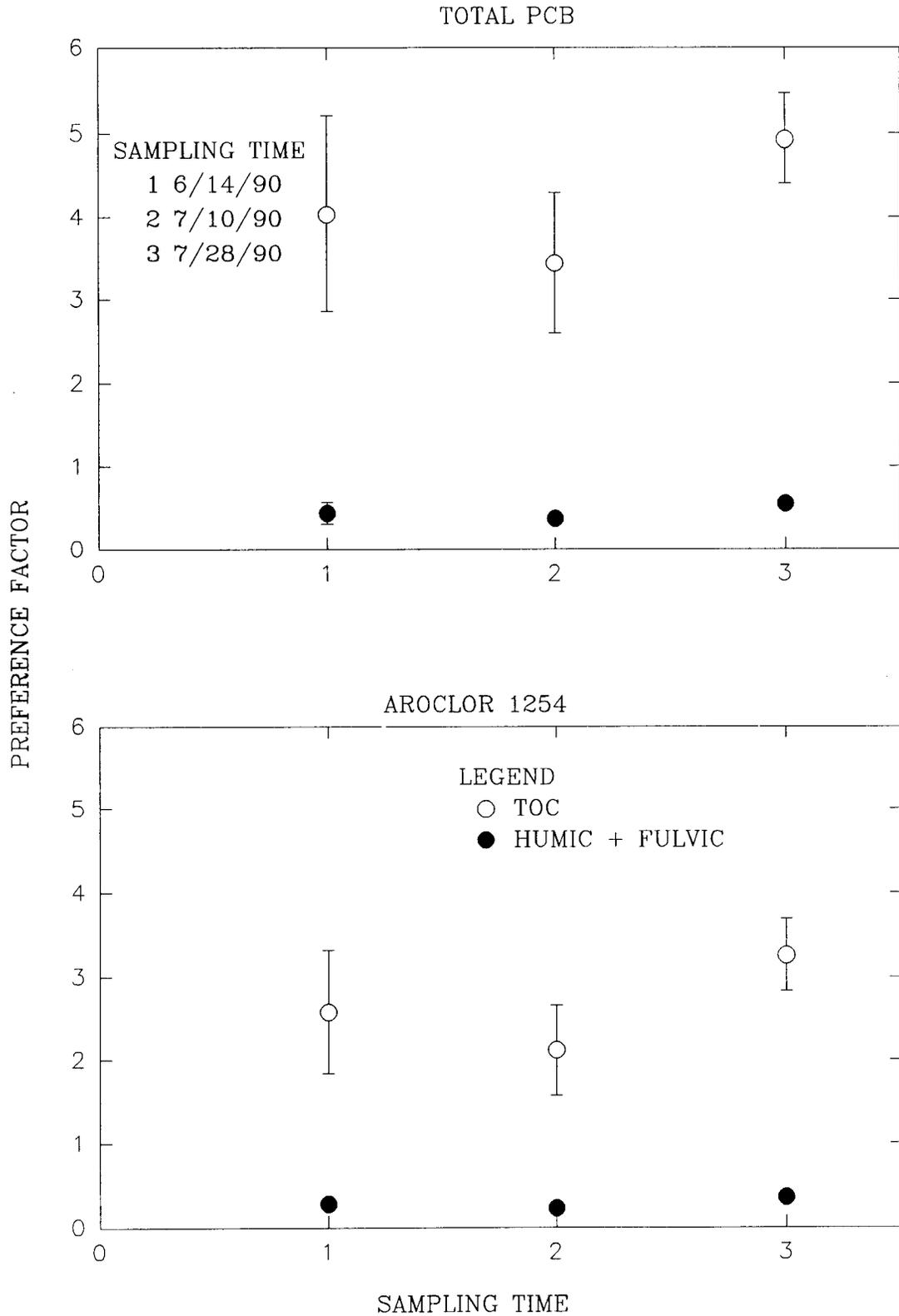


Figure 3. Preference factors for total PCB and Aroclor 1254 (TOC and humic + fulvic acid basis) for black bullhead in the Calumet CDF

Depuration of total PCB and Aroclor 1254, as reflected by changes in the preference factor computed using initial PCB and TOC exposure conditions, proceeded very slowly for total PCB and only marginally faster for Aroclor 1254 (Figure 4). Removal of PCB from the black bullhead does not follow any type of elimination rate constant for the time period studied (8 weeks). This lack of a pattern could be due to the fact that non-normalized PCB concentrations in the fish tissue were low, ranging from less than the detection limit to 1.4 $\mu\text{g/g}$ for total PCB, and 0.74 $\mu\text{g/g}$ for Aroclor 1254. However, these depuration results agree with findings of others (DeFoe, Veith, and Carlson 1978, Lieb, Bills, and Sinnhuber 1974) for fathead minnows and rainbow trout.

Depuration results indicate that attainment of steady-state will be slow when aquatic animals move from areas of high contamination to areas of low contamination. This may account for the much higher preference factors in the breakwater area than would be expected from sediment concentrations of PCB and TOC.

The equilibrium partitioning SQC approach currently under development is based on interstitial water exposure of benthic organisms. Results of this study indicate that attainment of steady-state exposure between benthic organisms such as worms (assuming that depuration rates are similar) moving into clean sediment after encountering contaminated sediment microzones would be slow. Previous results (Brannon and others 1989, 1991a,b) have shown that attainment of steady-state preference factors is rapid when "clean" animals are exposed to contaminated sediment. The reverse may not be true when contaminated animals are exposed to a clean environment.

Summary of Findings

Preference factors for total PCB in the Calumet CDF did not change significantly over the short term (months and weeks) or long term (years), indicating that steady-state conditions existed. Preference factors computed using the sediment humic + fulvic acid fraction, although exhibiting different absolute values, showed the same trends as those computed using TOC, but did not confer any apparent advantages.

Results also indicated that steady-state did not exist between sediment and aquatic organisms in higher energy environments outside the Calumet CDF. This was true even for organisms such as crayfish and black bullhead that are closely associated with the sediment. Application of equilibrium concepts for examining the partitioning of contaminants between sediment and aquatic organisms in such areas may not be warranted.

Depuration studies for black bullhead indicated that elimination of PCB proceeds very slowly. When aquatic animals move from areas of high contamination to areas of low contamination, attainment of steady-state with sediment can be slow, the opposite of what happens when clean animals are exposed to contaminated sediment. If contaminated microzones and localized contamination

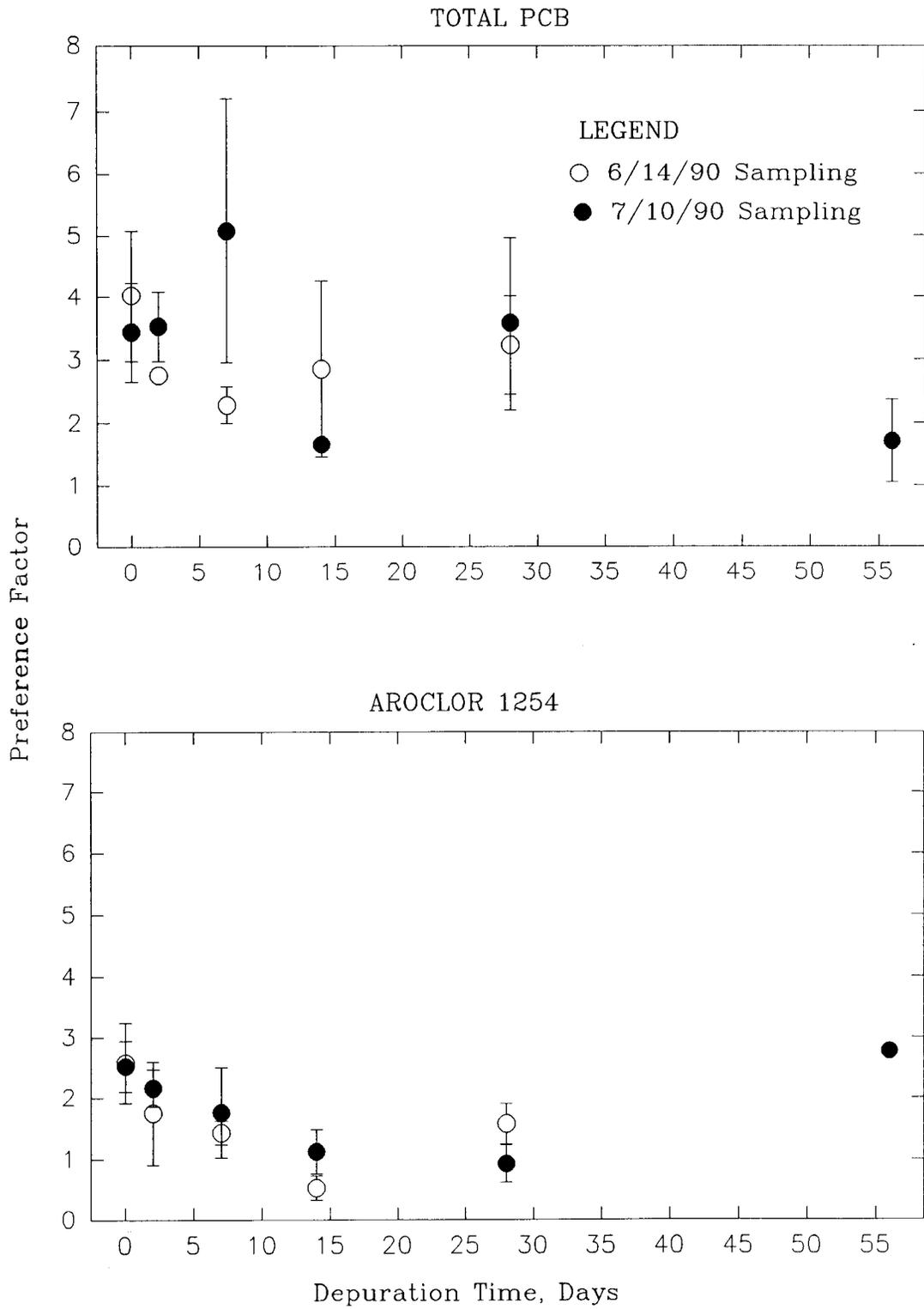


Figure 4. Effect of depuration time on total PCB and Aroclor 1254 preference factors in black bullhead

exist in sediment, the rate of attainment of steady-state between clean sediment and benthic organisms may be affected.

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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

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

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).

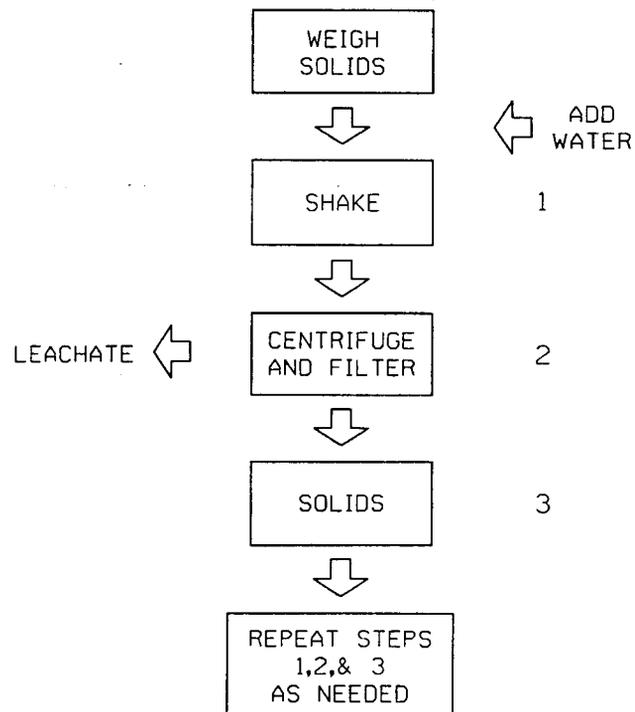


Figure 1. Schematic of WES sequential batch leach test

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.

