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**TECHNICAL REPORT D-86-4** 

# DEVELOPMENT OF A MODIFIED ELUTRIATE TEST FOR ESTIMATING THE QUALITY OF EFFLUENT FROM CONFINED DREDGED MATERIAL DISPOSAL AREAS

by

Michael R. Palermo

**Environmental Laboratory** 

DEPARTMENT OF THE ARMY Waterways Experiment Station, Corps of Engineers PO Box 631, Vicksburg, Mississippi 39180-0631

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The quality of effluent discharged from confined dredged material disposal areas is an environmental concern when the sediments to be dredged are contaminated. This report describes the development of a modified elutriate test procedure for prediction of the quality of effluent from confined dredged material disposal areas. The test was developed to simulate the physicochemical conditions in confined disposal areas which would affect the release of

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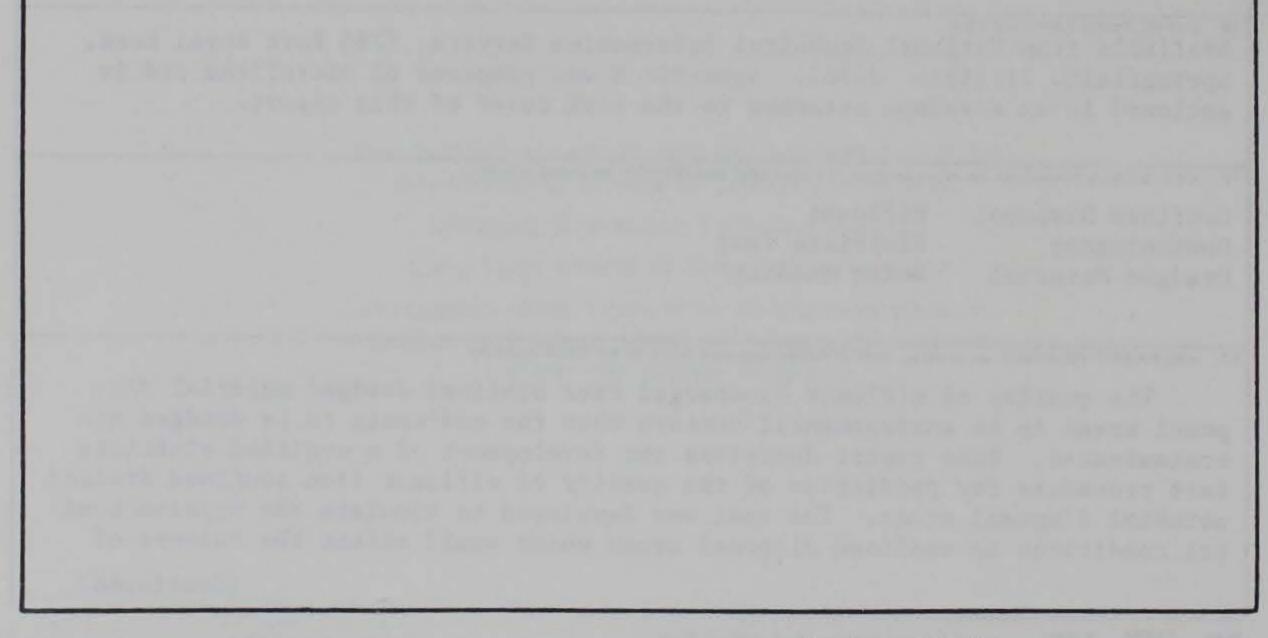
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20. ABSTRACT (Continued).

contaminants. The test development included experiments comparing suspended solids and particle grain-size distributions for test vessel selection. Factorial experiments were then conducted to select appropriate test factors for simulating the oxidizing conditions and retention times present in confined disposal areas. Limited field evaluations of effluent water quality were compared with the laboratory data. The test was found to adequately predict the dissolved concentration of contaminants and the fractions of contaminants associated with the suspended solids in the effluent.



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#### PREFACE

This work was conducted as part of the Long-Term Effects of Dredging Operations (LEDO) Program at the Environmental Laboratory (EL), US Army Engineer Waterways Experiment Station (WES), Vicksburg, Miss. The LEDO is sponsored by the Office, Chief of Engineers (OCE), US Army. This report was written as part of work unit 31775, Techniques for Predicting Effluent Quality of Diked Containment Areas. The OCE Technical Monitors were Drs. John Hall, William L. Klesch, and Robert Pierce and Mr. Charles W. Hummer.

The research was performed by Dr. Michael R. Palermo, Chief, Water Resources Engineering Group (WREG), of the Environmental Engineering Division (EED), EL. It served as a basis for his dissertation research. Guidance and technical review for this work were provided by the author's dissertation research committee: Drs. Edward L. Thackston, Frank L. Parker, Peter G. Hoadley, Antonis D. Koussis, and Horace E. Williams, all of Vanderbilt University, and Dr. Robert M. Engler, Ecosystem Research and Simulation Division, EL. Ms. Cheryl M. Lloyd, Ms. Kathy M. Smart, Dr. Paul R. Schroeder, and Mr. Anthony C. Gibson, all of WREG, provided technical assistance. The report was edited by Ms. Joyce H. Walker and Ms. Jamie W. Leach of the WES Information Products Division.

The work was performed under the general supervision of Dr. Raymond L. Montgomery, Chief, EED, and Dr. John Harrison, Chief, EL. Managers of LEDO within EL's Environmental Effects of Dredging Programs were Mr. Charles C. Calhoun, Jr., and Dr. Engler. Mr. Robert L. Lazor was the LEDO Coordinator.

COL Allen F. Grum, USA, was the previous Director of WES. COL Dwayne G. Lee, CE, is the present Commander and Director. Dr. Robert W. Whalin is Technical Director.

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Prediction of Effluent Quality . . . . APPENDIX B: DATA PLOTS FROM FACTORIAL EXPERIMENTS\* Page

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Appendix B was prepared on microfiche and is enclosed in an envelope \* attached to the back cover of this report.

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## CONVERSION FACTORS, NON-SI TO SI (METRIC) UNITS OF MEASUREMENT

Non-SI units of measurement can be converted to SI (metric) units as follows:

Multiply	By	To Obtain
acres	4,046.873	square metres
cubic yards	0.7645549	cubic metres
feet	3.785412	cubic decimetres
gallons	0.3048	metres
inches	2.54	centimetres
miles (US nautical)	1.852	kilometres
pounds (mass)	0.4535924	kilograms
tons (mass)	9,764.856	kilograms

## DEVELOPMENT OF A MODIFIED ELUTRIATE TEST FOR ESTIMATING THE QUALITY OF EFFLUENT FROM CONFINED DREDGED MATERIAL DISPOSAL AREAS

PART I: INTRODUCTION

## Background

1. Confined dredged material disposal has increased in recent years, primarily because of environmental constraints on open-water disposal of sediments classified as polluted. Release of contaminants in the effluent from confined disposal areas\* is dependent upon a number of physical and geochemical characteristics of the confined disposal process and of the dredged material. Guidance has been developed to predict contaminant release for proposed discharge of dredged material in open water (Engler 1980), but, prior to this study, no comparative guidance or procedures had been developed to predict contaminant levels in effluents from confined disposal operations.

2. The effluent from confined disposal sites that returns to waters of the United States is considered as a dredged material discharge under Section 404 of the Clean Water Act. The environmental impact of confined disposal of contaminated dredged material may be more severe than open-water discharge (Jones and Lee 1978; Gambrell, Khalid, and Patrick 1978). Water quality effects of effluents discharged from confined disposal areas have been identified as one of the greatest deficiencies in knowledge of the environmental impact of dredged material disposal (Jones and Lee 1978).

### Description of the Problem

3. Confined disposal areas are used to retain dredged material solids, while in most cases allowing the carrier water to be released from the disposal area. The two objectives inherent in the design and operation of a confined disposal area are: (a) to provide adequate solids storage capacity

\* The terms confined disposal area, confined disposal site, diked disposal area, containment area, and confined disposal facility are used interchangeably in the literature. to meet long-term dredging requirements, and (b) to attain the highest possible efficiency in retaining solids during the dredging operation in order to meet effluent suspended solids requirements. These considerations are basically interrelated and depend upon effective design, operation, and management of the disposal area.

4. Figure 1 shows the supernatant water interactions in an active confined disposal area. Dredged material placed in a confined disposal area undergoes sedimentation, resulting in a "thickened" deposit of settled material overlain by the clarified supernatant, which is usually discharged. The effluent may contain both dissolved and particle-associated contaminants. A large majority of the total concentration of contaminants is particle associated.

5. Release of supernatant waters from confined disposal areas occurs after a retention time ranging from hours to weeks. Procedures have been developed to predict total concentrations of suspended solids in the disposal area effluents, taking into account the settling behavior of the sediment in question and the design and operation of the area (Montgomery 1979). However, the physical behavior of fine suspended particles within the supernatant waters of confined disposal sites was largely not questioned prior to this study.

6. Several factors influence the concentration of suspended particles

present in supernatant waters, as shown in Figure 1. A dredged material slurry enters the ponded water as a density flow. Fine particles remain suspended in the disposal area water column at the point of entry due to turbulence and mixing. The suspended particles are partially removed from the water column by sedimentation. However, some of the settled particles reenter the water column because of the upward flow of water through the slurry mass during compaction (or thickening). Wind and/or surface wave action may also resuspend settled particles. If carrier water is released during disposal, all solids cannot be retained, and adsorbed and associated contaminants are transported with the particles in the effluent to the receiving water.

7. Prior to this study, no reliable method existed for the prediction of the concentration of contaminants in disposal area effluents during confined disposal operations. Such methods are required so that environmental impacts resulting from confined disposal operations may be properly assessed and evaluated prior to the dredging operation or permitting process.

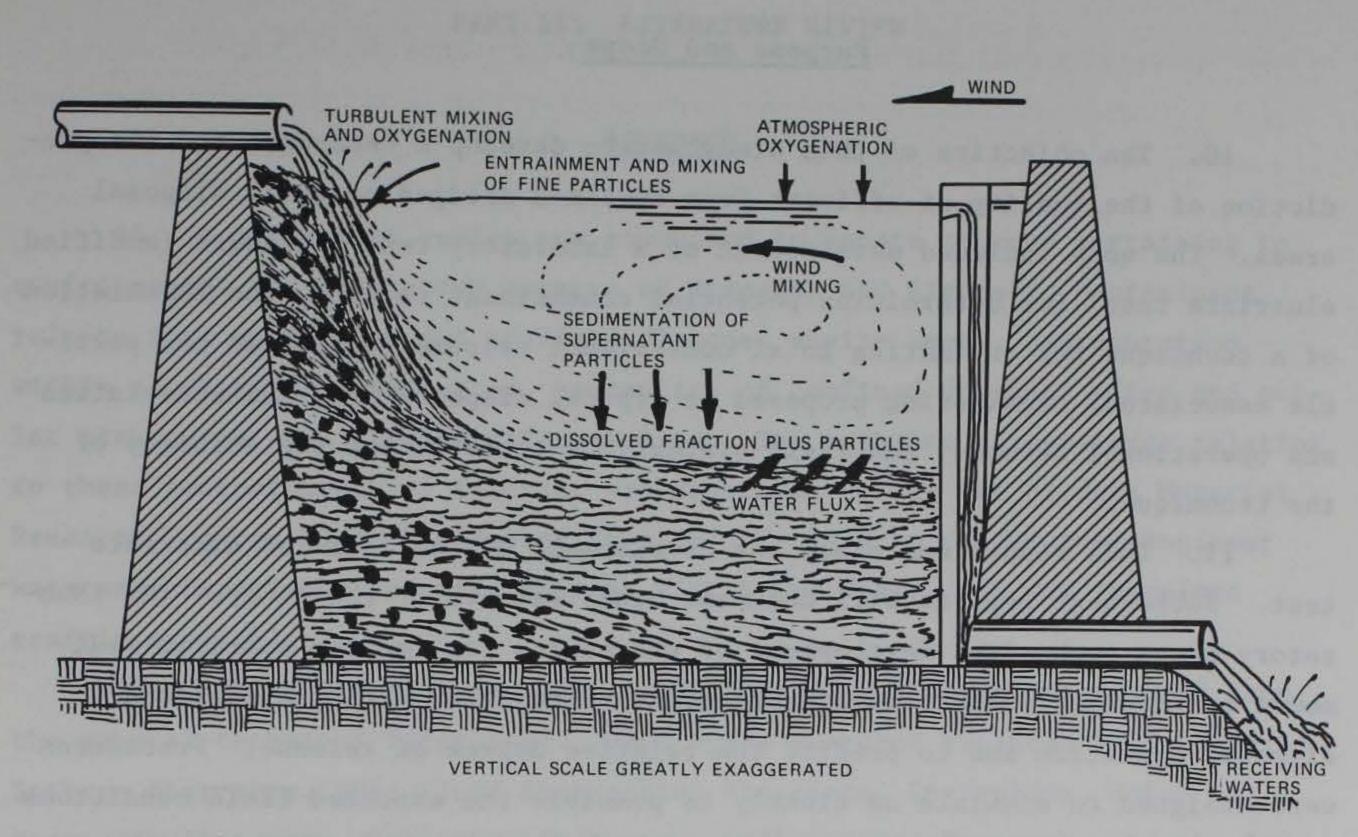


Figure 1. Schematic of ponded water interaction in an active confined disposal site

8. Several case studies involving confined disposal of highly contaminated sediments highlighted the need to predict concentrations of contaminants in effluents. Confined disposal operations connected with polychlorinated biphenyl (PCB) recovery on the Duwamish Waterway were closely monitored by the Environment Protection Agency (EPA) (Blazevich et al. 1977). For this case, the standard elutriate test failed to adequately predict PCB concentrations in the effluent discharged from a primary containment area. Since that time, several other cases have been proposed in which highly contaminated sediments will be placed in confined disposal areas (e.g., James River sediments containing kepone, mercury-contaminated sediments from Minamata Bay, Japan (Ishikawa and Yoshikazu 1980), and Superfund cleanup sites which will involve dredging).