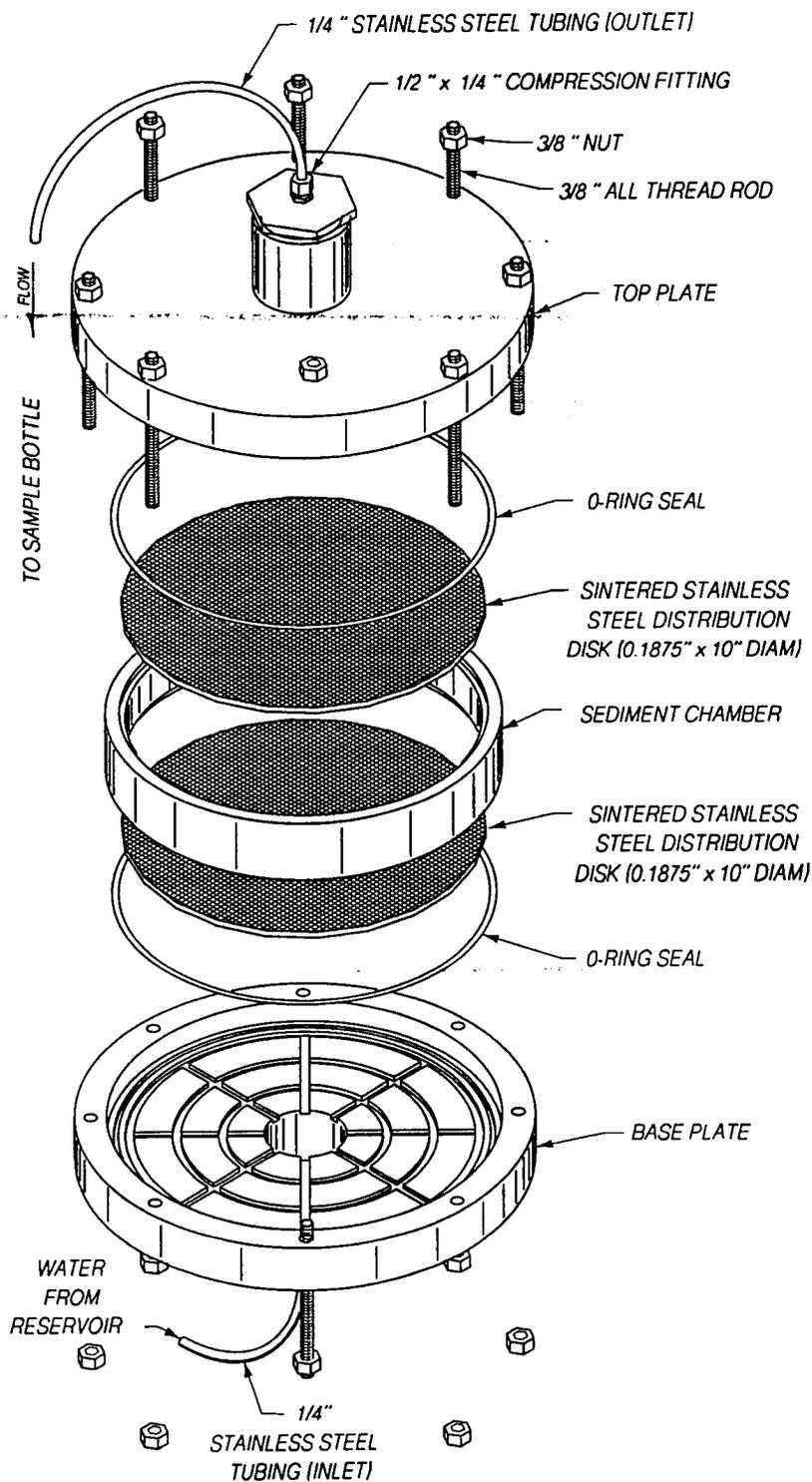


Figure 2. Schematic of column leaching apparatus for sediments

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^{-5} 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^{-5} 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^{-5} 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.

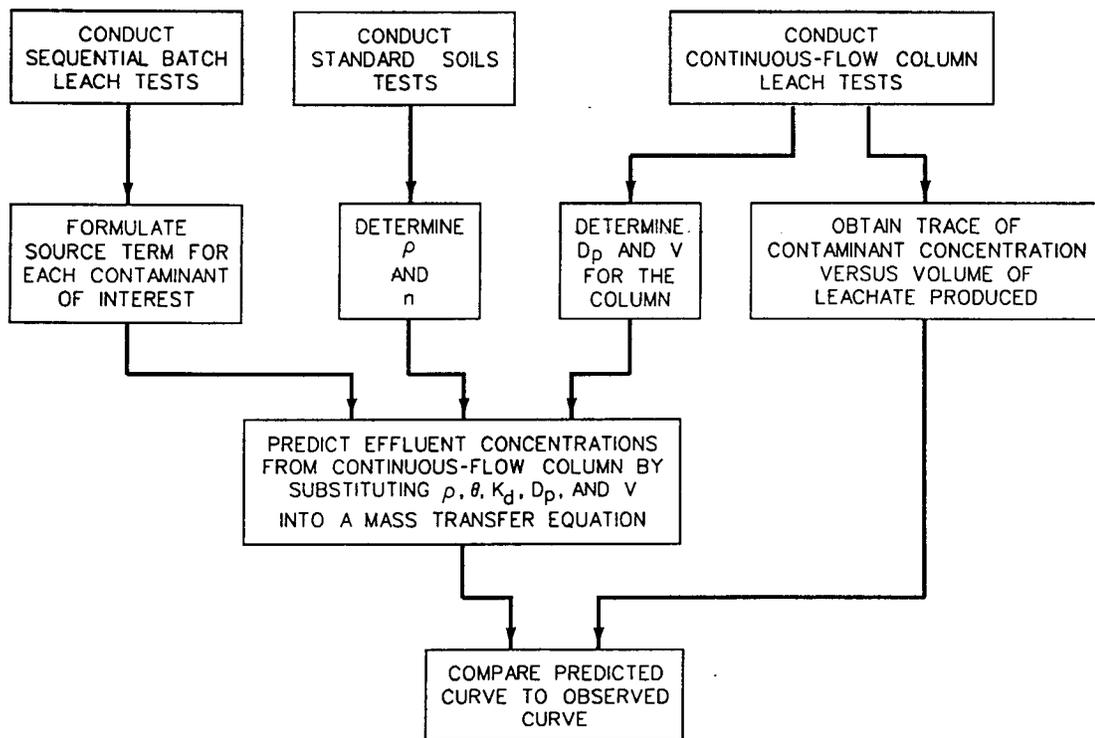


Figure 3. Integrated approach

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.

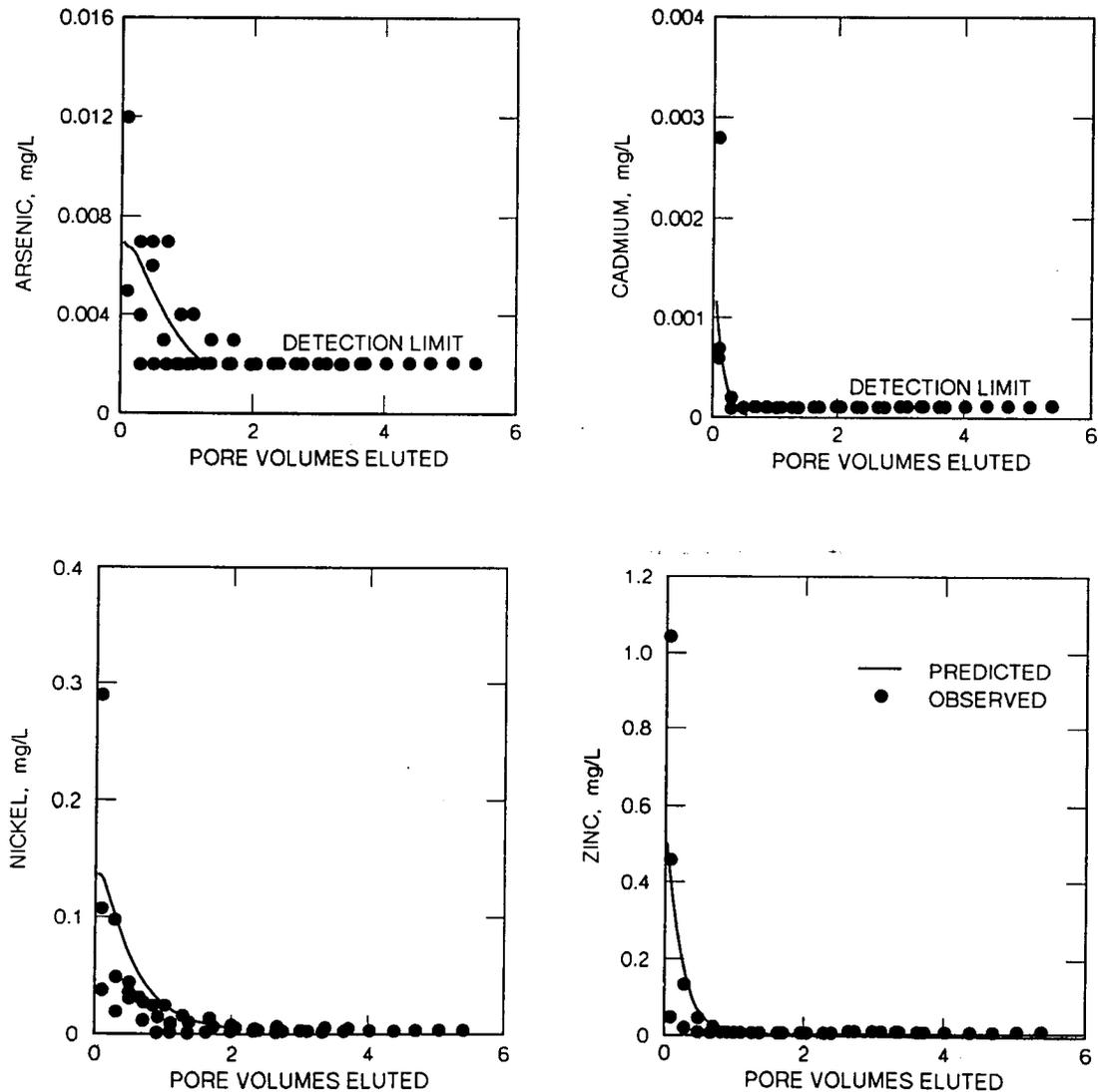


Figure 4. Predicted and observed column elution curves for Hamlet City Lake sediment

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

$$q = K_d C \quad (1)$$

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

$$q = K_d C + q_r \quad (2)$$

where q_r (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_d) and sediment metals concentrations in geochemical phases resistant to leaching (q_r) 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.

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

where

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

C_o = initial leachate contaminant concentration, mg/L

$A = \beta \rho_b (K_d^o - K_d^f)/n$ (variables are defined below)

β = empirical coefficient for change in K_d with T , dimensionless

$D = \rho_b (K_d^o - K_d^f)/n$ (variables are defined below)

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

T = number of pore volumes eluted, dimensionless

ρ_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

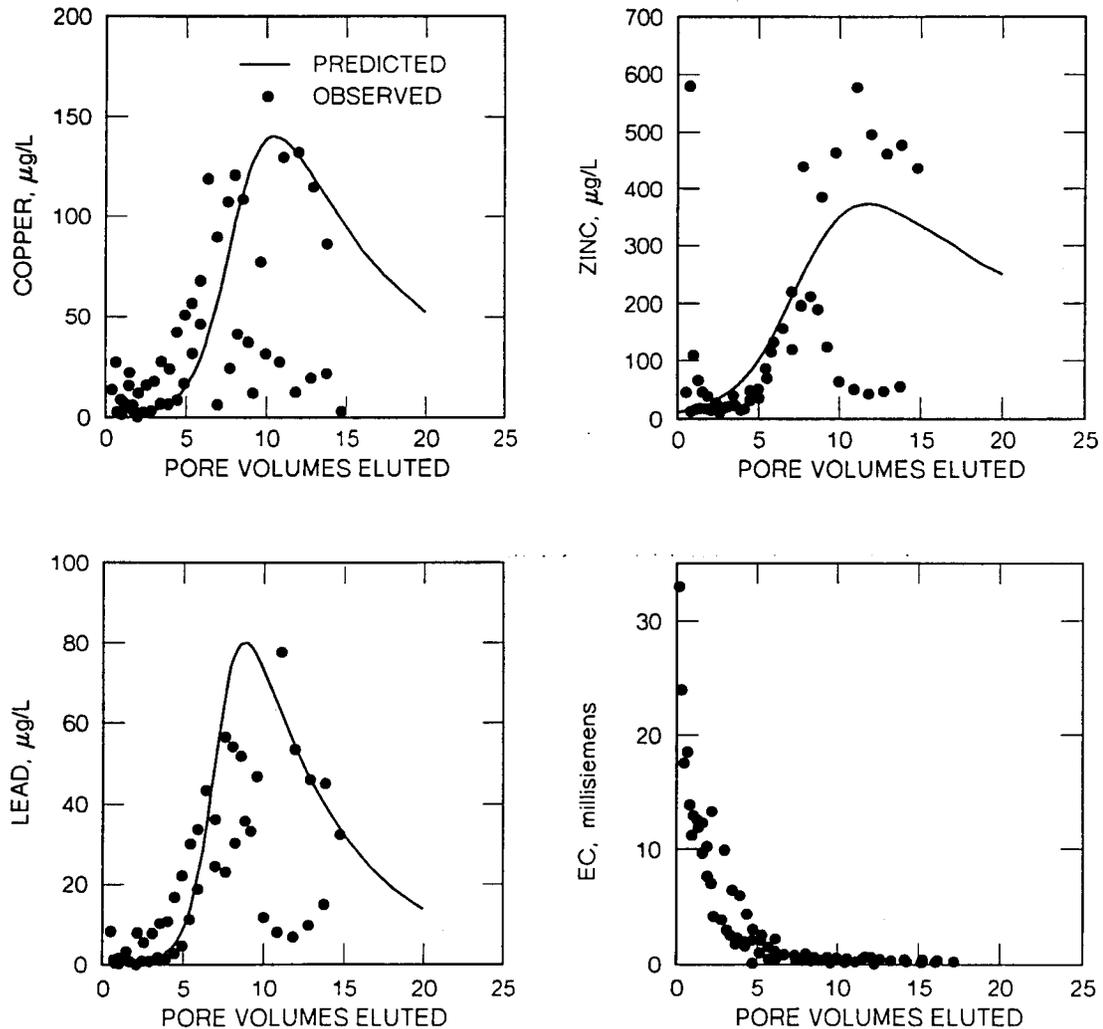


Figure 5. Predicted and observed elution curves for sediment from the West Richmond reach of J. F. Baldwin channel

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 β , K_d^f , and K_d^o .

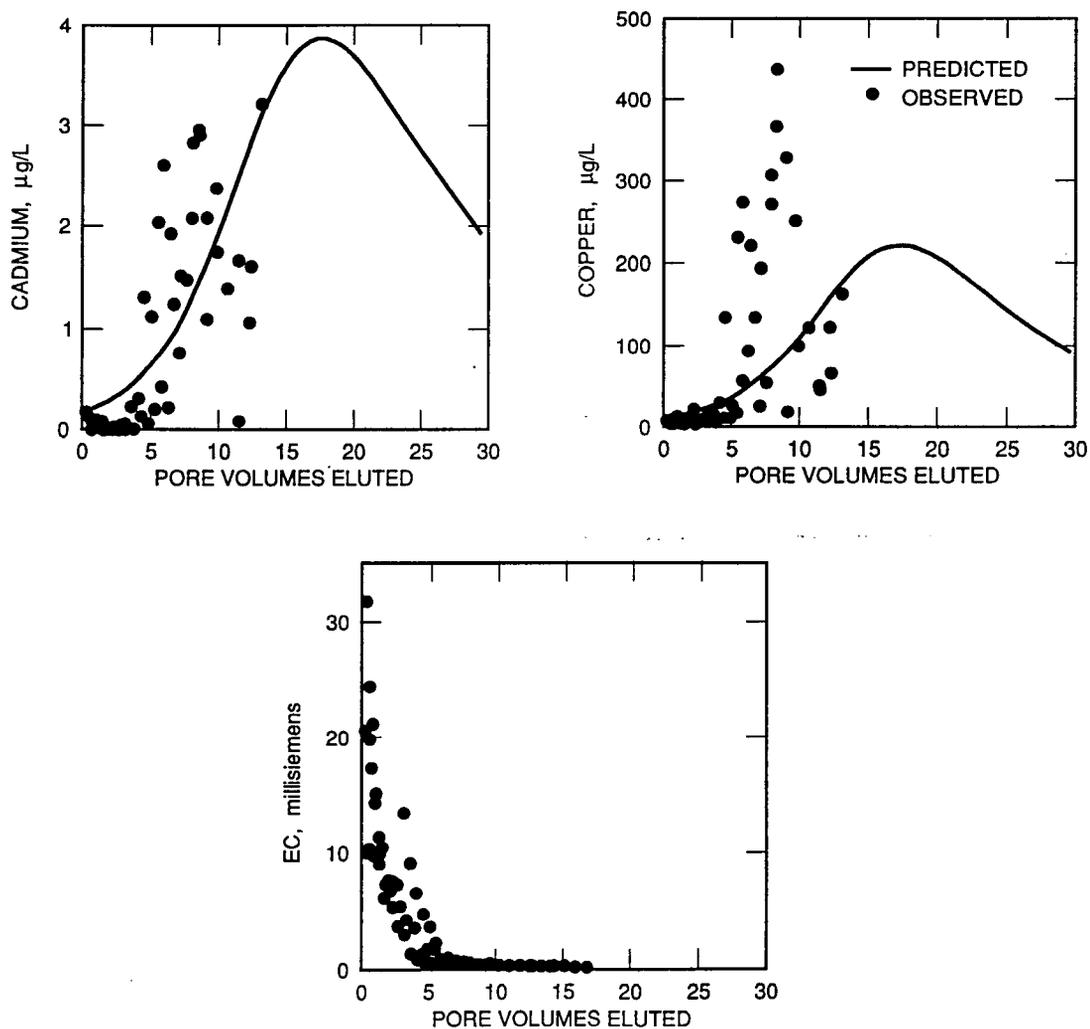


Figure 6. Predicted and observed elution curves for Richmond Harbor sediment, Santa Fe channel

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

$$K_d(T) = K_d^f + (K_d^o - K_d^f) \exp(-\beta T) \quad (4)$$

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~~ 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^{-5} 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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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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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.

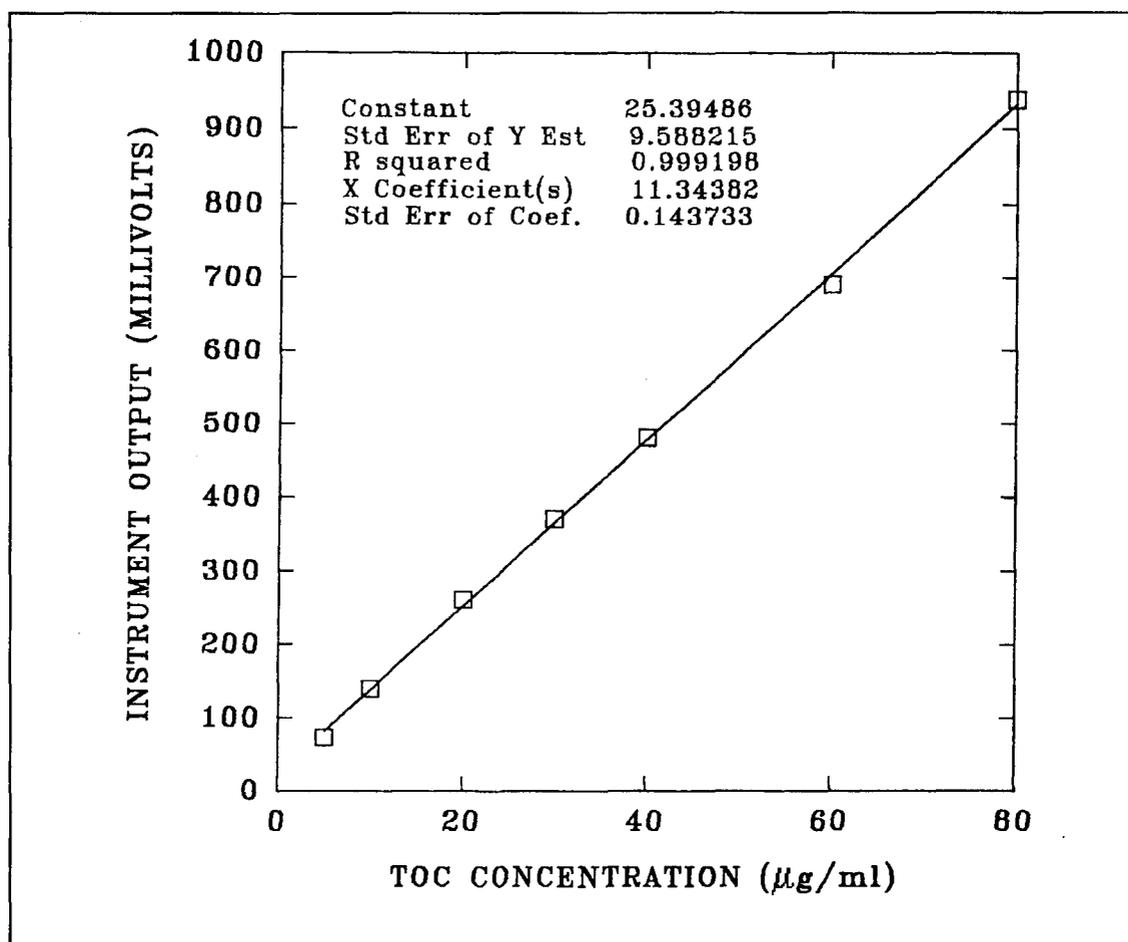


Figure 1. Total organic carbon standard calibration curve

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- $\mu\text{g}/\text{ml}$ 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 $\mu\text{g}/\text{ml}$ carbon with a standard deviation of 2.22 $\mu\text{g}/\text{ml}$ 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 $\mu\text{g}/\text{ml}$.

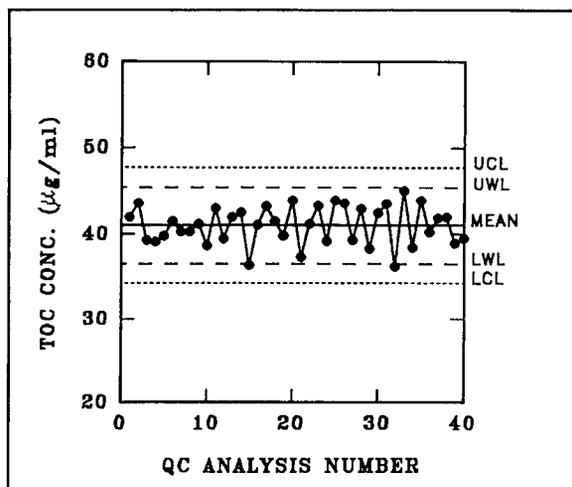


Figure 2. Quality control sample results

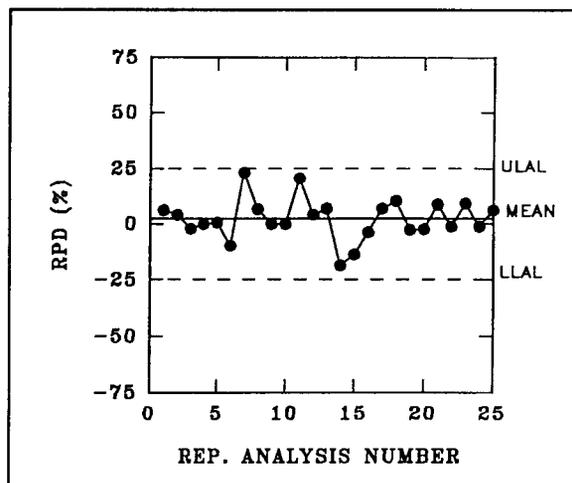


Figure 3. Replicate results for relative percent difference

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 $\mu\text{g}/\text{ml}$ TOC compared with a certified mean value of 67.9 $\mu\text{g}/\text{ml}$ with an LCV of 58 $\mu\text{g}/\text{ml}$ and a UCV of 78 $\mu\text{g}/\text{ml}$. The standard deviation was 3.2 $\mu\text{g}/\text{ml}$, with a method bias of 1.3 $\mu\text{g}/\text{ml}$, single operator bias of 0.8 $\mu\text{g}/\text{ml}$, and net bias of 1.9 percent. Comparison of the results obtained using this method with the published values for the CRM

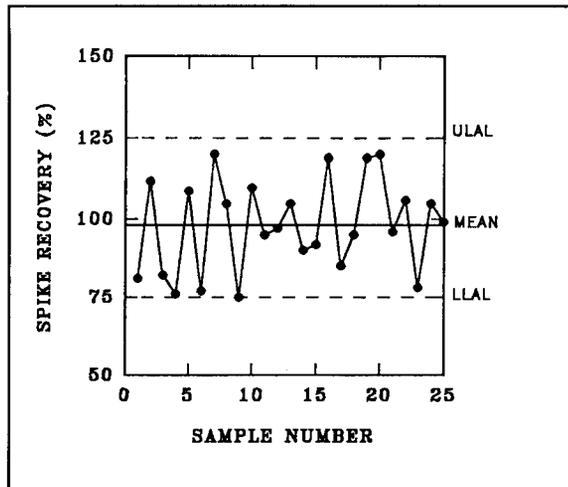


Figure 4. Spike recovery results

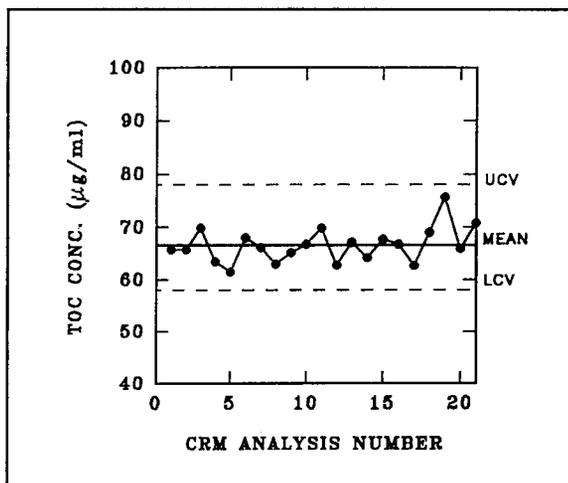


Figure 5. Analytical results for certified reference material

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.