9. In addition, proposed revisions (EPA 1980a) to the Section 404 guidelines call for setting criteria for contaminants in return flows in cases where dredging is used as a reclamation technique for highly contaminated sediments. Yet, no procedure had been developed for evaluation of the design and operation of disposal areas to ensure that the agreed-upon contaminant criteria could be met.

#### Purpose and Scope

10. The objective of this study was to develop a technique for the prediction of the quality of effluent from confined dredged material disposal areas. The work included development of a laboratory test procedure (modified elutriate test) for determining potential contaminant release, the formulation of a technique for estimating total contaminant release (dissolved and particle associated) considering proposed or typical disposal area characteristics and operational methods, and field evaluations to determine the accuracy of the technique.

11. This report describes the development of the modified elutriate test. Subsequent reports will document other aspects of the study. The laboratory phase emphasized development of procedures for testing specific sediments to identify which contaminants might be released during a confined disposal operation and to predict the relative degree of release. Procedures were designed to simulate as closely as possible the expected field conditions in confined disposal sites such as retention time, type of sedimentation, pH, and oxidation-reduction conditions.

#### Intended Use of Results

12. The technique for prediction of contaminant concentrations in disposal area effluents and the associated laboratory test procedures will become an integral part of the Corps of Engineers' (CE) regulatory program under Section 404 of the Clean Water Act. An implementation manual for Section 404 permit evaluations is proposed by the EPA/CE Technical Committee on Criteria for Dredged and Fill Material. The procedures developed during this study will be included in subsequent revisions of the implementation manual. Use of the procedures in the manual will be required when proposed revisions to the Section 404 regulations (EPA 1980b) become final.

13. The procedures will then be used by Corps field offices and permit applicants in the evaluation of all Category 3 (apparently contaminated material placed in confined disposal sites) disposal activities. Considering the present policy regarding confinement of contaminated sediments, the use of the modified elutriate test procedure and predictive technique should become quite extensive.

### PART II: LITERATURE REVIEW

#### Approach

14. A literature review was conducted to locate sources pertaining to environmental and regulatory aspects of dredging and disposal, contaminant release into open-water and confined disposal environments, sedimentation within confined disposal sites, hydraulics of confined disposal sites and outlet structures, and site-specific studies. The majority of knowledge relating to these general areas of interest was developed during the Dredged Material Research Program (DMRP) conducted from 1973 to 1978 by the US Army Engineer Waterways Experiment Station (WES) at Vicksburg, Miss., and was therefore readily available.

15. A DIALOG search was also conducted to supplement the sources from the general technical literature. Data bases searched included NTIS, Aquatic Science Abstracts, BHRA Fluid Engineering Abstracts, Enviroline, Water Resources Abstracts, Pollution Abstracts, SSIE Current Research, and the Army Engineer Private File. This search produced over 400 literature citations, most of which were environmental impact statements, or WES reports and other reports already collected in the literature review. Only eight of the documents were found to add to the pertinent information already collected for the literature review. Key word lists used in the search were as follows:

## dredge

or dredging		containment	contaminant
	and	or confinement and	or water quality
		or confined	or effluent
		or dike	or pollutant
		or pond	or parameter
		or lagoon	or release
in property in		or upland	or environmental impact

## Overview of Confined Dredged Material Disposal

16. Approximately 300 million cu yd\* of material are removed annually from Federal navigation channels in order to maintain authorized depths. Much of this material is placed in aquatic disposal sites, used in wetlands creation or nourishment, or placed in unconfined disposal areas. Although no breakdown of these figures is routinely maintained, about 30 percent of the total maintenance volume, or 90 million cu yd, is placed in confined disposal areas annually. This figure would include the majority of the maintenance dredging for major ports along the Atlantic and gulf coasts, including harbors at Baltimore, Norfolk, Charleston, Savannah, Mobile, Galveston, and Houston, and numerous harbors on the Great Lakes. Much of the confined disposal is required because the maintenance dredging sediments are contaminated.

17. The above-mentioned volume does not include material from non-Federal projects. Therefore, the total volume of sediments subject to confined disposal is potentially much larger. Confined disposal has also been identified as the most feasible means of disposal for most lake restoration projects (Loar et al. 1980). The typical lake sediments dredged from such projects may be contaminated in much the same manner as sediments from navigation projects. Therefore, similar problems must be considered.

18. The recent advent of environmental awareness related to dredged material disposal was sparked by the passage of the National Environmental

Policy Act (NEPA). Great attention was paid to potential environmental problems caused by open-water disposal, and a trend toward placement of contaminated material in confined sites began, including major construction efforts on the Great Lakes (Cable and Murden 1974). Concern for the environmental impacts of the confined disposal alternative lagged that for open-water disposal. As detailed guidance for the evaluation of open-water effects was evolving in the 1970s, the primary emphasis of the study of confined disposal was placed on the engineering aspects of site design, operation, and management. Detailed guidance for these aspects resulted from the DMRP (Palermo, Montgomery, and Poindexter 1978).

\* The US customary units of measurement are used in lieu of metric (SI) units for those cases common in dredging practice. A table of factors for converting non-SI units of measurement to SI (metric) units is presented on page 6. 19. Only limited field studies and laboratory test evaluations of the quality of effluents from confined disposal sites have been published (Hoeppel, Myers, and Engler 1978; Windom 1973; and others), although it is a major concern. Confined disposal areas are often located in environmentally sensitive nearshore areas where effluents are likely to have a greater-than-normal impact (Lee and Plumb 1974, Engler 1982). Reliable procedures for the prediction of the quality of effluent from confined disposal areas are needed to permit disposal in an environmentally acceptable manner and to fulfill legislative mandate.

#### Regulatory Aspects

#### Historical perspective

20. Engler (1980) presented an excellent summary of the historical evolution of regulatory criteria and guidelines regarding disposal of dredged material. Prior to the late 1960s, the regulation of dredging activities was limited to the authority of the CE regarding obstruction of navigable waterways under the River and Harbor Act of 1899. In the late 1960s, the CE expanded its review authority to include environmental considerations, and the passage of NEPA in 1969 set the stage for an expanded regulatory role. Regulatory guidelines

21. Regulation of disposal activities has now developed into extensive

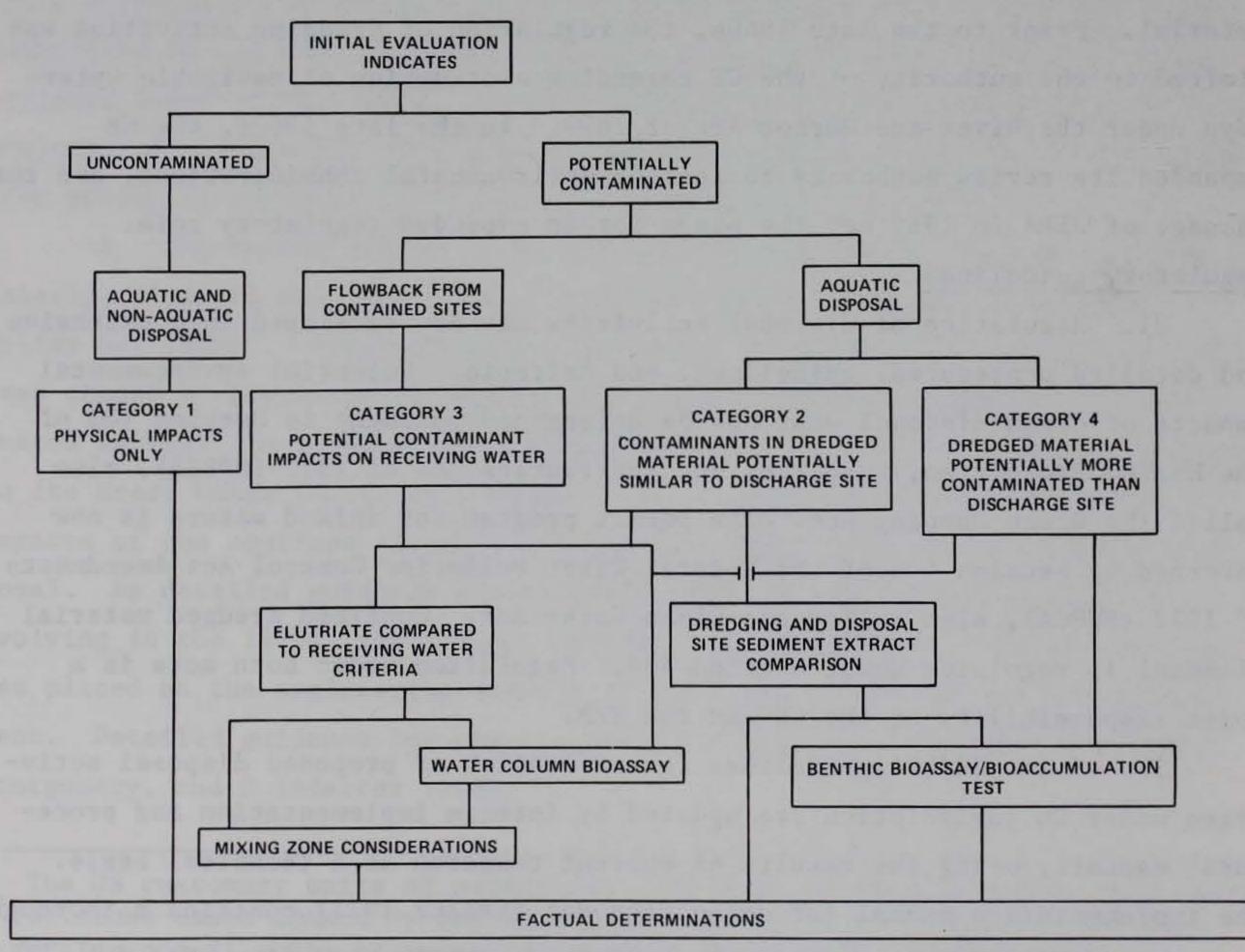
and detailed procedures, guidelines, and criteria. Potential environmental impacts of ocean disposal must now be determined pursuant to Section 103 of the Marine Protection, Research, and Sanctuaries Act of 1972 (MPRSA), also called the Ocean Dumping Act. The permit program for inland waters is now governed by Section 404 of the Federal Water Pollution Control Act Amendments of 1972 (FWPCA), also called the Clean Water Act. Confined dredged material disposal is regulated under Section 404. Regulation under both acts is a joint responsibility of the CE and the EPA.

22. Joint CE/EPA guidelines for evaluation of proposed disposal activities under CE jurisdiction are updated by interim implementation and procedural manuals, using the results of current research as a technical basis. The implementation manual for ocean disposal (EPA/CE 1977) contains a thorough explanation of sampling and testing procedures, while guidelines for Section 404 have been published only in interim form (Environmental Effects Laboratory (EEL) 1976). These guidelines are now overwhelmingly oriented toward evaluation of the effects of proposed open-water disposal. Short-term effects are estimated based on results of the well-known standard elutriate test (EEL 1976) and, in some instances, bioassays.