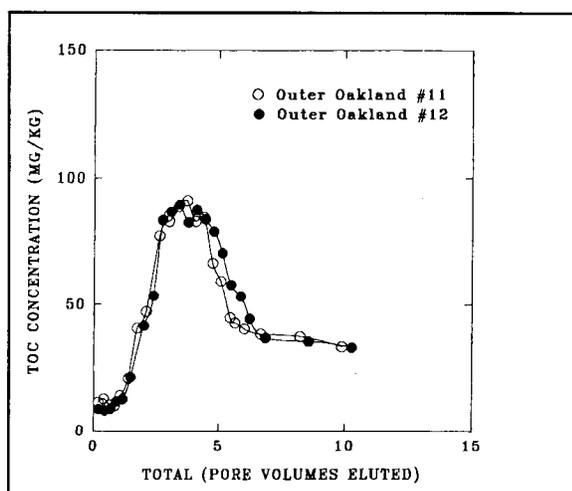


Figure 6. Total organic carbon elution curves

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

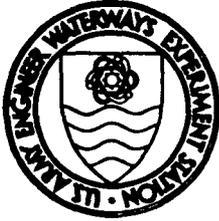
The test procedure described in this technical note can be used to make accurate and reproducible measurements of TOC concentrations in estuarine leachate samples. Acceptable bias, precision, and accuracy can be obtained with the procedure. Thus, this method eliminates the need to separately determine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



Natural Processes for Contaminant Treatment and Control at Dredged Material Confined Disposal Facilities

Purpose

This note examines the potential for natural processes to treat contaminants and maximize contaminant containment at dredged material confined disposal facilities (CDFs).

Background

CDFs are used by the Corps of Engineers to dispose contaminated dredged material from shipping channels and harbors in the Great Lakes, along the Atlantic and Gulf coasts, and to a limited extent along the Pacific coast. The nature and level of contamination in dredged materials disposed in CDFs vary widely on a project-to-project basis. Application of CDF technology has focused on containment effectiveness, and this focus will probably continue to be appropriate for many navigation maintenance projects. However, increasing attention is being directed to the containment effectiveness of CDFs for dredged materials that are viewed by resource agencies as highly contaminated (Petrovski 1995). One major criticism of CDFs is that they were not designed, nor are they managed, to treat the pollutants placed inside, but merely function as repositories from which there may be slow but long-term release of contaminants. In addition, many CDFs are now nearing or exceeding design capacity, and the Corps is in the process of developing new disposal options and evaluating closure requirements for existing CDFs.

Numerous phenomena affect contaminant containment efficiencies at CDFs and, in some cases, degrade contaminants or retard contaminant migration. Some of these phenomena occur without intervention by humans and are referred to as natural processes. The effects that natural processes have on contaminant containment and the potential for enhanced effects, however, are

rarely considered during design, construction, operation, and management of CDFs. With increasing concerns about the effectiveness of contaminant containment at CDFs, the need for improved CDF technology also increases (Petrovski 1995). Better understanding of natural processes could provide a basis for developing improved CDF technology.

Additional Information

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Natural Process Overview

Treatment by natural processes is defined as the in situ biological transformation of contaminants to less harmful forms by microorganisms and the in situ physicochemical alteration of contaminants to less mobile forms. Processes such as biodegradation and photolysis reduce organic contaminant concentrations through chemical transformation reactions.

Figure 1 is a schematic showing some of the natural processes that alter contaminant concentrations and mobility in CDFs. Some natural phenomena tend to clean the site by moving contaminants offsite. Processes such as leaching, volatilization, and runoff reduce contaminant concentrations by removing pollutant mass from the CDF. Still other natural phenomena tend to reduce contaminant migration. For example, desiccation reduces volatilization by increasing tortuosity, and self-weight consolidation minimizes leaching by reducing hydraulic conductivity. Other natural processes not shown in Figure 1 include sorption, hydrolysis, microbially mediated oxidation-reduction reactions, and abiotic reactions. Of these various processes, in situ natural biodegradation is the process with most promise for treating organic contaminants in CDFs.

Biodegradation

Application Potential

Natural biodegradation (aerobic and anaerobic) uses in situ, naturally occurring microorganisms to degrade contaminants (Norris and others 1994). The microorganisms are mainly bacteria but can be fungi. The ability of indigenous microorganisms in fresh and salt water, soils, and groundwater to chemically transform a wide variety of organic contaminants is well known (Wise 1988; Ehrlich and others 1992; King, Long, and Sheldon 1992; National Research Council 1993; Norris and others 1994). These same microorganisms may also be capable of transforming contaminants in CDFs, aerobically in the vadose zone and in the capillary fringe where oxygen is not limiting and anaerobically in the saturated zone (Figure 1).

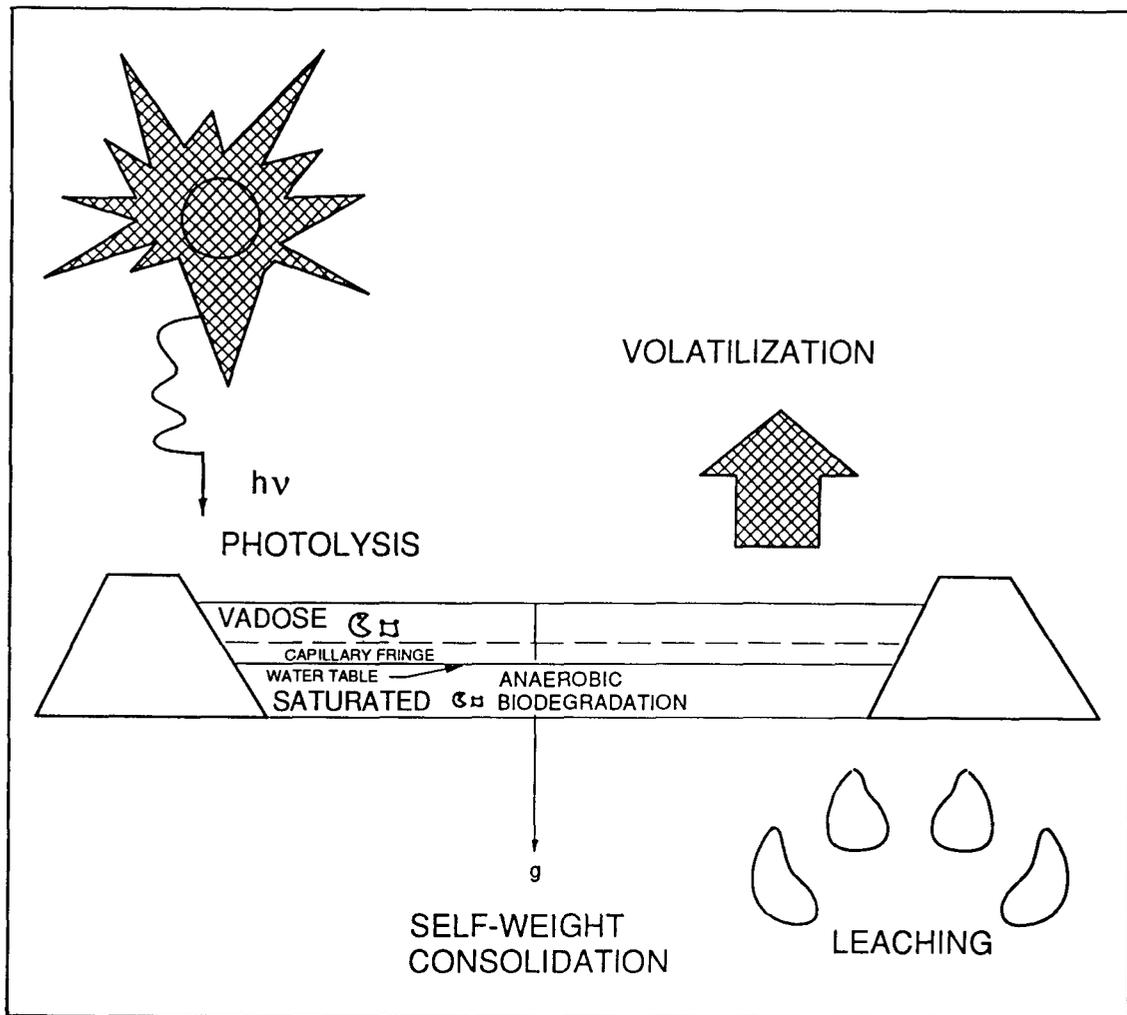


Figure 1. Natural processes affecting contaminants in CDFs

Organic chemicals can be classified into two groups: halogenated and nonhalogenated. Chlorine and bromine are halogens. Thus, halogenated organics are organic chemicals with either chlorine or bromine in their molecular structure. As a general rule, organic molecules containing halogens are more difficult to biodegrade than the same molecules without halogens present.

Petroleum hydrocarbons and nonhalogenated solvents such as alcohols, ketones, ethers, carboxylic acids, and esters are readily biodegraded (National Research Council 1993, Norris and others 1994). Monoaromatic compounds such as benzene, toluene ethylbenzene, and xylenes (BTEX compounds) are more rapidly degraded than the two-ring compounds such as naphthalene, which are in turn more easily degraded than the three-, four-, and five-ring polycyclic aromatic hydrocarbons (PAHs). Dredged material contaminated with creosote, coal tar, and heavier petroleum products often contains higher molecular weight PAHs (fluorene, phenanthrene, chrysene, etc.). These chemicals have limited solubility in water, adsorb strongly, and degrade at rates much slower than other hydrocarbons.

For years it was thought that halogenated organics, such as dichloro-diphenyl-trichloroethane (DDT) and polychlorinated biphenyls (PCBs), were persistent and did not biodegrade. However, laboratory and field studies have shown that biodegradation of these contaminants occurs and that degradation is affected by environmental conditions, such as pH and oxidation-reduction potential. For example, DDT degrades more rapidly under anaerobic conditions typical of saturated dredged material than under aerobic conditions (Guenzi and Bread 1967, Gambrell and others 1984). Anaerobic dechlorination of PCBs in sediments has also been reported (Brown and others 1987); however, PCB mineralization rates are higher under aerobic than anaerobic conditions (Pardue, Delaune, and Patrick 1988).

Metals do not biodegrade, but biological processes may incidentally mobilize mercury, arsenic, and selenium or immobilize other metals through oxidation-reduction reactions. Generally, the presence of metals has little direct effect on bioremediation rates. While some metals such as mercury can be toxic, microbial populations frequently adapt to the concentrations present (Ahrling and Wastermann 1988).

Performance Evaluation

Questions concerning treatment effectiveness remain. There is very little operating history to judge the effectiveness of natural bioremediation for CDFs. It is therefore necessary to develop a performance track record before the potential of natural bioremediation can be realized as a component of an improved CDF technology. Development of such a track record requires an evaluation framework to quantify when natural biodegradation processes are working or have worked.

The National Research Council Committee on In Situ Bioremediation recommends an evaluation strategy that builds a consistent, logical case based on converging lines of independent evidence (National Research Council 1993). The strategy includes three types of information: documented loss of contaminants from the site, laboratory assays showing that microorganisms from site samples have the potential to transform contaminants under site conditions, and one or more pieces of information showing that the biodegradation potential is actually realized in the field. A critical factor in deciding whether bioremediation is working or has worked is whether the contaminants are susceptible to biodegradation by the organisms at the site. This must be demonstrated in either laboratory or field tests performed on site-specific samples and may require continual monitoring of contaminants and transformation products indicative of bioremediation.

For natural bioremediation to be effective, biodegradation must proceed faster than contaminant migration processes such as leaching and volatilization. These processes are discussed below.

Leaching

Leaching is a contaminant migration pathway that lowers contaminant concentrations in CDFs. The process is usually very slow in CDFs containing fine-grain dredged material because the hydraulic conductivity of fine-grain dredged material is low (10^{-5} to 10^{-9} cm/sec) and hydraulic gradients are low (near 1) after filling. Organic carbon contents of polluted dredged materials are usually high ($f_{oc} > 0.01$) so that sorption coefficients and retardation factors are large.

Dredged material specific tests (Brannon, Myers, and Tardy 1994) have been developed for obtaining site-specific sorption coefficients. These tests can be used in lieu of estimation techniques to obtain retardation factors.

Seepage rates can be estimated using minimal site-specific information and the Hydrologic Evaluation of Landfill Performance (HELP) model (Schroeder and others 1994a, 1994b), or more accurate estimates can be obtained using site-specific piezometer data and a groundwater model. First-cut seepage velocities can be obtained using Darcy's law, typical dredged material hydraulic conductivities of 10^{-5} to 10^{-9} cm/sec, and a hydraulic gradient of 1 (Figure 2). This simple approach usually overestimates seepage because hydraulic gradients in CDFs can be less than 1.

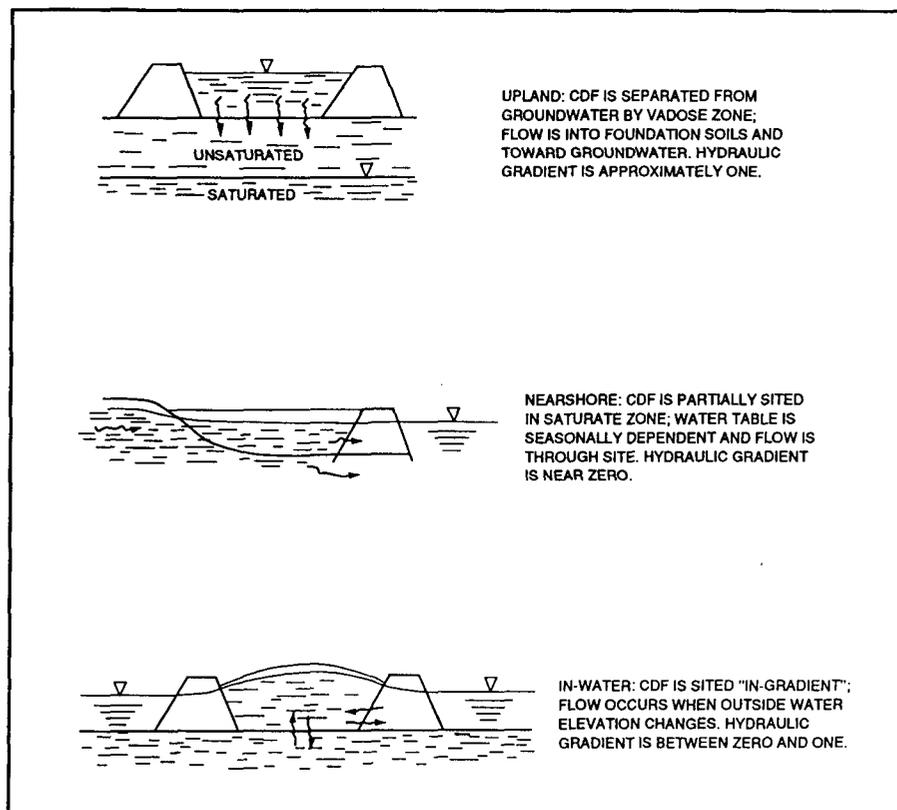


Figure 2. Long-term average hydraulic gradients in CDFs

Contaminant losses by leaching are usually of minor significance relative to effluent losses during filling operations and volatile losses from exposed, fresh dredged material. In spite of the low loss potential relative to other contaminant loss mechanisms, leaching can adversely impact groundwater, depending on site geohydrological conditions. For example, if the CDF foundation soils are sandy or there is a sand wedge in the CDF as a consequence of long-term hydraulic placement of sandy dredged material at one location, contaminants originally in the dredged material may eventually appear in the water table aquifer beneath the CDF.

Volatilization

Many organic chemicals will vaporize from the surface of freshly exposed dredged material. This natural process is often referred to as volatilization. Unless a cap is placed on freshly exposed dredged material, organic chemicals will volatilize. A common misconception is that the tendency for organic chemicals to volatilize from dredged material is indicated by vapor pressure. The tendency for chemicals to volatilize from dredged material depends on the Henry constant (Thibodeaux 1989), which is a function of water solubility and vapor pressure. Thus, organic chemicals with low vapor pressures and low water solubilities can have sufficiently high Henry constants for volatilization to be significant.

Simmler (1990) evaluated the tendency for PCBs to volatilize from dredged material in a CDF and suggested that PCB losses via volatilization could exceed PCB losses by other contaminant migration pathways. Myers and others (1993) estimated PAH losses for a CDF and suggested that volatilization was a major contaminant migration pathway. Both Simmler's work and the estimates made by Myers and others (1993) were based on theoretical models developed by Thibodeaux (1989). There are no field data available to verify the estimated tendency of these chemicals to volatilize from dredged material.

Volatile losses can be estimated using theoretical models, but the reliability of such estimates is unclear. Model uncertainty is high. In addition, the estimates are large, suggesting that the first millimeter of aged dredged material (1 year exposure to the atmosphere) should be substantially reduced in organic chemical contamination via volatilization alone. Unfortunately, there are no published reports that confirm or refute this prediction.

Photolysis

Photolysis refers to molecular chemical change due to absorption of light energy. Laboratory studies of photolysis in aqueous solutions have led to increasing attention to photolysis as an important process in determining the fate of many organic chemicals. For example, surface water half-lives of 21 to 118 hr have been estimated for photolysis of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) (Podoll, Jaber, and Mill 1986). In a CDF, photolysis would be expected to be of little significance since light cannot penetrate dredged material.

Exceptions may be photochemical reactions in ponded water and on frequently tilled dredged material. (Dredged material tilling is not a common practice in the United States.) Photolysis in the vapor state, that is after volatilization, is potentially more significant than photolysis in the aqueous phase. The half-life of TCDD in the vapor state has been estimated to be as low as 58 min (Podoll, Jaber, and Mill 1986).

Self-Weight Consolidation/Desiccation

Self-weight consolidation is compression of dredged material under its own weight. During self-weight consolidation, bulk density increases and the void ratio and hydraulic conductivity decrease. Since the solid particles do not compress, reduction in void ratio involves release of water from the pores in the dredged material. The direction of water movement is governed by pore pressure gradients as influenced by hydraulic conductivities. Water usually moves upward into the negative pore pressure zone of the desiccated crust, if present. If the pressure is lower in the underlying materials than in the consolidating layer due to the presence of drainage material such as sand, water will tend to move down.

During desiccation of the surface layer, negative pore pressures develop which cause fine-grain dredged material to shrink. A hard crust can form that has low hydraulic conductivity, low evaporative rates for water, and low volatilization rates for organic chemicals. The crust also acts as overburden and generates excess pore pressures in the lower saturated material, increasing hydraulic gradients. When new dredged material is placed on top of previously desiccated material, an overconsolidated interior sublayer remains which does not behave as the normally consolidating material above and below. The desiccated and overconsolidated material will initially behave as a semipermeable drainage boundary that resists downward movement of water.

The bottom boundary of consolidating dredged material in a CDF can sometimes be compressed to the point that the layer is an effective liner. Figure 3 shows the relationships between void ratio and effective stress and hydraulic conductivity and void ratio for three dredged materials. At the minimum void ratio (about 2) achieved at about 95 percent of ultimate consolidation, hydraulic conductivities are on the order of 10^{-8} cm/sec for clay material. The time needed to achieve 95 percent of ultimate consolidation is about 1 year for a drainage length up to 1 meter (Cargill 1985). For CDFs that are permanently maintained, self-weight consolidation can be very effective in controlling leaching losses.

Relative Significance of Biodegradation

When the naturally occurring rate of contaminant biodegradation is faster than the rate of contaminant migration, natural bioremediation can provide significant treatment. The relative rates of natural bioremediation and contaminant migration depend on types and concentrations of contaminants, the

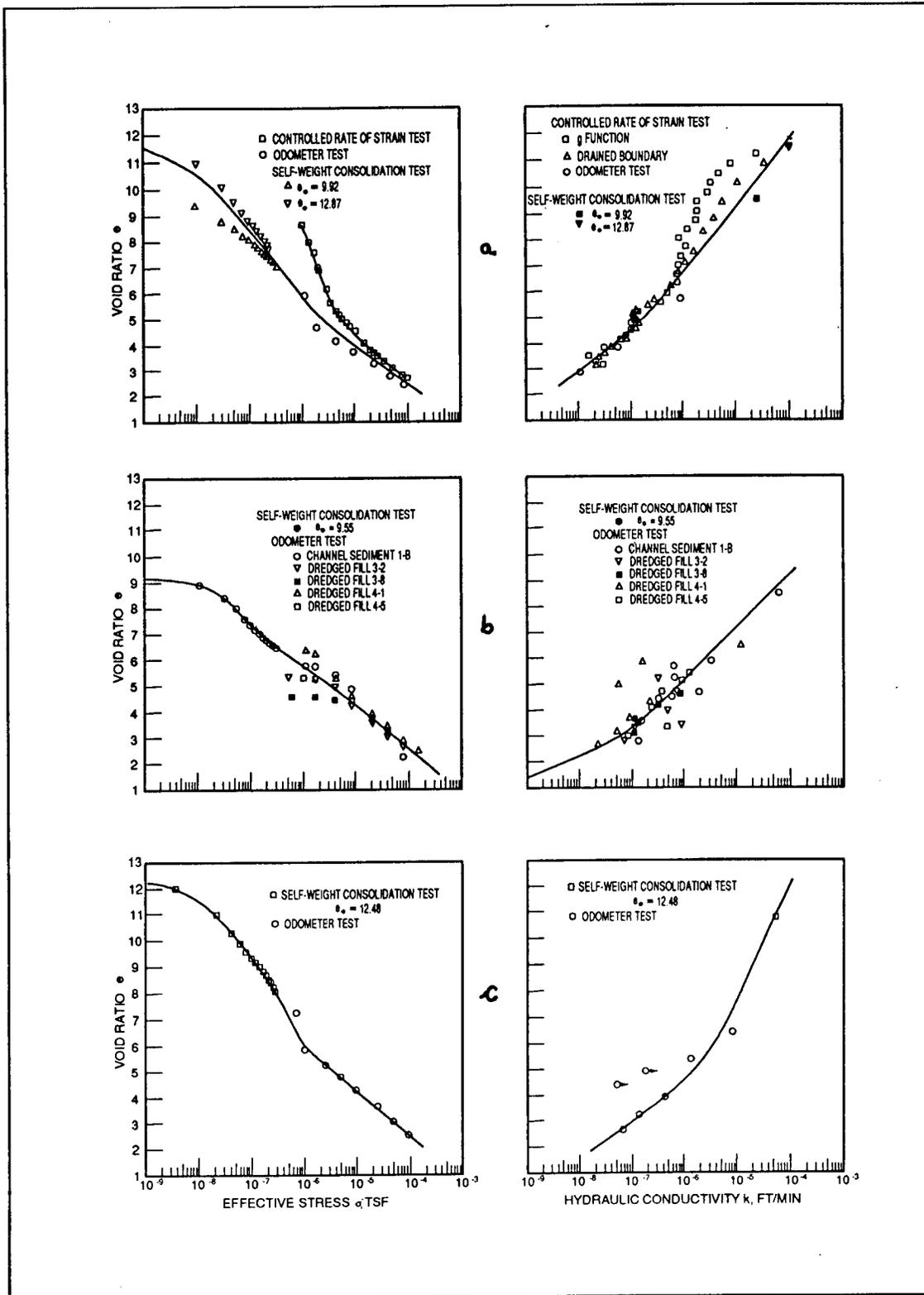


Figure 3. Stress, void ratio, and hydraulic conductivity relationships in three dredged materials: (a) Canaveral Harbor, Florida, (b) Craney Island, Virginia, and (c) Drum Island, South Carolina (from Cargill 1985)

microbial community, CDF design and operation, and various other site-specific conditions.