23. The EPA has published interim final guidelines for testing requirements under Section 404 (EPA 1975) and a revised guidelines and testing requirements package (EPA 1980a and 1980b) to reflect the 1977 Amendments to Section 404 of the Clean Water Act.

24. Proposed testing requirements (EPA 1980b) define dredged material according to four categories, as shown in Figure 2. Category 3 (see Figure 2) includes contained or confined disposal with "potential for contamination of the [receiving] water column only." These proposed testing requirements call

#### EVALUATION AND TESTING OF DREDGED MATERIAL SCHEMATIC REPRESENTATION OF TESTING CATEGORIES



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Figure 2. Section 404 testing flowchart (EPA 1980b)

for a "modified elutriate test" to evaluate short-term water column impacts of disposal area effluents. Specifically, the requirements are worded as follows:

> The potential for short-term water-column impacts is assessed in Category 3 by an elutriate test, or under the special circumstance described below, by a water-column bioassay. Generally, the appropriate test is a chemical comparison of the concentration of contaminants in the elutriate of the proposed dredged material with the concentration in the receiving water. These concentration values are then used with the appropriate water quality standards or criteria to calculate a mixing zone. Where retention time within the containment area will be of short duration, the standard elutriate test can be used to estimate the concentration of those contaminants that will be released in the effluent. Where the containment area is managed for maximum solids retention and, consequently, the liquid is retained for long periods, a modified elutriate test should be used, considering biological, chemical, and physical changes that may occur in the containment area. Settleability tests should be conducted to simulate the actual retention time (EPA 1980b).

The modified elutriate test mentioned in these guidelines was developed as a part of this study. The test was essential in the overall strategy for predicting contaminant concentrations in disposal area effluents. Water quality criteria

25. Predictions of the quality of the effluent may be used with appropriate water quality criteria to determine the required dimensions of a mixing zone necessary to dilute the concentrations of contaminants in the discharge to an acceptable level. Water quality <u>criteria</u> may be described as data concerning effects of a given contaminant concentration on a specific water use, such as for fish and other aquatic life, while water quality <u>standards</u> may be described as legal limits on such concentrations (Thackston 1978). The proposed Section 404 testing requirements (EPA 1980b) call for use of state water quality <u>standards</u> (Section 303 of the Clean Water Act) or, in their absence, EPA water quality criteria (EPA 1976 and 1980c).

26. The Federal water quality criteria as given by EPA (1976 and 1980c) are summarized for selected parameters in Table 1. These criteria are guidelines for the maximum concentrations in order to ensure protection of aquatic life in either the marine or freshwater environment.

27. It should be noted that the EPA criteria usually refer to concentrations in a total water sample, which would include suspended particles. The criteria for aquatic life often refer to the "total recoverable" concentration, which would also be obtained from the total water sample. This poses a serious problem where suspended soil mineral material will be analyzed as a pollutant and interpreted as the same when, in fact, this mineral fraction (containing numerous metals) has no environmental impact. Consequently, only the solution or liquid phase should be compared with water quality criteria or standards for a realistic assessment of potential for harm.

#### Revisions

28. Changes to the proposed Section 404 requirements have been recently drafted which do not specifically mention Federal water quality criteria.\* The chemical comparison protocol in the drafted change is as follows:

> Chemical analyses shall be conducted on the receiving water and on the elutriate of the dredged material. The location and number of sampling stations and replicates shall be designed specifically for the dredging and disposal sites. . .Test results shall be used to determine whether, after consideration of mixing, the discharge will substantively increase concentrations of those contaminants in solution at the disposal site.

#### State regulatory requirements

29. State standards are often more restrictive than Federal criteria. As an example, a water quality permit granted by the State of Florida (Florida Department of Environmental Regulation 1980) sets standards of 0.0004 mg/l

mercury and 0.06 mg/l copper at the point of effluent discharge (no mixing zone granted). State water quality standards were also required for other contaminants, allowing for a 50-ft mixing zone. The permit also required daily monitoring for turbidity and an initial effluent sample analysis for PCB and 15 metals.

#### Mixing zone

30. Mixing zone requirements may be used in making "factual determinations" regarding the acceptability of the discharge. EPA (1980b) describes the mixing zone determination as follows:

> The size of the mixing zone will be calculated for the contaminant requiring the greatest dilution volume as determined from the elutriate analyses, to meet applicable water quality standards or, if none, Federal water quality criteria

\* Memorandum, Office of Federal Activities, 11 January 1983, EPA, Washington, DC.

established by EPA. The selected standard or criteria shall define the perimeter of the mixing zone.

## The definition for a mixing zone is as follows (EPA 1980a):

The term 'mixing zone' means a limited volume of water serving as a zone of initial dilution in the immediate vicinity of a discharge point where receiving water quality may not meet quality standards or other requirements otherwise applicable to the receiving water.

A mixing zone may or may not be allowed by certain states administering the regulatory program. It should be noted that regulatory agencies usually specify a mixing zone in terms of an acceptable dimension in which the necessary dilution will be allowed to occur.

## Sediments and Contaminants

#### Contaminants of interest

31. Major classes of contaminants associated with some dredged material include heavy metals, nutrients, pesticides, petroleum hydrocarbons, and chlorinated hydrocarbons. There may also be natural background levels of metals far in excess of water quality standards or criteria. Gambrell, Khalid, and Patrick (1978) observed that most highly contaminated sediments will be contaminated with more than one toxic material because sediments in industrialized or urbanized harbor areas are exposed to contaminants from a variety of domestic, agricultural, and industrial sources. Therefore, evaluation of pollution potential must consider all contaminants present and the relative environmental threat of each. He stated that higher priority should be given to sediments believed to be contaminated with mercury, cadmium, and certain organics. On the other hand, sediments with high levels of nitrogen, phosphorus, and iron generally pose little environmental threat. Lead, copper, zinc, nickel, chromium, arsenic, manganese, and petroleum hydrocarbons can have variable environmental effect, depending on several factors. Sediment sampling and analysis

32. <u>Sampling</u>. Generalized procedures for sediment sampling and analysis were described by Plumb (1981). He discussed appropriate sampling locations; trade-offs between sample number, costs, and statistical reliability of results; and sources of error associated with sampling. Brannon et al. (1976) indicated that the largest source of variation between dredged material samples is the vertical and horizontal distribution of samples. Based on this fact, the Section 103 implementation manual recommends collection of a minimum of three samples within the area to be dredged.

33. General guidance on sample preservation for water or sediment samples was also presented by Plumb (1981). The Section 103 implementation manual specifies that all samples for use in the elutriate test should be collected and immediately stored at 4° C, and all samples should be processed within 2 weeks of sample collection. However, it has been shown (Michnowsky et al. 1982) that routine storage times for preserved samples may not be valid for water samples containing suspended particles. Michnowsky found that such samples were stable during the first week of storage, but showed significant changes between 7 and 100 days of storage. For this study, the samples obtained by laboratory extraction were filtered immediately prior to preservation to obtain subsamples for analysis of dissolved and total concentrations. The field samples were similarly processed and analyzed within a few days of collection.

34. <u>Analysis.</u> Plumb (1981) presented detailed procedures for the chemical analysis of sediment and water samples. The interim guidance for Section 404 (EEL 1976) also contains procedures for total or bulk sediment analysis. The Section 103 implementation manual contains an appendix for the step-by-step standard elutriate test procedure, and a second appendix presents

guidance on the chemical analysis of the liquid phase produced by the elutriate test. Guidance is given summarizing the appropriate chemical analyses procedures to be used in analysis of heavy metals and other constituents, and for pesticides and PCB materials.

35. The manual recommends the preparation and analysis of three replicates for reporting the liquid phase concentration of contaminants and recommends that all concentrations be reported in milligrams per litre. Much of this guidance is directly applicable to the analysis phase of the tests developed as a part of this study.

36. Analysis of sediment samples for physical and engineering properties is routinely performed. These analyses should be performed in accordance with standard soils testing procedures (Office, Chief of Engineers 1970). Bulk sediment criteria

37. Even though bulk sediment analysis is not considered a valid criterion for impact evaluation of a given dredged material discharge, it can be used as a general screening tool for determining an inventory or the presence or absence of specific contaminants. Bulk sediment analysis cannot be used to evaluate or establish cause and effect.

38. The EPA (1977) has established rough guidelines based on bulk analysis of Great Lakes sediments which can be used to classify a sediment as heavily polluted, moderately polluted, or nonpolluted. The guidelines are shown in Table 2. The EPA states that the use of these guidelines for roughly classifying a sediment should be based on a composite of all sample constituents, except in the case of PCBs or mercury. Engler (1980) has pointed out, however, that many of the concentrations listed in these criteria are exceeded by the average concentration of the elements in the earth's crust, rendering the EPA (1977) criteria virtually useless.

39. The EPA also offers general guidance on sediment quality based on field observation as follows:

- a. Color. The lighter the color, the cleaner the sediment.
- b. <u>Texture</u>. The finer the material, the more likely it is to be polluted.
- <u>c</u>. <u>Odor</u>. A lack of odor, a beach odor, or a fishy odor tends to denote clean sediment.
- d. <u>Detritus</u>. High detritus content usually denotes pollution from natural sources.
- e. Oil content. Samples showing visible oil are usually highly contaminated.

## Contaminant Mobility

## General

40. Factors which influence the mobility of contaminants in sediments (i.e. the movement of contaminants from one phase or species to another, e.g. from particle-associated to dissolved) include salinity, oxidation-reduction potential (Eh), hydrogen ion concentration (pH), and chemical composition of the interstitial water (Hoeppel, Myers, and Engler 1978; Gambrell, Khalid, and Patrick 1978).\* The physical properties of the sediment, including grain-size

\* Much of the pertinent literature up to 1978 concerning contaminant mobility in sediment-water systems and specifically in confined disposal areas was summarized or referenced by Hoeppel, Myers, and Engler (1978) and Gambrell, Khalid, and Patrick (1978). The detailed literature citations from these references are not given in this section for the sake of simplicity. distribution and clay mineralogy, are also major factors.

41. Both heavy metals and organics tend to have a greater affinity for clay and silt-size particles with high relative surface areas and negative surface charges (Dossis and Warren 1981; Gambrell, Khalid, and Patrick 1978). This same trend has been observed for available heavy metals in natural soils (Nair and Cottenie 1971).

42. Most of the discussion regarding contaminant mobility in this section refers to sediment or dredged material which is predominantly fine grained (i.e., silts and clays). With the exception of toxic spills, contaminants are rarely associated with coarse-grained sediments. It is apparent that, if a coarse-grained sediment containing high concentrations of a contaminant were dredged, relatively high release would occur in almost any disposal environment.

#### Sediment-water phases

43. Engler (1980 and 1982) identified several components, or phases, in the sediment-water system which are relevant to contaminant mobility. These include:

- <u>a</u>. <u>Interstitial water</u>. May be considered an integral part of the sediment prior to dredging and is at equilibrium with other phases. The interstitial water may frequently be enriched in chemical constituents, compared to overlying waters.
- b. <u>Mineral exchange phase</u>. That phase which can be removed from the cation exchange sites of the sediment using a standard ion-

exchange extractant, i.e., dilute acid.

- <u>c.</u> <u>Reducible phase</u>. Contains certain hydrous oxides or hydroxides of iron or manganese which are soluble under reducing (anaerobic) conditions but will precipitate under oxidizing (aerobic) conditions. Other metals may be bound with this phase as occlusions or coprecipitates under aerobic conditions.
- d. Organic phase. That phase which will be solubilized after destruction of organic matter. Elements may be either loosely bound or tightly bound in this phase.
- e. <u>Residual phase</u>. Solid particles of mineral which can only be solubilized in a total digestion, i.e., with hot acid.

A contaminant can be present in any of the above phases (partitioned), and therefore more or less susceptible to release under a given set of disposal conditions. For this reason, it was recognized by investigators in the early 1970s that the bulk concentration of a contaminant in a sediment is not indicative of the environmental availability of a contaminant (Keeley and Engler 1974, Lee and Plumb 1974). 44. Other terms can be used to describe various sediment-water phases. Skougstad et al. (1974) described laboratory extraction methods for watersuspended sediment mixtures to desorb and solubilize readily acid-soluble metals. They stated that if  $\geq$ 95 percent of the analyte to be determined is solubilized, the concentration should be reported as "total." If <95 percent is solubilized, the concentration should be reported as "total extractable." The "dissolved" phase of sediment-water or dredged material systems is commonly considered that phase which passes a 0.45-µm filter (Plumb 1981). Partitioning coefficients

45. Several investigators have used partitioning coefficients to express the relative concentrations of contaminants in various phases. Such coefficients may be calculated in a variety of ways. A general form of metal partitioning between aqueous and solid phases was proposed by O'Connor (1976) in which the fraction of metal associated with particles is inversely proportional to pH, but directly proportional to surface area available for adsorption (higher for small particle sizes) and to the stability of the reaction once it occurs.