To illustrate the potential for natural bioremediation, a simple analysis of the contaminant loss due to biodegradation and leaching is provided as follows:

$$F_L = 1 - e^{\left(\frac{-vt}{LR}\right)}$$

$$F_B = 1 - e^{(-K_b t)}$$

where

F_L = fraction of initial contaminant mass lost due to leaching

v = average seepage velocity, m/day

t = time, day

L = dredged material thickness, m

R = retardation coefficient, dimensionless

$$= \rho_b K_d / n$$

ρ_b = bulk density, kg/L

K_d = equilibrium distribution coefficient, L/kg

$$= 0.411 f_{oc} K_{ow} \text{ (Karickhoff, Brown, and Scott 1979)}$$

n = porosity, dimensionless

f_{oc} = fraction organic carbon, dimensionless

K_{ow} = octanol-water partitioning coefficient, L/kg

F_B = fraction of initial contaminant mass lost due to biodegradation

K_b = overall first-order biodegradation constant, day⁻¹

The above process relationships are not coupled, that is, the expression for F_L assumes leaching to be the only removal process, and similarly the expression for F_B assumes biodegradation to be the only removal process. From these relationships, times required for half of the initial contaminant mass to be removed either by leaching or biodegradation (but not both) can be estimated as follows:

$$t_{\frac{1}{2},L} = \frac{0.69 L R}{v}$$

$$t_{\frac{1}{2},B} = \frac{0.69}{K_b}$$

where

$t_{1/2,L}$ = time required for leaching to remove one-half of the contaminant mass initially present

$t_{1/2,B}$ = time required for biodegradation to remove one-half of the contaminant mass initially present

Table 1 shows times required for half of the initial mass of fluoranthene (a PAH), TCDD, and hexachlorobiphenyl to disappear by leaching only and anaerobic biodegradation only. The calculations were made for $L = 10$ m, three seepage velocities, and a range of octanol-water partitioning coefficients. Anaerobic biodegradation half-lives in Table 1 are suggested values based on scientific judgment (Howard and others 1991). Data on anaerobic biodegradation of many toxic organics are so sparse that biokinetic constants and half-lives are not usually available. Table 1 shows that for even very slow anaerobic degradation rates, biodegradation can be significant for CDFs that must be maintained into perpetuity. As shown in Table 1, the potential significance of anaerobic biodegradation versus leaching is substantial. Anaerobic biodegradation could be 1,000 to 100,000 times faster than leaching, depending on the chemical considered and seepage velocity.

Table 1. Leaching Versus Anaerobic Degradation					
Chemical	Anaerobic Biodegradation Half-Life ¹ (thousands of years)	Octanol-Water Partitioning Coefficient, ² $\log K_{ow}$ (L/kg)	Retardation Factor, ³ R , dimensionless	Seepage Velocity, v (cm/sec)	Half-Life for Leaching (thousands of years)
Fluoranthene	0.005 - 0.48	4.70 - 650	648 - 41,000	10^{-5}	1.4 - 89
				10^{-6}	14 - 890
				10^{-7}	142 - 8,900
TCDD	0.01 - 1	5.38 - 7.70	3,100 - 647,000	10^{-5}	6.8 - 1,400
				10^{-6}	68 - 14,000
				10^{-7}	678 - 140,000
PCB (Hexachlorobiphenyl)		6.70 - 6.80	64,000 - 81,000	10^{-5}	142 - 180
				10^{-6}	1,420 - 1,800
				10^{-7}	14,200 - 18,000

¹ Minimum biodegradation half-lives for fluoranthene and TCDD are best-judgment estimates suggested by Howard and others (1991) for anaerobic biodegradation of these chemicals. Maximum values were obtained by multiplying the minimum values by 100. Anaerobic biodegradation half-lives for hexachlorobiphenyl are not available.

² Mackay, Shiu, and Ma (1992a, 1992b).

³ Retardation factors were calculated using bulk density = 1.1 kg/L, fraction organic carbon = 0.02, and porosity = 0.7.

The simple half-life comparison method discussed above is useful for generating planning-level approximations, but is a gross simplification of the complex phenomena affecting leaching and biodegradation. Site-specific factors, such as heterogeneities in dredged material properties and inhibitory conditions such as low pH, could reduce the relative significance of anaerobic biodegradation. Though many site-specific factors potentially alter the relative

significance of biodegradation, factors of 1,000 to 100,000 are large enough to indicate significant potential for field biodegradation rates to exceed leaching rates.

In Situ Natural Treatment Engineering

Districts choosing to approach CDF design, operation, and management as natural process treatment facilities will have to use sound scientific and engineering judgment since specific guidelines are not available. The potential exists, however, to design, operate, and manage CDFs to achieve the following:

- Self-cleaning on the surface.
- Self-sealing on the bottom.

It may also be possible to recover storage capacity through reclamation of cleaned dredged material.

Fully meeting these objectives may require operation and management of CDFs to enhance natural treatment processing of dredged material. Some of the techniques used in land treatment of wastes may be applicable to enhancing natural process rates in CDFs (Ferdinandy-van Vierken 1995). Land treatment techniques include tilling (reduces mass transfer limitations on oxygen availability and volatile emissions), liming for pH adjustment, nutrient and alternative electron acceptor addition, and water budget management (control of oxidation-reduction potential and volatile emissions). The unique nature of CDFs, for which in situ natural treatment may be particularly applicable, makes consideration of land treatment techniques warranted.

Summary

A myriad of natural processes that deplete organic contaminants are potentially active in CDFs. Natural surface-cleaning processes include aerobic biodegradation, volatilization, runoff, and photolysis. Anaerobic biodegradation and leaching are solids-cleaning processes that may be important in the saturated zone of CDFs. Self-weight consolidation is an important process that reduces leaching potential.

Engineering of CDFs (design, construction, operation, and management) to achieve in situ natural processing of contaminants is a promising concept. However, before full-scale, natural processes remediation of contaminated dredged material in CDFs can become engineering practice, a number of hurdles must be overcome. Some of the major hurdles include:

- Demonstrated effectiveness in spite of significant chemical heterogeneity in contaminated sediments.
- Development of design, operation, and management guidelines.
- Development of beneficial uses for decontaminated dredged material.

- Acceptance by regulatory agencies and the public.

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Environmental Effects of Dredging Technical Notes



Vertical Strip Drains to Increase Storage Capacity of Confined Dredged Material Disposal Facilities

Purpose

This technical note describes the use of vertical strip drains for improved management of confined dredged material disposal areas.

Background

Fine-grained dredged material usually enters a confined disposal facility (CDF) in a slurry consisting of 10 to 25 percent soil particles (i.e., 440 > water content > 110 percent). After the slurry spreads over the CDF, the fine-grained material starts undergoing sedimentation. At some point in the sedimentation process, the soil particles begin touching each other and, eventually, a continuous soil matrix is created. From this condition, the settlement of the surface of the matrix is determined by the densification of the soil matrix. Densification is governed by a process called primary consolidation. At the start of primary consolidation, the soil matrix is extremely soft and usually has a void ratio of 10 to 20 and a saturated unit weight of 10.2 to 11.8 kN/m³ (65 to 75 pounds per cubic foot).

Excess pore water pressures are induced in the soil matrix by the weight of overlying dredged material creating pressures in excess of the hydrostatic water pressures. The primary consolidation process through which excess pore water pressures are dissipated involves forcing water from the soil matrix. Once the excess pore water pressures have dissipated and consolidation is completed, a hydrostatic condition is established in which no further flow or primary consolidation occurs.

Relationships describing the one-dimensional consolidation process, as developed by Terzaghi (Terzaghi and Peck 1967), show that the rate of consolidation

(rate of settlement of the surface of the soil matrix) is a function of the ratio C_v/H_{dr}^2 , where C_v is the coefficient of consolidation and H_{dr} is the length of drainage path. The total amount of consolidation (settlement of the surface) that a soil mass can experience is a constant; however, the rate of consolidation can be increased by increasing the value of C_v or by decreasing the length of the drainage path. Suffice it here to state that decreasing the drainage path is much easier than increasing the value of C_v . Note also that if the length of drainage path is halved, for example, the rate of consolidation is increased by a factor of four. The main objective of installing vertical strip drains in a confined dredged material management area is to reduce the length of the drainage path.

As pore water is expelled from the soil matrix, the volume of the matrix decreases, causing a settlement of the surface and thereby increasing the storage capacity and soil shear strength, both desired effects. The main purpose of installing vertical strip drains in a confined dredged material management area is to reduce the length of the drainage path, thereby accelerating the primary consolidation process.

Additional Information

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Introduction

In the last 5 to 10 years, vertical strip drains have replaced conventional sand drains as the preferred method to accelerate the consolidation of soft cohesive soils. Most strip drains are modeled after the cardboard strip drain developed by Kjellman (1948). Strip drains are band-shaped and have a rectangular cross section approximately 100 mm wide and 4 to 5 mm thick. A plastic core with grooves, studs, or channels is surrounded by a filter fabric. The filter fabric is most commonly a nonwoven geotextile that prevents soil particles from entering and clogging the core. The core carries expelled pore water to the dredge fill surface or underlying drainage layer.

Vertical strip drains have been used in many projects throughout the United States to accelerate consolidation of soft cohesive soils, including the recent expansion of the Port of Los Angeles (Jacob, Thevanayagam, and Kavazanjan 1994), the Seagirt project in Baltimore Harbor (Koerner, Fowler, and Lawrence 1986), the construction of dredged material containment areas in the Delaware River near Wilmington, DE (Koerner and Fritzinger 1988, Fritzinger 1990), and the New Bedford Superfund site near New Bedford, MA (Schimelfenyg, Fowler, and Leshchinsky 1990).

Strip drains arrive at the site in large rolls and are installed using a hollow mandrel (Figure 1). The end of the strip drain is threaded down the inside of the mandrel, which must be as long as the depth to which the strip drains are to be installed. At the bottom of the mandrel, the strip drain is threaded through a baseplate and inserted into the mandrel (Figure 2). The baseplate is used to keep the strip drain at the bottom of the mandrel (to prevent soil from entering the mandrel during the insertion process) and to keep the strip drain

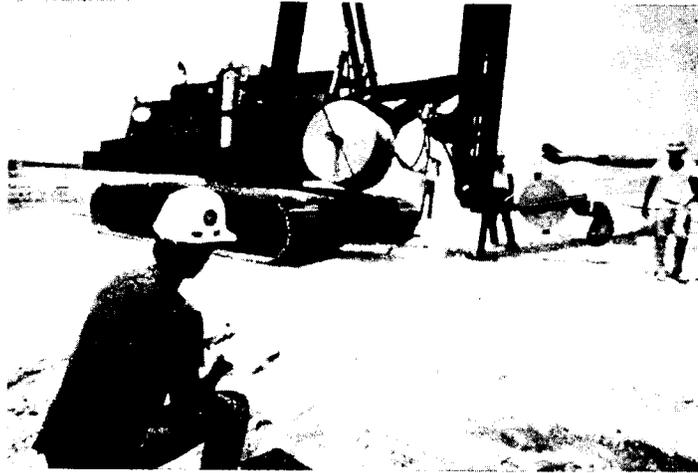


Figure 1. Typical vertical strip drain installation equipment



Figure 2. Vertical strip drain installation procedure

at the desired depth as the mandrel is withdrawn. When the mandrel is withdrawn from the ground, the strip drain is cut, and the process is repeated at the next location. This insertion cycle is rapid (1 to 3 min) and only the strip drains, baseplates, and a cutting tool are required.

Use of Vertical Strip Drains at Craney Island Dredged Material Management Area

The Craney Island Dredged Material Management Area (CIDMMA) is a confined disposal facility (approximately 8.9 km²) located near Norfolk, VA. Dredged material has been placed in the management area almost continuously since construction of the original dikes was completed in 1957. The facility was initially designed to store $76.4 \times 10^6 \text{ m}^3$ ($100 \times 10^6 \text{ yd}^3$), which at the time was thought adequate for a 20-year period of operation.

Increased dredging in the Norfolk channel has required the capacity of the CIDMMA to be increased by raising the dikes on three separate occasions. The dikes were raised from elevation +2.4 to 5.2 m mean low water (mlw) in 1969, to elevation +7.9 m mlw in 1980, and to elevation +10.4 m mlw in 1988. The final dike raising required the placement of an underwater stability berm (305 m wide) along the outer toe of the west perimeter dike and large dike setbacks along the north and east perimeter dikes to ensure stability of the perimeter dikes (Figure 3). The dike setbacks are usually 60 to 90 m, which results in approximately 0.08 to 0.12 km² of lost storage capacity during each dike raising.

Interior dikes were built within the CIDMMA to create three containment areas. This design improves sedimentation in the compartment being filled, while allowing the dredged materials in the other two compartments to desiccate and consolidate faster. The removal or evaporation of surface water accelerates the desiccation and increases the amount of consolidation because the effective density of the soil increases as the pore water evaporates. Construction of the interior dikes was completed in 1983. On the average, $3 \text{ to } 3.8 \times 10^6 \text{ m}^3$ of dredged material is placed in a compartment each year. Dredging results in a net increase in dredged fill thickness of 1 to 2 m per year in each compartment being filled.

After the dikes were raised for the third time, the U.S. Army Engineer Waterways Experiment Station (WES) conducted an extensive consolidation and desiccation analysis to predict the remaining service life of the CIDMMA (Palermo and Schaefer 1990). This study was conducted using the 1989 version of the microcomputer program entitled Primary Consolidation and Desiccation of Dredged Fill -PCDDF89 (Stark 1991) and revealed that the current capacity of the CIDMMA will be exhausted near the year 2000. Because the perimeter dikes are at their maximum height (as controlled by the stability of the foundation) and the CIDMMA cannot be expanded or replaced (based on a ruling by the Virginia State Legislature), new techniques were sought for increasing its storage capacity.

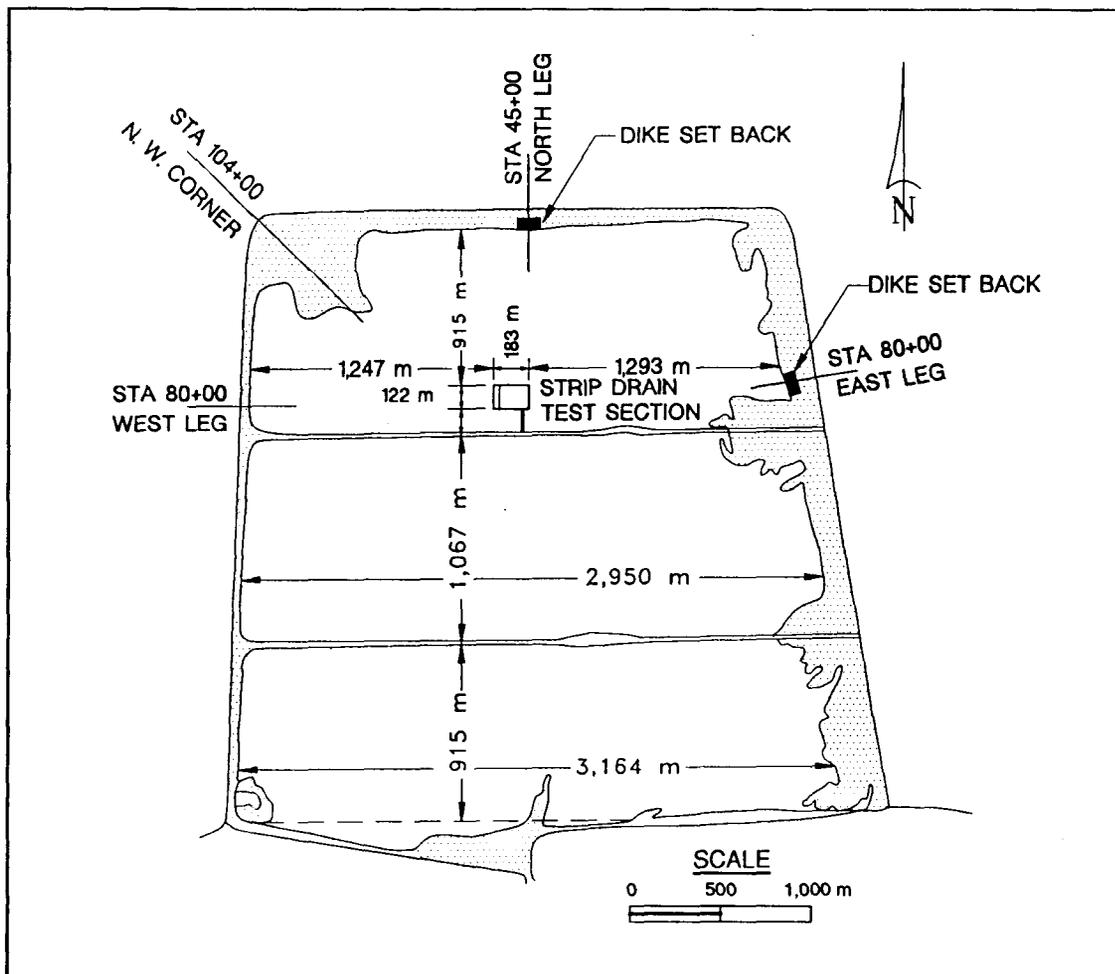


Figure 3. Plan view of Craney Island and location of vertical strip drain test section

Piezometers installed in the perimeter dikes at CIDMMA revealed that large excess pore water pressures exist in the underlying dredged fill and soft foundation clay. In February 1991 the excess pore water pressures in the foundation clay along the west perimeter dike typically exceeded the ground surface by 6 to 8 m. Although it was anticipated that excess pore water pressures also existed in the foundation clay underlying the dredged material inside the containment area, piezometers could not be installed to confirm their existence, because of the low shear strength of the dredged material.

Figure 4 shows the generalized subsurface profile at the location of the vertical strip drain test section at Craney Island (shown in Figure 3). The thickness of the dredged material and foundation soft marine clay is approximately 44 m. Therefore, the maximum vertical drainage path is approximately 22 m because the site is drained at the top and bottom of the deposit. Installation of vertical strip drains, as shown in Figure 5, will result in radial flow as well as vertical flow. As a result, the maximum drainage path will be reduced to one half the strip drain spacing instead of one half the compressible layer thickness. This

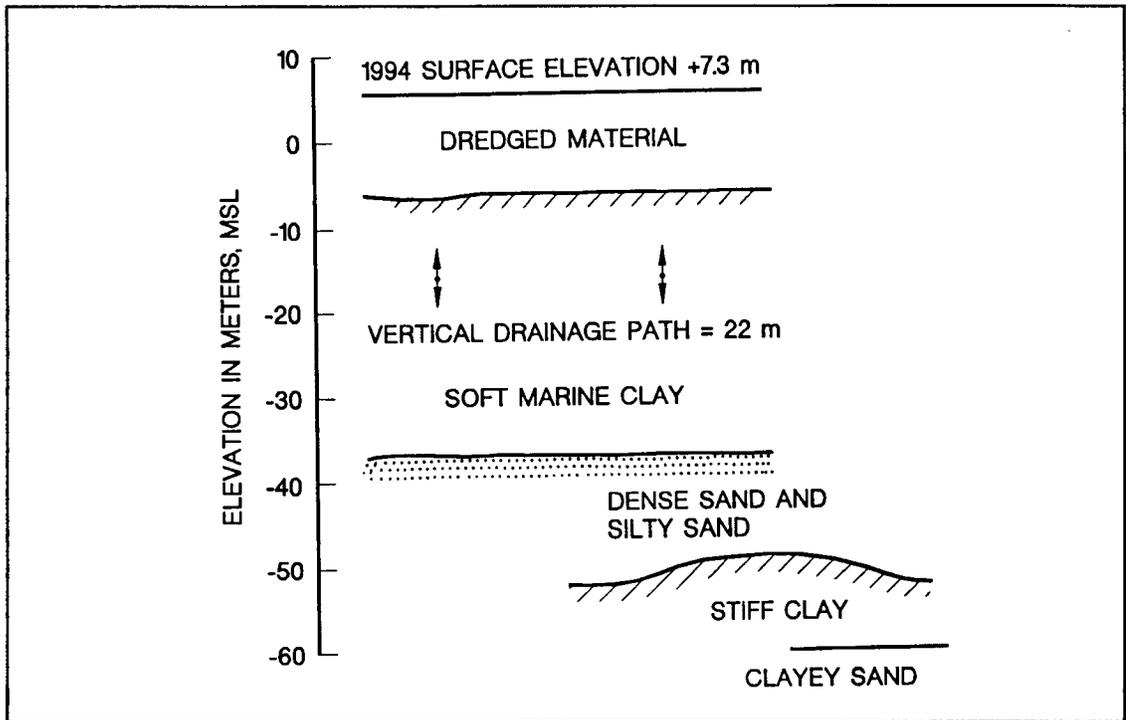


Figure 4. Generalized subsurface profile at the Craney Island vertical strip drain test section

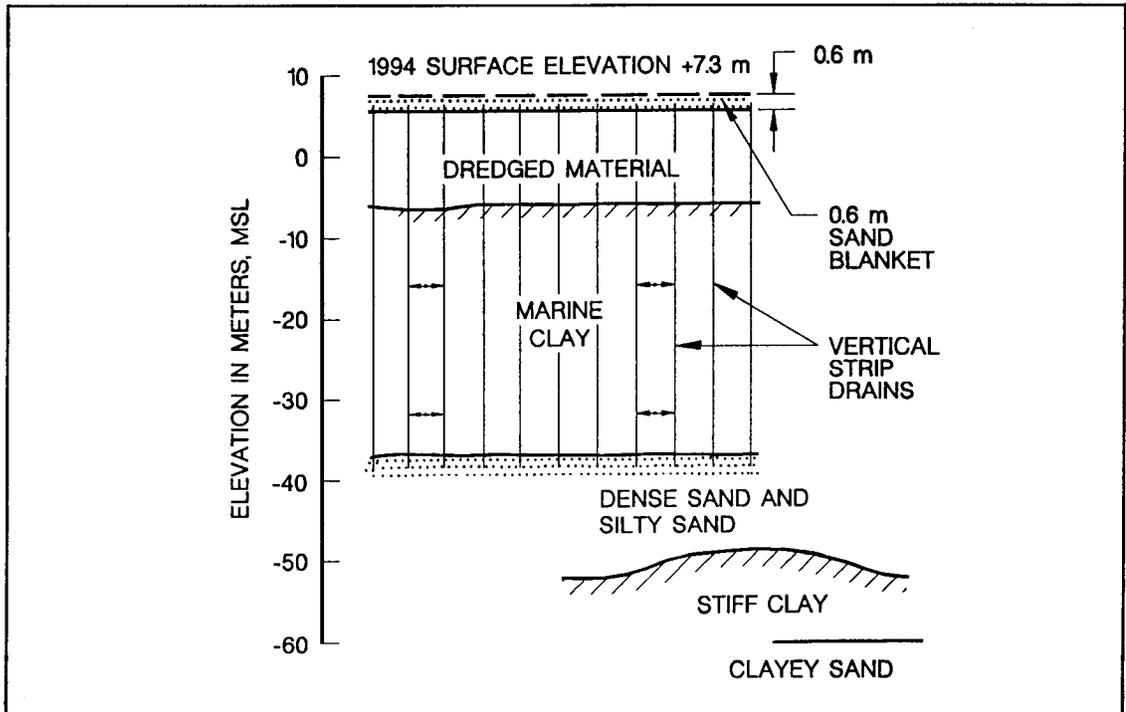


Figure 5. Radial drainage pattern using vertical strip drains

reduction is significant since the rate of consolidation is a function of the squared length of drainage path. The shorter drainage path will result in a substantial reduction in the time required to consolidate the dredged fill and underlying foundation clay.