## Typical sediment conditions prior to dredging

Stratification. Sediments normally encountered in highly industri-46. alized ports are generally fine grained, contain organic matter, and are anaerobic. However, a thin surface layer (approximately 1 cm) may become oxidized, resulting in the typical sediment profile shown in Figure 3. This stratified profile is sometimes clearly visible in sediment box cores. The thin oxidized layer is visually apparent as a yellowish-brown or reddish-brown layer which derives its color from precipitation of various oxidized iron compounds. Beneath this surface layer, microbial decomposition results in the formation of organic and inorganic sulfide compounds, an accumulation of ammonia nitrogen, orthophosphorus, and numerous reduced iron and manganese complexes. The lower layer is typically grey colored in older (new area dredging) sediments because of the presence of iron disulfide (pyrite), or is typically black for newer (old area maintenance dredging) sediments because of the presence of iron sulfide and other reduced iron complexes (Hoeppel, Myers, and Engler 1978).

47. <u>Sediment-water equilibrium</u>. Cycling of chemical constituents at the sediment-water interface under undisturbed conditions tends to favor

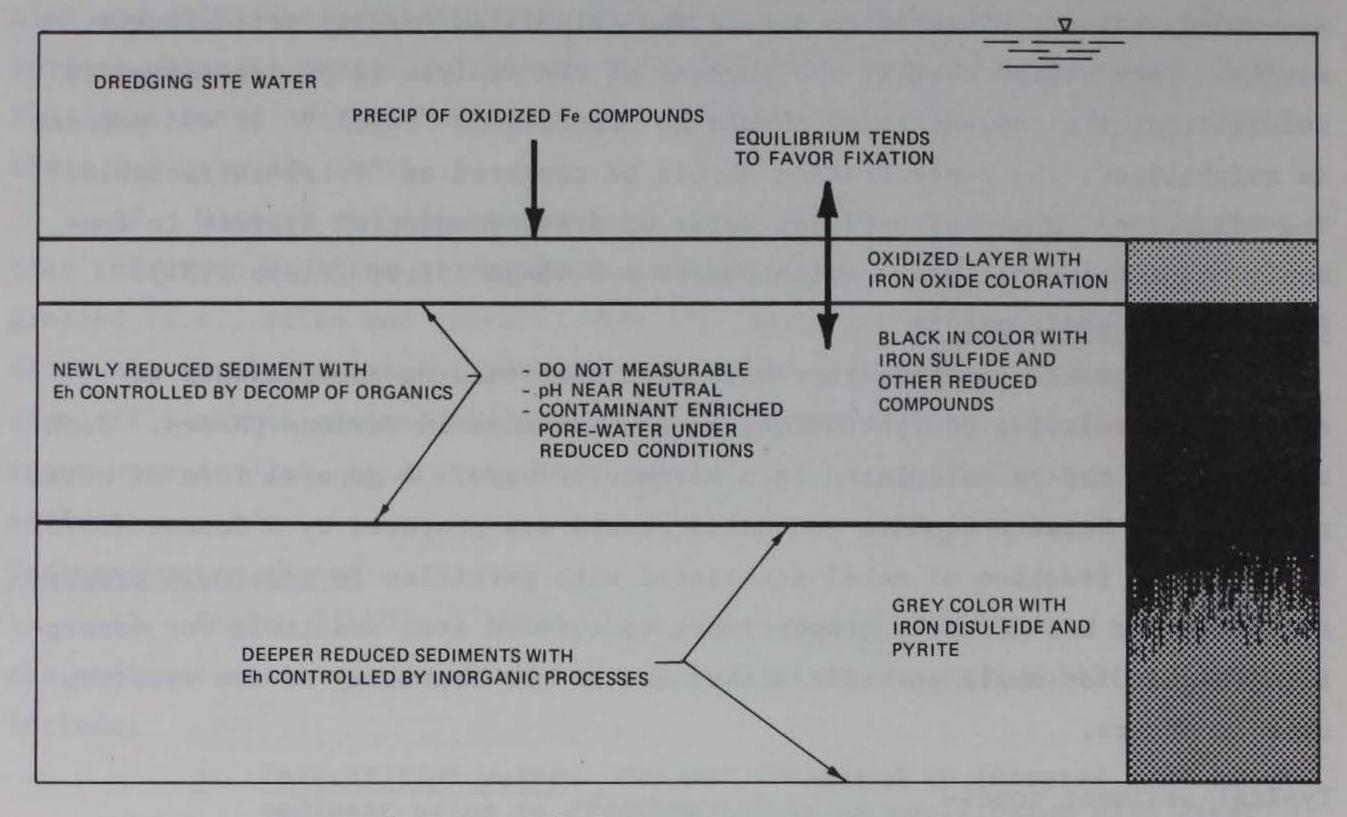


Figure 3. Typical fine-grained sediment profile

fixation in the sediment, leaving only trace concentrations in the water column (Hoeppel, Myers, and Engler 1978). Many chemical constituents tend to

be somewhat fixed in sediments beneath the thin oxidized surface layer. Wave and current action, deposition, erosion, and bioturbation may tend to upset these complex stratified formations. If this dynamic equilibrium is intensely disturbed by the mixing induced by dredging, the contaminant-enriched pore water could be released into the water column or could be released at the disposal site. If the pore water contains high concentrations of reduced soluble contaminants, the oxidizing conditions in a confined disposal area would promote rapid precipitation of iron compounds if retention times are sufficiently large (Hoeppel, Myers, and Engler 1978).

48. <u>Control of reducing conditions.</u> Populations of microorganisms in sediments prior to dredging are well developed due to relatively high organic content. Microorganisms (bacteria and fungi) and benthic macrofauna (worms, clams, etc.) are very active in the aerobic surface sediments, and facultative populations can extend into moderately reduced anaerobic sediments. Microorganisms are capable of biologically reducing both organic and inorganic compounds through energy-producing and respiratory functions. These processes usually result in a reducing or anoxic condition in the sediment by creating an oxygen demand exceeding supply. The influence of microorganisms tends to decrease with depth into the sediment because the organic compounds are more resistant to attack and microbial populations decrease. At the deeper depths in the sediment (approximately 20 cm), oxidation-reduction reactions involving inorganic (e.g. iron, manganese, and sulfur) compounds become more important. Sediment pH is also controlled by the types of compounds produced by biological activity (Hoeppel, Myers, and Engler 1978).

## Change in environmental conditions

49. When hydraulic dredging and disposal occur, the sediment is violently mixed with overlying water and is then subjected to sedimentation within the disposal area. The stratification described above is completely disrupted. The resulting influent into the confined disposal site is a mixture of mostly reduced sediment and entrained water, and oxygen-rich water from the overlying water column. However, the oxygen demand of the dredged material generally consumes the available oxygen from the overlying water. This has been indicated by field measurements of influents which indicate little or no dissolved oxygen. The environmental factors which existed in both the sediment mass and the water column are therefore subject to major changes,

with resulting changes in contaminant mobility.

50. Chen et al. (1976) and Gambrell et al. (1976) showed that the greatest release of sediment-bound elements may occur under changing environmental conditions, such as fluctuating pH or oxidizing conditions. Gambrell stated that much of the dredged material removed during maintenance dredging operations is anaerobic, relatively high in organic material and sulfide, and is both biologically and chemically active. The indirect effect of pH can be seen through an increase in the concentration or activity of toxic metals at low pH values and through an increase in highly toxic free ammonia at high pH values.

51. Ion exchange is the reversible process by which cations and anions are exchanged between solid and liquid phases (Bear 1964). Colloidal (clay) and small silt-sized mineral soil and organic particles generally have a high specific surface area and carry a net negative surface charge. This charge varies as a function of the pH of the system, with the net negative charge

(adsorbing force) tending to be less negative with decreasing pH (actually caused by an increase in positive charge). Electrochemical changes such as changes in Eh or pH can therefore result in either the solubilization or precipitation or sorption or desorption of many elemental species (Gee et al. 1976, Engler 1980).

52. If sediment is oxygen-free and therefore chemically reducing, reactions of toxic metals and some organics will be different from those under oxygenated conditions. For example, metals bound by sulfide in oxygen-free and sulfide-rich sediments may be released if the sediment is placed in an oxidized environment such as a confined disposal area where oxidation of sulfide may occur and a sharp decrease in pH occurs. A high sediment concentration of carbonates, common to some sediments, will negate the pH influence. Sorption of contaminants on particles

53. Suspended solids from sediments consist of clay minerals, inorganic precipitates, and organic matter, usually <10 µm in diameter. Placement of sediments and entrained water in confined disposal areas produces a supernatant water with suspended solids. However, the nature of these suspended solids may be different from the original sediments because of chemical changes occurring as the largely reduced sediments are exposed to oxidizing conditions. For example, dispersion and resedimentation studies indicate that a cycling between ferric hydrous oxide solids and insoluble sulfides occurs (Chen et al. 1976, Gambrell, Khalid, and Patrick 1978).

54. Affinity of contaminants for particles of various sizes, clay minerals, and organic matter can also be an important consideration. Solids of different sizes may also exhibit different densities and may have different exchange capacities and different mineralogy. Generally, particles less than 2 µm in diameter have the greatest affinity for metals. However, some metals will become fractionated with various particle sizes. Increased crystallinity tends to produce a decrease in surface adsorption of ions due to decreased surface area, but also produces a decreased tendency of precipitates to resolubilize (Hoeppel, Myers, and Engler 1978).

55. Association of metals and organics with various particle sizes has been determined for studies of ocean discharge of wastewater (Chen and Lockwood 1976). The concentration of contaminants in confined disposal area effluents should therefore be directly proportional to solids content, with the correlation stronger with surface area of particles than with total solids weight (Choi and Chen 1976). Also, different compounds may have affinity for various particle size or density fractions (Chen and Lockwood 1976).

56. The mobility of contaminants in sediment water systems is highly dependent on the way in which the contaminant is associated with solid particles. While biological and/or chemical reactions tend to result in long-term binding, free ions or soluble chemical complexes are bound only by physical sorption, resulting from actual or induced charges. A simplified concept of these processes is illustrated in Figure 4.

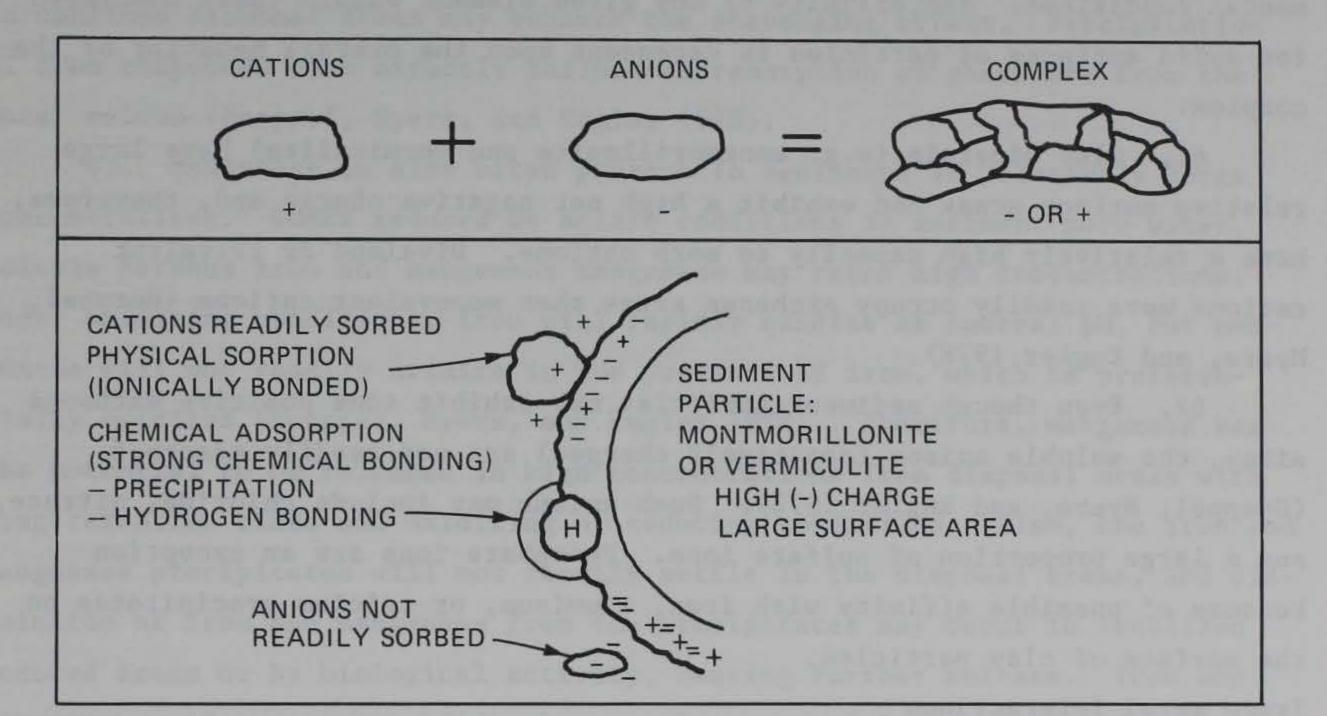


Figure 4. Conceptual illustration of contaminant sorption processes

57. Metal oxihydroxide formation can result in chemical precipitation on the particle surface. The precipitation of iron oxihydroxides under oxidizing conditions is a common example. This process is both time and pH dependent, and the resulting chemical adsorption is irreversible due to the strong chemical bonding (Hoeppel, Myers, and Engler 1978).

58. Organic complexes can be bound to particle surfaces through physical absorption or hydrogen bonding (protons shared between the complex and the surface site). These reactions are strongly influenced by pH. The relatively large surface areas of organic complexes may account for most of the ion exchange capacity in sediments (Hoeppel, Myers, and Engler 1978).

59. Physical adsorption in which bonds are formed by van der Waals forces results in relatively weak bonds, and reversible desorption of ions is possible. This process is dependent on the type of particles and the charge of the ions.

60. Marine waters have very high ionic strength. Cations (positive ions) can form soluble complexes with other ions, including anions (negative ions), in such an environment. These complexes can have a net positive or negative change and can display a variety of properties depending on environmental conditions. The affinity of any given element within these complexes for solid surfaces of particles is dependent upon the overall behavior of the complex.

61. Clay minerals (e.g. montmorillonite and vermiculite) have large relative surface areas and exhibit a high net negative charge and, therefore, have a relatively high capacity to sorb cations. Divalent or trivalent cations more readily occupy exchange sites than monovalent cations (Hoeppel, Myers, and Engler 1978).

62. Even though sediment particles may exhibit some positive exchange sites, the soluble anions (negatively charged) are not readily adsorbed (Hoeppel, Myers, and Engler 1978). Such anions may include chloride, nitrate, and a large proportion of sulfate ions. Phosphate ions are an exception

because of possible affinity with iron, aluminum, or calcium precipitates on the surface of clay particles.

#### Trace metal interactions

63. Iron plays a very significant role in the cycling of heavy metals, phosphorus, and organic compounds because of its prevalence and high concentrations in most natural soils and sediments (up to several percent of bulk composition) and its ability to form different complexes of varying solubility with many chemical compounds. Iron readily forms ferric precipitates in an aerated water column, and limited microbial oxidation of iron can occur even in the absence of molecular oxygen if oxidized chemical compounds are present. The formation of iron complexes is affected by pH and oxidizing conditions (as measured by Eh), and results in dissolution and precipitation of different iron compounds. The iron precipitates generally have large surface areas and high charges, which enable them to adsorb various complexes and to bind with particles (Hoeppel, Myers, and Engler 1978).

64. In a natural water column, the concentration of many trace metals is often one or two orders of magnitude lower than the concentrations in sediment pore water. This is largely the result of the ferric iron sorbing trace metals in the aerobic environment of the water column. This process is controlled by the absorption and coprecipitation of metal ions or hydroxides with iron hydroxides which form coatings on the surface of particles. The large surface area of these precipitates is even more effective in scavenging when they are freshly formed. Thus, dredging operations and placement of material in confined disposal areas may enhance the scavenging effect. Precipitation of iron compounds also directly influences resorption of phosphate from the water column (Hoeppel, Myers, and Engler 1978).

65. Manganese is also often present in sediments in relatively large concentrations. Under reduced or acidic conditions in sediment pore water, soluble ferrous iron and manganous manganese may reach high concentrations. Under oxidizing conditions, iron will rapidly oxidize at neutral pH, but manganese will not readily oxidize in the presence of iron, which is preferentially oxidized (Hoeppel, Myers, and Engler 1978). Therefore, manganese has the potential to be released in high concentrations from disposal areas with long retention times and oxidizing or reducing conditions. Also, the iron and

manganese precipitates will not readily settle in the disposal areas, and dissolution of iron and manganese from the precipitates may occur in localized reduced areas or by biological activity, causing further release. Iron and manganese oxides can also bind other metals to particle surfaces (Lion, Altmann, and Leckle 1982).

#### Nutrient interactions

66. Nitrogen is a nutrient associated with the presence of organic matter in water bodies. In photosynthetically active water bodies, including confined disposal areas where pH is unusually high, ammonium ions  $(NH_4^+)$  begin to revert to free ammonia, a compound which is toxic to many organisms (Hoeppel, Myers, and Engler 1978).

67. Organic nitrogen is mineralized through microbial decomposition processes and may be released as ammonium ions. Ammonium ions are easily but loosely adsorbed by sediments, and nitrogen may be fixed in this form in anaerobic sediments. Under oxidizing conditions, ammonium ions may be oxidized to soluble nitrate. If the nitrate migrates to the anoxic zone, it can be converted to nitrogen gas and lost to the atmosphere (denitrification). This process may result in a net loss of nitrogen in confined disposal areas (Hoeppel, Myers, and Engler 1978).

68. Phosphate release follows a pattern similar to iron. Dredging will release orthophosphate in reduced sediments, but under oxidizing conditions, sediments will scavenge soluble phosphate, forming iron phosphate precipitates. Poorly soluble oxidized iron phosphate precipitates will again release soluble phosphate if reducing conditions recur in the containment area. Organic interactions

69. Organic matter in sediments is composed primarily of the reworked and recycled plant and animal debris resulting from metabolism. Most of this material consists of complex condensates which do not closely resemble cellular constituents of aquatic organisms and is collectively called humic matter. The structure of these complexes can be quite varied (Hoeppel, Myers, and Engler 1978).

70. Humic matter can interact with metal ions and clay minerals to form soluble or insoluble complexes, depending on Eh, pH, salinity, and other factors. Mobility of contaminants can be either decreased or increased by this binding with organic matter, depending on Eh, pH, and the particular contaminant involved (Hoeppel, Myers, and Engler 1978).

71. Chlorinated hydrocarbons such as PCB or DDT are synthetic compounds

which have generated much controversy because of their environmental persistence and their toxicity to certain organisms. These substances are present in many sediments. Chlorinated hydrocarbons may undergo transformations with changing pH, temperatures, and association with organic matter. Generally, chlorinated hydrocarbons are relatively insoluble and hydrophobic and are closely associated with sediment particles.

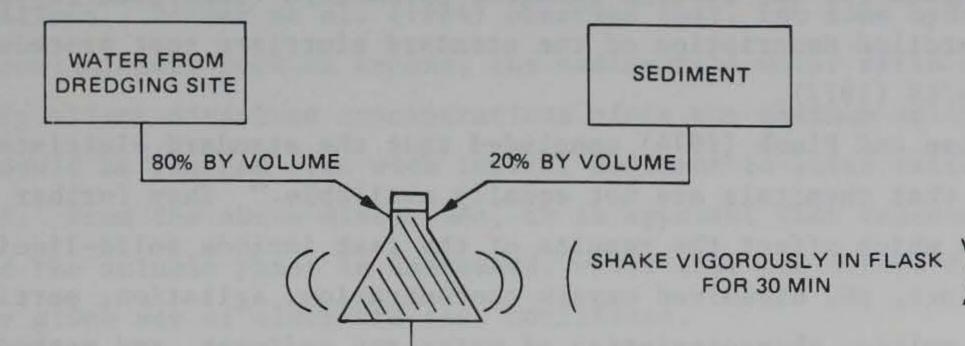
72. Petroleum hydrocarbons are also present in many sediments. The composition of petroleum hydrocarbons is very diverse. Solubility of these substances generally decreases with increasing molecular weight, and some structures become less soluble with increasing salinity. Hydrocarbons associated with sediments may decrease the adsorption or sorbtive capacity of sediment particles by masking adsorptive sites (Hoeppel, Myers, and Engler 1978).

#### Laboratory Studies

## Elutriate test development

73. The overall basis for evaluation of the potential for contaminant release for open-water disposal is the standard elutriate test (EEL 1976). Figure 5 depicts the major elements of the test. Keeley and Engler (1974) discussed the rationale behind the elutriate test development as follows:

> ...regulatory agencies faced with the legislative requirement of establishing dredged material criteria, must strive to establish meaningful criteria based on the best possible knowledge, and avoid the tendency to set forth criteria that precede the current technical state-of-the-art. Furthermore, regulatory criteria should be based on laboratory procedures that can be performed satisfactorily in routine testing laboratories as opposed to complicated procedures that can only be conducted in sophisticated research-level laboratories.



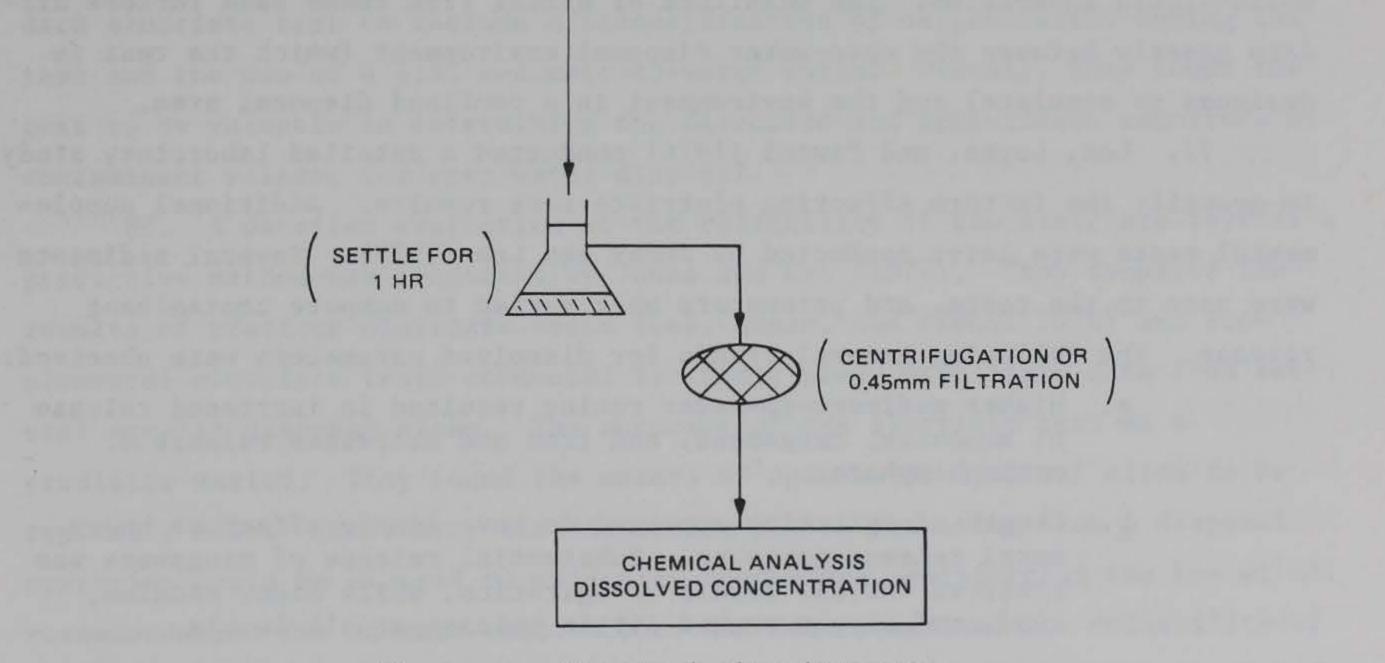


Figure 5. Standard elutriate test

Finally, in order to be equitable, the criteria should not be prohibitively expensive.

74. Personal communications with the principal developers of the test indicated that the above quote summarizes the rationale behind a laboratoryoriented evaluation procedure, as opposed to a theoretical or model-oriented procedure, for determining contaminant release. These concepts were considered in developing the laboratory procedures for this study.