The recommendation of strip drains to increase the consolidation rate at the CIDMMA was novel for several reasons: strip drains had never been installed in an active dredged material management area; a drain length of 47 to 49 m would be close to the longest drain ever installed (58 m), and the installation equipment could not exert a ground pressure greater than 10.4 kN/m². (Typical installation equipment (Figure 1) exerts a ground pressure of 27.6 to 34.5 kN/m², which could not be supported by the soft dredged material.) The installed cost of vertical strip drains in the test section was \$1.60 to \$2.00 per linear meter. The time required for consolidation of the dredged fill and foundation clay is controlled by the spacing of the drains. Therefore, value engineering can be used to determine the optimal spacing of the drains to produce a certain increase in surface settlement, that is, storage capacity, in a specified time.

Effectiveness of Vertical Strip Drain to Increase Consolidation Rates

A field test section was completed in the north compartment in February 1993 to evaluate the effectiveness of vertical strip drains to increase the consolidation rate of the dredged material and foundation clay. The test section was 122 by 183 m (Figure 3) and was divided into two sections. A 0.6-m-thick sand blanket was constructed in the main area (122 by 152 m). A sand blanket was not placed in the mobility test section (31 by 122 m, located on the west side of the test section). The mobility test section was used to determine if the low-ground pressure equipment could operate on the desiccated crust without a sand blanket.

Strip drains were pushed through the dredged fill and foundation clay into the underlying permeable foundation sands. This installation procedure allowed the expelled water to exit the strip drains at the dredged fill surface and into the underlying dense sand.

Settlement plate readings from the main section and mobility section are presented in Figures 6 and 7, respectively. Installation of the vertical strip drains in the test section was completed on February 19, 1993. As of April 6, 1995 (that is, after approximately 775 days), the maximum consolidation settlement in the test section was approximately 2.5 m. Without strip drains, the test section would have settled less than approximately 0.15 m. Therefore, the strip drains are responsible for the majority of the observed settlement. It should be noted that strip drains were installed in the northern portion of the test area first. As a result, the settlement plates in the northern part of the main test section (SP1, SP5, and SP7) show a faster response than the other settlement plates. For example, settlement plates SP1 and SP7 show a significant

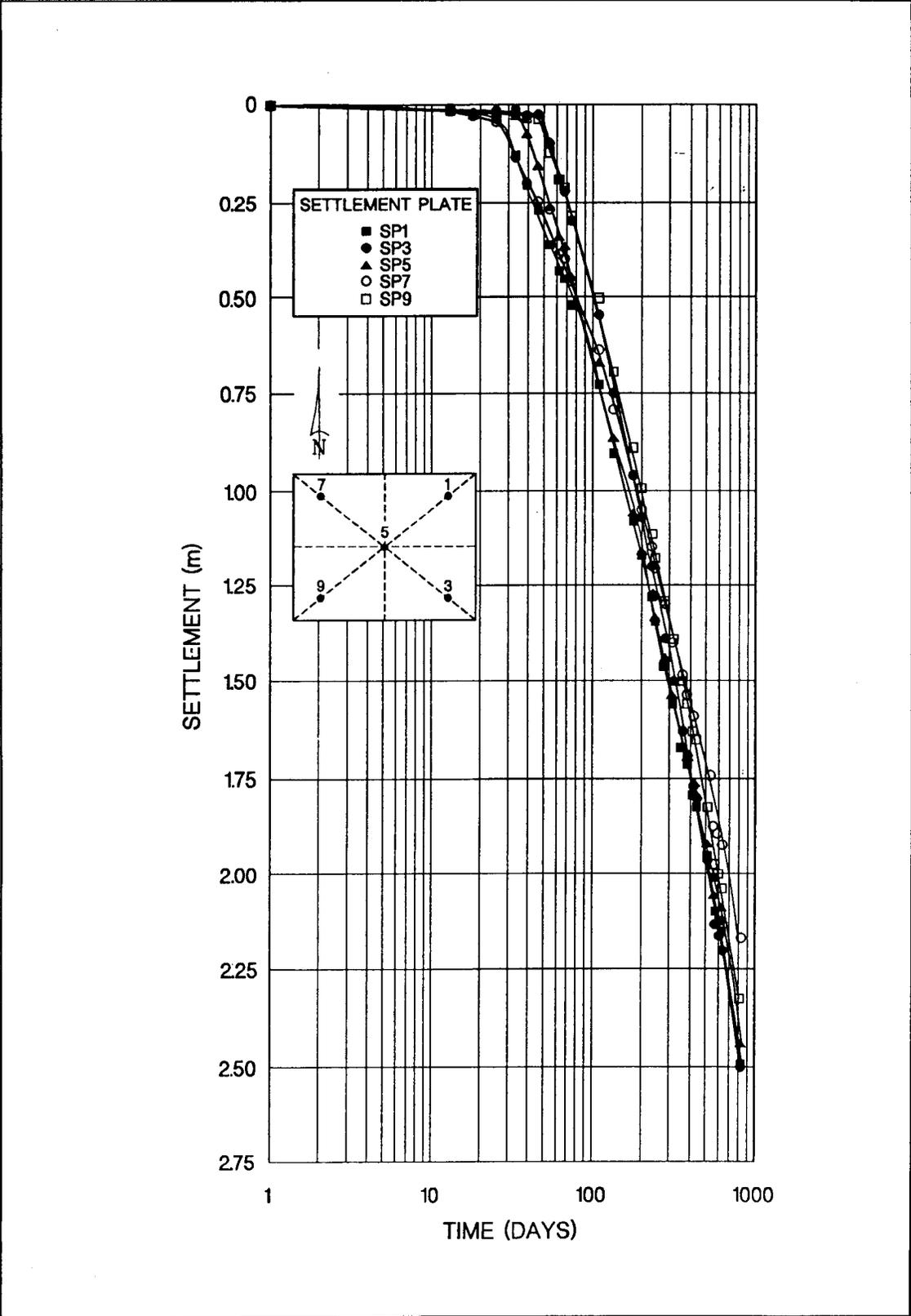


Figure 6. Semilogarithmic presentation of settlement plate measurements in main section

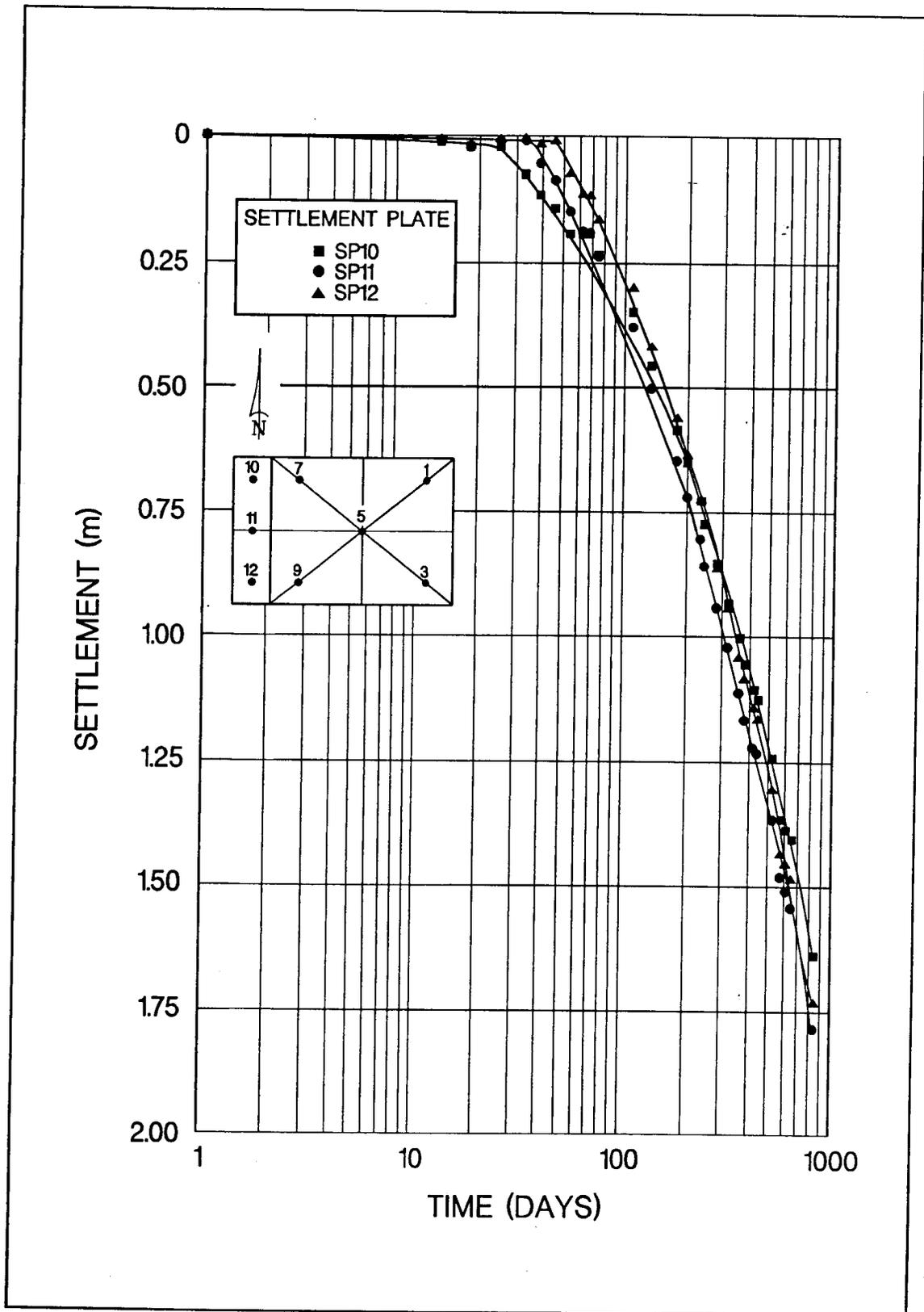


Figure 7. Semilogarithmic presentation of settlement plate measurements in mobility section

decrease in elevation after only 20 to 30 days. Conversely, settlement plates SP3 and SP9 did not show a significant decrease in elevation until 40 to 50 days after installation of strip drains began.

The end of primary consolidation is identified by a decrease in the slope of the settlement-time relationship. Therefore, as shown in Figures 6 and 7, none of the settlement plates indicates that the end of primary consolidation has been reached, and more settlement should occur in the future.

The mobility section was developed to demonstrate that a sand blanket is not required to support the strip drain installation equipment. A comparison of Figures 6 and 7 provides an insight into the effect of the sand blanket on consolidation of the dredged fill and marine clay. Settlement of plate SP10, located at the northern end of the adjacent mobility section, can be compared with settlement of plates SP1 and SP7 located at the northern end of the main section. Settlement plates SP1 and SP7 have settled 2.2 to 2.5 m, while settlement plate SP10 has settled approximately 1.6 m. Therefore, it can be concluded that the additional surcharge provided by the sand blanket results in a significant increase in consolidation settlement.

Future Research

A technical report describing the vertical strip drain test section, field measurements, and data analysis is being developed by WES. In addition, a micro-computer program that describes Primarily consolidation, Secondary compression, and Desiccation of Dredged Fill (PSDDF) is being completed by WES and the first author of this technical note. This computer program uses the finite strain consolidation theory, a secondary compression model based on Mesri, Lo, and Feng (1994), and an empirical desiccation model. This program can be used to estimate the remaining service life of a facility, the effect of dredging operations on storage capacity, and the effectiveness of dewatering techniques. The finite strain consolidation model, PCDDF89, is being modified to incorporate radial flow to simulate the installation of vertical strip drains.

Conclusions

Using vertical strip drains to consolidate dredged fill and soft foundation soils will significantly increase the consolidation rate, resulting in a corresponding rapid increase in storage capacity and soil shear strength. The strength gain will allow perimeter dikes to be constructed to higher elevations without setbacks or stability berms.

The installation of vertical strip drains will reduce the height of existing management areas, possibly allowing a new management area to be constructed on top of the existing area. The installed strip drains also will accelerate consolidation of the existing dredged fill and foundation clay as new dredged material and perimeter dikes are placed. Strip drains have also been proposed to consolidate inactive management areas for future development.

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