75. The standard elutriate test procedure is generally intended to simulate the release of dissolved constituents into the receiving water column during open-water disposal operations. The main steps of the test include mixing one part of sediment with four parts of water (by volume), agitation for a period of 30 min, a settling period of 1 hr, and finally centrifugation and/or filtration. The filtrate is considered the standard elutriate, which is then analyzed for the desired chemical parameters (dissolved fraction only). A detailed description of the standard elutriate test procedure is found in EPA/CE (1977).

76. Lee and Plumb (1974) concluded that the standard elutriate test "recognizes that chemicals are not equally available." They further stated that factors which affect the results of the test include solid-liquid ratio, time of contact, pH, dissolved oxygen concentration, agitation, particle size, handling of solids, characteristics of water and sediment, and method of solid-liquid separation. The magnitude of effect from these same factors dif-

fers greatly between the open-water disposal environment (which the test is designed to simulate) and the environment in a confined disposal area.

77. Lee, Lopez, and Piwoni (1976) conducted a detailed laboratory study to quantify the factors affecting elutriate test results. Additional supplemental tests were later conducted by Jones and Lee (1978). Several sediments were used in the tests, and parameters were varied to compare contaminant release. The following general trends for dissolved parameters were observed:

- <u>a</u>. Higher sediment-to-water ratios resulted in increased release of ammonium, manganese, and iron and decreased release of orthophosphate.
- b. Length of agitation appeared to have little effect on heavy metal release patterns. Substantial release of manganese was observed for all levels of agitation, while zinc, cadmium, lead, and copper showed little release at all levels.
- c. Sample size and method of agitation (stirring versus shaking) were found to be insignificant factors in metal release with

the exception of iron, which showed higher release with stirring than with shaking.

- <u>d</u>. Compressed air agitation, creating oxidizing conditions, showed significant increased release of manganese; little change in copper, cadmium, lead, and iron; and significant removal of zinc from solution as compared with mechanical agitation.
- e. Compressed nitrogen agitation, creating reducing conditions, showed significant increases in release of manganese, iron, and lead as compared with mechanical agitation.

78. O'Connor (1976) investigated the effect of pH on zinc release during elutriate tests and concluded that lowered pH values caused a dramatic increase in zinc release. Chen et al. (1976) also conducted a series of laboratory tests to investigate release of metals during open-water disposal. They found increased release of iron and manganese under reducing conditions and increased release of cadmium, copper, nickel, lead, and zinc under oxidizing conditions. Bender et al. (1984) observed that, for some hydrophobic organic contaminants such as kepone, the sediment-to-water ratio may not significantly affect dissolved concentrations since the maximum soluble concentration could be reached even with initial sediment-to-water ratios of l percent. From the above discussion, it is apparent that release of some metals to the soluble phase is increased, while that for others is decreased, under any given set of elutriate test conditions.

79. Lee, Lopez, and Piwoni (1976) also recommended changes in the stan-

dard elutriate test to include a standardization of oxygen status during the test and the use of a 1:20 sediment-to-water ratio. Overall, they found the test to be valuable in determining the direction and approximate magnitude of contaminant release for open-water disposal.

80. A detailed evaluation of the reliability of the elutriate test as a predictive method was conducted by Jones and Lee (1978). They compared the results of previous elutriate tests (Lee, Lopez, and Piwoni 1976) and supplemental elutriate tests conducted for their study with field data from several aquatic disposal sites. The accuracy of the elutriate test as a predictor varied. They found the waters of open-water disposal sites to be typically oxic. Therefore, the dispersion plumes resulting from a disposal operation could be exposed to oxidizing conditions, reinforcing the Lee et al. recommendation for an oxic test. Jones and Lee summarized the reliability of the test for various predictions by stating that the elutriate test predicted the "behavior" of heavy metals and ammonia "with a reasonable degree of reliability [and within] the general order of magnitude of release found in the field," and was "an indication of the behavior" of phosphorus. For chlorinated hydrocarbons, the test "gave an indication of whether sorption or release may occur." These statements indicate the difficulty of comparing laboratory test results with field behavior, which is subject to dynamic changes, as are open-water disposal sites.

81. Brannon et al. (1976) conducted a study using a selective extraction procedure to partition sediments into the major phases, as described earlier by Engler (1980). Good mass balance for the partitioning was obtained. Results showed that the standard elutriate represented the phases most mobile and biologically available in the aquatic environment. The dissolved oxygen concentrations in the water during the test affected the results, and a standardization of oxidizing conditions to reflect the disposal site was recommended.

82. Lee and Plumb (1974) observed that any application of the elutriate test to evaluation of confined disposal should consider those particle sizes which would not settle during the retention time available in the disposal area. More discussion of the elutriate test as an evaluation tool for confined disposal is found later in this report.

#### Other tests

83. Several investigators have conducted limited laboratory tests involving settling and analysis of settled material and/or supernatant waters.

Krizek (1974) tested two freshwater sediments and analyzed settled material and supernatant water for 12 pesticides. He found close association of pesticide concentration with solids concentration, with, however, pesticide concentrations in the supernatant being several orders of magnitude lower than in the settled material.

84. Reimers et al. (1975) conducted a series of settling tests in  $2-\ell$  cylinders using sediments from five freshwater sites. The concentrations of metals and nutrients in supernatant water were compared with the sediment concentration. Removals of most heavy metals and nutrients were reported to be in excess of 98 percent.

85. Gee et al. (1976) used a modification of the elutriate test to predict dissolved metal concentrations for effluent from a proposed confined disposal project on the Potomac River. Sediment slurry was mixed in 2-& beakers for 30 min using a jar test apparatus, and allowed to settle for 12 hr. Supernatant water was decanted, filtered using 0.45-µm filters, and analyzed for 11 metals. A high potential for release of some metals was predicted. However, no field data were available to verify the predictions.

86. Yoshida and Ikegaki (1976) conducted settling tests in 2- $\ell$  cylinders on mercury-contaminated sediments from Minamata Bay, Japan. They measured the total concentration of mercury in supernatant water as a function of time for various initial concentrations. Mercury remained closely associated with particles, but total concentrations remained above 0.5  $\mu$ g/ $\ell$  even with prolonged settling times.

87. The Chicago District, CE,\* has utilized a settling test in a l-l graduated cylinder to evaluate the effectiveness of sand filtering systems used on many of the confined disposal areas on the Great Lakes. The supernatant was analyzed for total contaminant concentrations. A supernatant sample was then passed through a sand filter, and the filtrate was analyzed. This test is designed to simulate the final water quality attained when effluent is passed through sand filters.

88. O'Reilly (1980) proposed the use of a small-scale settling test in 1- or 2-L cylinders to determine the settling rates for dredged material removed from a Wisconsin lake. He also proposed chemical analysis of the supernatant water for evaluating effluent water quality.

89. Tofflemire, Hetling, and Quinn (1979) documented the results of

laboratory studies conducted prior to dredging PCB-contaminated sediments on the Upper Hudson River. Several types of laboratory studies were conducted to determine the sediment-water interaction and partitioning of PCB between the sediment and soluble phases. Elutriate tests were conducted using  $2.8-\ell$  jars and at sediment-water ratios of 1:10. The supernatants were analyzed for various settling times, and a direct relationship between dissolved PCB and suspended solids was found. Tofflemire summarized the results of these studies and those by other investigators and concluded that partitioning coefficients (dry sediment concentration/soluble water concentration) were lower for elutriates than for tank simulation tests in which water flowed over sediments. A lower partitioning coefficient indicates a higher release of PCB to the dissolved phase. The soluble concentrations were determined by analyzing samples

 \* Solicitation No. DACW23-78-0063, 1979, Description or Specification for Laboratory Services. filtered through 0.45-um filters. No analyses of the suspended particle fractions were performed.

90. Jones and Lee (1978) conducted settling tests on sediments from two sites to evaluate the relation of chlorinated hydrocarbon concentrations to particle size. The tests consisted of placing sediment in 1-L cylinders and shaking them for 1 min. Samples of the supernatant were withdrawn by a syringe at 2, 12, 24, and 48 hr from separate cylinders. All chlorinated hydrocarbons were removed to low levels after 48 hr of settling, indicating their strong association with particles.

91. Chen, Lu, and Sycip (1976a and 1976b) conducted a study designed to simulate the mobility of contaminants resuspended and resettled during openwater disposal operations. As with the laboratory studies on elutriate tests, only the soluble fraction was of concern. A 5-ft-long, 9.5-in.-diam plexiglass column was used in the tests. Sediments were mixed with water at a 1:20 ratio and allowed to settle, and samples were extracted from the supernatant at times of 0, 1/2, 1, 2, 4, 8, 12, 24, and 48 hr. The soluble fraction was obtained by filtering and was analyzed for metals, nutrients, and chlorinated hydrocarbons. Some of the test columns were continuously bubbled with air or nitrogen prior to sample extraction to simulate oxidized or reduced conditions. Chen et al. found that the dissolved oxygen of the mixed slurry was initially zero, but recovered to initial water concentrations within 2 to 4 hr of continuous bubbling with air. In a testing situation where bubbling precedes quiescent settling, oxidizing conditions in the supernatant water would be achieved quicker than by surface reaeration alone. This was also shown by the tests conducted in this study.

92. The findings of Chen, Lu, and Sycip are summarized as follows:

- a. Under oxidizing conditions, lower concentrations of soluble iron were observed, indicating formation of insoluble ferric oxides.
- b. For quiescent tests, metals displayed an initial release to the soluble phase followed by gradual removal through precipitation or readsorbtion.
- <u>c</u>. Iron, manganese, and nickel showed the highest releases, while other metals exhibited little or no release.
- d. Generally, higher release of metals to the soluble phase was found under reducing conditions.
- e. Most of the chlorinated hydrocarbons exhibited no release to

the soluble phase and were therefore concluded to be associated with fine particles.

<u>f</u>. Little difference was found in the release of metals and nutrients to the soluble phases between the resettled and continuously agitated tests with similar redox conditions. This indicates that redox conditions are the controlling factor rather than physical characteristics of the sediment.

# Effluent Quality Field Studies

# Physicochemical environment of confined disposal areas

93. The physicochemical environment of confined disposal areas can be site specific due to differences in design and operation. For this reason, confined disposal can be considered more complex than aquatic disposal from an environmental standpoint (Engler 1981). Gambrell, Khalid, and Patrick (1978) described conditions relating to contaminant mobility for subaqueous, intertidal, and confined disposal. They determined that short-term impacts for confined sites (those associated with toxicity or biological stress during and shortly after disposal) will be due to elevated levels of contaminants associated with particles in the effluent. They also stated that management of the disposal operations to reduce the total level of suspended solids in the effluent will tend to reduce potential short-term release of contaminants.

94. Gambrell, Khalid, and Patrick (1978) further state that the oxidation-reduction process is critical for the confined disposal condition since dredged material may become well oxidized in mass due to deep penetration of atmospheric oxygen by both mixing and gaseous diffusion. The fact that sediments that were initially reduced undergo oxidation within the confined disposal sites indicates that changes in the mobility of several contaminants are likely to occur. Changes in pH may also occur in confined disposal sites. These changes are related to changes in chemical components such as iron or sulfur. Such changes in pH also affect the mobility of contaminants.

95. Prior to the mid 1970s, field data on the quality of effluent from confined disposal areas was limited to site-specific studies. As the potential problems associated with effluent from confined disposal areas became apparent, more general investigations at multiple sites were conducted. Routine monitoring accomplished as part of the regulatory processes also yielded valuable data on field behavior. Results of such studies are summarized in the following paragraphs.

## Studies by Windom

96. Windom (1972) compared dissolved metal concentrations in the effluent from a diked disposal area in Savannah, Ga., with ambient river water. He found that the quality of the effluent (dissolved) was essentially identical with that of the river and noted that the precipitation of iron oxides may have a scavenging effect on other dissolved metals. Windom (1973) later published results of monitoring conducted at five disposal areas along the Georgia and Carolina coasts (including the Savannah Harbor site used for field evaluations in this study).

97. Windom found that some parameters (such as ammonia) were apparently controlled by biological activity. Ammonia was found to increase by an order of magnitude, with resulting increases in phytoplankton and algae. He attributed the observed increases in dissolved oxygen to photosynthesis, and the slight increases in pH to uptake of carbon dioxide. He also found that initially reduced iron present in the sediments oxidized and formed iron oxides, initially scavenging dissolved metals. At longer retention times, dissolved metal concentrations increased. Windom attributed this to the interaction of settled material in the reduced state with the overlying water column. Windom concluded that significant variations in effluent quality could be expected, depending on retention time, and longer retention times may not necessarily improve effluent quality with respect to concentrations of dissolved contaminants.

## WES effluent/leachate field studies

98. Hoeppel, Myers, and Engler (1978) performed a monitoring study of effluents and leachates at nine confined disposal areas. Two additional sites were later added in a related study (Lu et al. 1978). Results of influent and effluent samples at eight of the nine sites are summarized in Figure 6. Large net decreases were observed for most major elements and metals, generally correlating well with the retention of solids within the disposal area. However, as shown in Figure 6, considerable variability exists among specific chemical parameters. Furthermore, many contaminants now known to be associated with sediments were not studied. Hoeppel also developed some data regarding particle-size fractionation and found that some constituents may have affinities for different particle sizes and specific gravities. This may be

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\*EXCHANGEABLE AMMONIUM-N + <0.45 µm AMMONIUM-N

Figure 6. Percent increase or decrease of physical and chemical parameters in total and soluble phase effluent dredged material based on influent-effluent samples from eight land containment areas (after Hoeppel, Myers, and Engler 1978) explained by the larger relative surface areas involved with smaller particles and by differences in surface chemistry.

- 99. Specific findings of Hoeppel's study may be summarized as follows:
  - a. Total digests of influent and effluent samples showed a net decrease of all nutrients, chlorinated and petroleum hydrocarbons, and most elements and trace metals.
  - b. The net reduction in total concentration of most elements was proportional to the reduction in total filterable solids.
  - <u>c</u>. Residence time and salinity may not be the most significant factors in nutrient and metal release in confined disposal areas. Of course, increased residence time resulted in higher removal of particle-associated contaminants and resulted in increased oxidation of surface waters.
  - d. Salinity does not appear to have a major effect on contaminant release since no major changes in salinity were observed during confined disposal.
  - e. Temperature rose an average of only 2° C at the observed sites during confined disposal. However, this parameter could take on increased significance during the summer months, especially in disposal areas with shallow ponding depths and large retention times.
  - f. Dissolved oxygen levels in disposal area effluents averaged 5.3 mg/l. Influent measurements showed no measurable dissolved oxygen.
  - g. An overall increase in pH was observed during confined disposal, averaging 6.6 for the influent and 7.15 for the effluent. Generally, sediments were found to be close to neutral pH, while dredging site water was often slightly acidic.
  - h. The cation exchange capacity showed an average increase from 50.9 meq/100 g of suspended sediment for the influent to 82.5 meq/100 g for the effluent. This is probably due to the overall decrease in particle size and increase in relative surface area of effluent particles compared with all of those in the influent.
  - i. Removal percentages of the following parameters (total concentration) closely approximated the total suspended solids removal: iron, zinc, cadmium, copper, nickel, arsenic, vanadium, lead, total organic carbon, organic nitrogen, total phosphorus, and chlorinated hydrocarbons (e.g. DDT and PCB).
  - j. Removal of the following parameters (total concentration) was less than the total suspended solids removal: manganese, calcium, titanium, sodium, potassium, magnesium, and mercury.
  - k. Most soluble phase parameters showed a slight decrease during confined disposal, indicating a particle scavenging effect. The following parameters showed slight increases: potassium, calcium, copper, chromium, and zinc. The most dramatic increase was shown by nitrate and nitrite-nitrogen

(94 percent). These data substantiate the assumption that most soluble phase contaminants are discharged in the effluent.

100. The above findings are based on a general examination of data from nine disposal sites. The findings for metals are generally compatible with the laboratory data developed during elutriate test evaluation studies (Lee, Lopez, and Piwoni 1976; Jones and Lee 1978).

# Field studies with limited objectives

101. Several studies characterizing contaminant concentrations in disposal area effluents have been conducted for selected sites. Most of these studies were performed for general monitoring purposes and were limited in their objectives. However, they contain results which increase the overall knowledge of effluents and associated contaminants.

Mobile Harbor. May (1974) analyzed sediments prior to dredging 102. and monitored the effluent from four diked containment areas along the upper Mobile River (including the North Blakely or Upper Polecat Bay site used for field evaluation in this study). He observed that dissolved oxygen in the influent was zero and hydrogen sulfide was present, indicating reducing conditions. The dissolved oxygen in the effluent ranged from 4 to 5 mg/l and was attributed to atmospheric reaeration. Dissolved metal concentrations in the effluent were found to be lower than are found in Mobile Bay. May concluded that processes in the disposal area are largely controlled by the redox conditions, and the contaminants are strongly associated with particles and not readily soluble. 103. Toledo Harbor. Krizek, Gallagher, and Karadi (1976) conducted a study of the water quality effects of a confined disposal site at Toledo Har-Influent to this site was an intermittent pump-out from a hopper dredge. bor. Total concentrations of metals and nutrients were monitored for influent and effluent. Based on the relatively large number of samples, Krizek found that variations in effluent quality were lower than those in influent quality. The range of contaminant concentrations for any particular parameter was large, and particular samples could only be considered representative in a statistical sense. Krizek's study pointed to the need for a large number of samples before statistically sound conclusions can be reached. Krizek found that the confined disposal process "does effectively improve the water quality ... [and that] many of the contaminants apparently associate with solid particles,

thereby settling out of suspension with the solids and reducing significantly the concentrations of polluting materials."

104. <u>Duwamish Waterway.</u> In September 1974, approximately 250 gal of PCB transformer fluid was spilled into the Duwamish Waterway near Seattle, Wash. Initial cleanup efforts with hand suction pumps removed only 80 gal. Therefore, hydraulic dredging was used as a cleanup technique. This operation was extensively monitored in a cooperative EPA/CE effort. Blazevich et al. (1977) documented the EPA monitoring efforts, as follows:

> Apparently most pollutants were associated with or scavenged by particulate matter and settled with the aid of a flocculent to the bottom of the disposal ponds. Comparisons of these observations with predictive tests used to estimate the amount of a pollutant released during dredging is good. Considering the degree of accuracy possible for this type of estimate the "standard elutriate test" appears to be valid for most metals, nutrients, and oil and grease... [The] tests failed to accurately predict the amount of PCB released.

However, the results indicate that only one-half of the pollutants tested were predicted within a factor of two of the observed concentration in the effluent. These results may be valid in predicting which contaminants will be released, but clearly are not adequate for use in predicting the magnitude of release of specific contaminants from a regulatory standpoint.

105. <u>Upper Hudson River.</u> Capacitor manufacturing plants located on the Upper Hudson discharged approximately 500,000 lb of PCBs into the river in the 1960s and '70s. Several studies pertaining to potential removal of hot spots by dredging have been conducted. Tofflemire, Hetling, and Quinn (1979) summarized the results of both laboratory studies and field monitoring for the Upper Hudson.

106. The PCB distribution in bottom sediments was extensively mapped to determine hot spot locations. This work determined that the PCBs were typically found in higher concentrations in the finer sediments near the banks than in the coarse sediments in the main channel. Areas with concentrations of 50 mg/g or higher were considered as hot spots. Routine channel maintenance dredging was conducted and the material was placed in three disposal sites. Both influent and effluent were monitored daily for 1 to 2 months. Polymer was added by pipeline injection during portions of the disposal. Results showed that PCB concentrations in the effluent were proportional to the suspended solids levels. The addition of polymer by pipeline injection cut the effluent concentrations roughly in half.

107. O'Brien and Gere Engineers (1980) monitored additional dredging operations on the Upper Hudson River for the New York District. The sediments in situ contained relatively high concentration of PCBs. The study included monitoring the retention of PCBs and other contaminants within the disposal areas and the use of the standard elutriate test as a predictor of contaminant levels in the effluent. The results indicated that PCB retention was generally proportional to solids retention. However, no direct measurements of influent levels were made.

108. <u>Craney Island</u>. A comprehensive water quality monitoring program was conducted at the Craney Island disposal area in Norfolk, Va. (a site used for field evaluations in this study), from December 1973 to March 1976 (Adams and Young 1975, Adams and Park 1976). The major objective of the studies was to monitor and evaluate the quality of water and associated particles discharged from the Craney Island site during active disposal operations.

109. Comparison of total suspended solids and nutrient data for influent and effluent indicated that the Craney Island site was very effective in retaining these constituents. The fractions of contaminants in the suspended solids in the effluent were higher than those in receiving waters. As with the nutrients, the low effluent suspended solids levels were indicative of the efficiency of the site in retaining particle-associated metals.

The sampling schedule for this study consisted of weekly or 110. monthly sampling conducted over periods of several months. This approach is valid as far as evaluating the changing nature of influent and effluent quality over long time periods. However, the nature of the sampling schedule presents problems when attempting to establish a mean concentration for constituents of influent and effluent under a given set of operational conditions, because the influent and effluent samples are not taken from the same parcel of water. The authors calculated means and standard deviations for various parameters, and a high degree of variability was observed in the data. Changing operational and environmental conditions during the total sampling period probably account for most of this variability. Over the course of several months, the location of the dredge, nature of material dredged, ponding conditions, and climatic conditions will all substantially change. Therefore, the comparison of samples taken during such a long period is questionable from a statistical standpoint.

111. A better approach for such sampling would involve a number of samples taken during a sampling period in which operational and environmental conditions would remain practically constant. A set of such samples could be thought of as taken from the same population. Therefore, sample means, standard deviations, and other statistical parameters could be developed on a sounder basis. The efficiency of the site in retaining contaminants during typical disposal conditions could then be calculated based on a comparison of mean influent and effluent concentrations.

#### Routine monitoring

112. Monitoring the effluent water quality from confined disposal sites is now required by many state and local/regional regulatory agencies. In the case of the states, such monitoring may be requested as part of the water quality certification (Florida Department of Environmental Regulation 1980). The total cost to the government of such monitoring programs is difficult to estimate. However, the development of reliable predictive tests may serve to significantly reduce the cost of monitoring, especially in those cases where effluent water quality will clearly not violate Federal or state standards.

113. Most routine monitoring consists of physicochemical parameters, nutrients, and metals. Samples are normally taken at specified time intervals (Sacramento District 1974, Detroit District 1980). Results of these routine monitoring studies invariably support the findings of the generalized studies described in the previous paragraphs in that the contaminants in the effluent

are largely associated with particles, and the retention is found to be proportional to the retention of solids within the disposal area.

# Physical Aspects of Confined Disposal Affecting Contaminant Release

# Sedimentation behavior

114. Recent research has greatly advanced the state of the art regarding confined disposal area design, considering ponded water depth, ponded surface area, and hydraulic efficiency. Much of this work has some degree of application to prediction of contaminant release. The most comprehensive work regarding dredged material sedimentation behavior in confined disposal areas has been conducted by Montgomery (1978 and 1979).

115. The sedimentation process can be categorized according to three

basic classifications (Thackston 1972; Montgomery 1978; Montgomery, Thackston, and Parker 1983): (a) discrete settling, in which the settling particle maintains its individuality and does not change in size, shape, or density during the settling process; (b) flocculent settling, in which particles agglomerate during the settling period with a change in physical properties and settling rate; and (c) zone settling, in which the flocculent suspension forms a lattice structure and settles as a mass, exhibiting a distinct interface between it and the relatively clear supernatant during the settling process.

116. Studies in the early 1970s examined discrete settling theories as a means to describe settling behavior of dredged material. Fitzpatrick, Atmatzidis, and Krizek (1977) proposed discrete settling design in conjunction with studies on filtration of effluents. Mallory and Nawrocki (1974) had earlier proposed similar designs as part of an overall evaluation of solidliquid separation technology as related to dredged material. Montgomery (1978) later showed that either flocculent or zone settling, not discrete settling, governs the sedimentation behavior of fine-grained dredged material.

117. The important factors governing the sedimentation of fine-grained dredged material solids are the initial concentration of the slurry and the flocculating properties of the slurry (Montgomery 1978). Because of the high influent solids concentration and the tendency of dredged material fine-

grained particles to flocculate, either flocculent or zone settling behavior governs the gross sedimentation behavior (sedimentation of the entire slurry mass) in containment areas. Discrete settling describes the sedimentation of sand particles, and in some cases fine-grained suspensions at concentrations much lower than those found in dredged material containment areas.

118. It should be noted that Montgomery's description of settling classifications was made considering the settling characteristics of the entire slurry mass. The lowered concentration of fine-grained particles remaining in the supernatant waters may not follow the processes described above. This concept was further investigated as a part of this study and will be documented in a later report.

# Development of testing procedures

119. Montgomery developed a column settling test to describe either flocculent or zone settling behavior of dredged material slurries. The tests provide numerical values for the design criteria, which can be used to design the containment area. It is important that the sediment slurry tested have characteristics in the settling column similar to those that it will have in the containment area. This becomes increasingly difficult as the sediment slurry becomes more flocculent and as solids concentrations increase.

120. Montgomery conducted column tests using several sediments to develop appropriate test procedures and to characterize the sedimentation regimes governing dredged material slurries. Column diameter, column (initial slurry) height, and initial slurry concentration were varied in the test series.

121. Multiconcentration tests were performed at concentrations of 26 to 366 g/l in 4-in.-diam columns at a slurry height of 1.12 ft. Results indicated that the settling velocity decreased with increasing slurry concentration. As part of this series, Montgomery conducted tests directly comparing settling characteristics of a sediment sample taken prior to dredging and the same material after discharge into a containment area. Regression analysis performed on data for settling velocity versus concentration indicated no significant difference. Therefore, settling tests conducted on sediment samples taken prior to dredging were found to be valid for defining the settling behavior of dredged material within a containment area.

122. Multidiameter tests were performed at column diameters from less than 4 in. to 31 in. at a slurry height of 1.12 ft. Montgomery found that wall effects apparent in the tests were probably due to the relatively high concentrations of dredged material slurries. Bridging effects in small diameter columns tended to decrease settling velocities. At high slurry concentrations, the upward flow of water displaced from the bottom of the column in channels along the column wall tended to decrease friction between the wall and the solid mass and thus to increase settling velocity. Montgomery's data indicated that wall effects are significant at slurry concentrations greater than about 50 g/ $\ell$  for column diameters less than 6 in. Therefore, he concluded that columns 8 in., or more, in diameter should be used in tests for sedimentation area design.

123. Multiheight tests were performed at slurry heights from 1.2 to 4.0 ft at constant initial slurry concentration. The data indicated that, at concentrations less than about 50 g/ $\ell$ , slurry height had little effect on settling velocity. At greater slurry concentrations, column height had a pronounced effect, with significantly increased settling velocities resulting from higher slurry heights. Montgomery concluded that tests for sedimentation design should be conducted at a slurry height to match the depth expected in the field.

124. The test column recommended by Montgomery for routine evaluation of dredged material sedimentation is an 8-in.-diam sectional column with side extraction valves. Field verification work conducted by Montgomery has shown that the column test procedure adequately simulates field settling behavior of fine-grained dredged material. However, the large column size and the column materials present difficulties in preparation (acid cleaning, etc.) required for the chemical analytical work and the volume requirements for the test replication required in this study for prediction of contaminant release. New test procedures were developed as part of this study to overcome these problems.

125. Montgomery also developed procedures for containment area design and evaluation based on works of Coe and Clevenger (1916), McLaughlin (1959), Thackston (1972), Dick and Ewing (1969), Yoshioka et al. (1957), and Vesilind (1968). The design procedures for flocculent settling, as proposed by Montgomery, rely on the measurement of suspended solids concentrations within the test column as a function of depth and time. This procedure allows determination of suspended solids "gradients" as a function of time. These data are then used to establish required retention times for a desired suspended

solids removal.

126. Design procedures for zone settling are based on the measurement of the interface position as a function of time and the subsequent calculation of its settling velocity. Montgomery states that the zone settling design procedure will result in effluent suspended solids levels of 1 to 2 g/l. However, the testing procedures for zone settling do not provide any information on the solids or contaminant composition of supernatant waters.

127. Additional insight into the sedimentation behavior of fine-grained slurries may be gained by investigations of the behavior of tailings sludge (Dusseault and Scott 1983, Scott and Dusseault 1982). The thin sludges in the tailings streams from oil-sand processing are placed in large tailings ponds. The thin sludge flow consisting of a silt/clay/bitumen/water mixture enters the pond as a density current. Once in the pond, the sludge undergoes a zone sedimentation process, transitioning to consolidation, in a manner similar to dredged material. Scott and Dusseault (1982) have also utilized a large diameter, multiport column test to define sedimentation and consolidation characteristics of oil-sands tailings sludge.

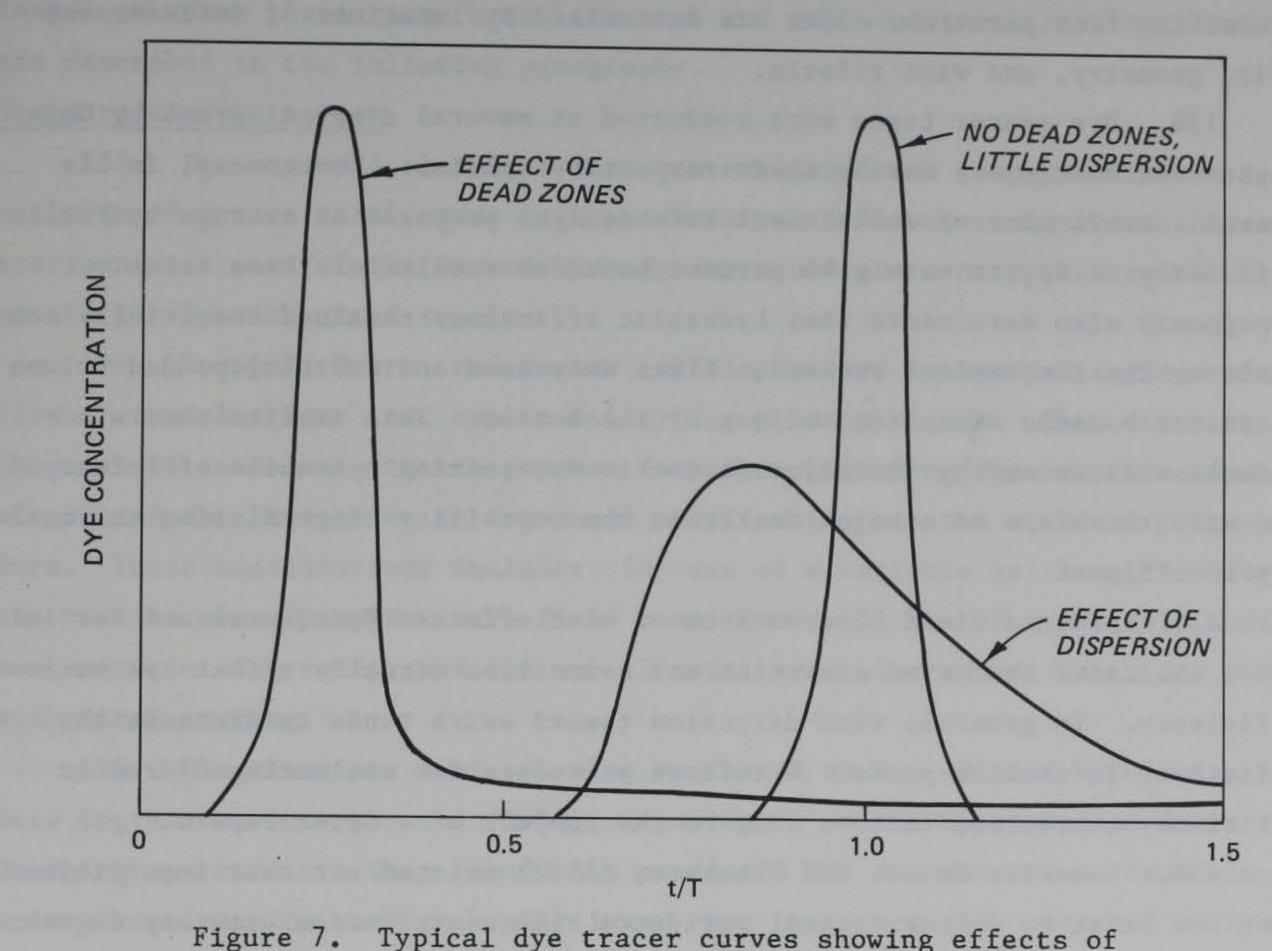
128. The density current behavior described for oil sands tailings was also observed in dredged material disposal areas during this study. Clear water overlying settled material is observed near the influent points in dredged material disposal sites where saltwater sediments are dredged, indicating that the flow enters as a density current. This significantly complicates the determination of the necessary ponded volume and the relationship between theoretical and mean retention times since a portion of the settled material is also flowing.

#### Hydraulic considerations

129. A laboratory settling test performed under quiescent conditions could be directly applied to the case of plug flow, in which retention time would be equal to the theoretical retention time V/Q. However, shortcircuiting from "dead zones" and dispersion occur in disposal areas. Therefore, the actual retention time of a portion of the slurry is less than V/Q, while some portions are retained for times greater than V/Q. This requires that some estimate of the overall hydraulic efficiency, the ratio of actual to mean theoretical retention times, be considered in evaluation of dredged material containment area design.

130. In an actual confined disposal facility, there are dead zones where flow velocities are significantly less than the average flow velocities. These zones do not act as fully involved flow paths, thereby reducing the volume of ponded water effectively involved with the flow. Dead zones exist behind spur dikes, in corners, or in shallow, rough, or vegetated areas (Koussis, Saenz, and Thackston 1982). Dead zones can also be created by a prevailing wind which causes a net velocity increase in one portion of the basin and/or a net decrease in other portions. Short-circuiting caused by dead zones is illustrated by a change in the ratio of theoretical to actual mean retention time as illustrated by a shifting of a typical tracer curve (see Figure 7). The resulting field mean retention time in a disposal area is therefore less than the theoretical or volumetric retention time. The portion of the slurry or ponded water which is subject to flow is also difficult to determine because of the density flow phenomenon described above.

131. Short-circuiting caused by longitudinal dispersion differs from that caused by dead zones in that the ratio of actual mean to theoretical



gure 7. Typical dye tracer curves showing effects o dispersion and dead zones

retention times is unaffected. However, some portions of a given parcel of

fluid entering the basin will exit faster than the average, while other portions will exit slower. This phenomenon can best be illustrated by a change in shape of the tracer curve (see Figure 7).

132. Longitudinal dispersion is caused by velocity gradients in the area involved in flow due to roughness of the bottom and sides of a basin. Fluid moving near the surface or near the center tends to move faster, exiting the basin earlier than water flowing near the bottom or sides of the basin. Observed flow velocities in disposal areas are much larger than average net velocities determined from volumetric flow rate and average cross-sectional areas.

133. Brian J. Gallagher and Co. (1978) provided a detailed treatment of hydraulic efficiency, including a theoretical analysis of basin hydraulics and discussions of outlet structures, wind effects, and the influence of interior or spur dikes. He stated that hydraulic efficiency is directly influenced by prevailing flow patterns, which are determined by locations of influent and weir, geometry, and wind effects.

134. Dye tracer tests were conducted at several disposal areas by Gallagher and Montgomery during their respective studies. Montgomery, in his overall development of containment area design, proposed an average hydraulic efficiency of approximately 40 percent based on results of these tests. Montgomery also determined that hydraulic efficiency remained essentially constant as the theoretical retention times decreased and as total ponded volume decreased because of solids buildup of the bottom. This implies that windinduced effects may be the major factor in determining hydraulic efficiency and will therefore be a major factor in the capability of predicting the quality of effluent.

135. Limited field observations of wind effects (Poindexter and Perrier 1980) indicated that wind direction and velocities directly affect hydraulic efficiency. In general, wind direction toward weirs tends to decrease the efficiency in shallow ponds. A refined procedure for estimating hydraulic efficiency correction factors will be the subject of a later report.

136. Koussis, Saenz, and Thackston (1982) pointed out that insufficient data now exist to define typical residence time distribution with any degree of certainty. A more exact estimate of hydraulic efficiency would be possible with a mathematical model. Gallagher stated that no exact mathematical solution for flow field could be obtained because flow in disposal areas was turbulent. Therefore, he proposed no numerical solution or computational procedure for determining hydraulic efficiency. Koussis, Saenz, and Thackston (1982) investigated the feasibility of modeling containment area hydrodynamics and model availability. They concluded that a steady-state, two-dimensional, vertically averaged model could be used for routine use in design and site evaluations, but that a three-dimensional model would be necessary to completely describe the various phenomena. Development of such improved techniques for prediction of hydraulic efficiency is still under study.

# Effluent Quality Prediction

137. In the absence of proven techniques for predicting contaminant concentrations in disposal area effluents, the standard elutriate test or other proposed methods have been used as indicators of potential release. Specific instances where these tests have been used and the subsequent results obtained are described in the following paragraphs.

Standard elutriate test

138. The standard elutriate test was evaluated and compared with an analysis of interstitial water as a predictor of effluent contaminant concentrations as a part of the Duwamish study described previously (Blazevich et al. 1977), with mixed results.

139. Hoeppel, Myers, and Engler (1978) provided a more realistic evaluation of the elutriate test applicability for predictive use. They state that the test is inadequate in its present form for predicting the concentrations of contaminants and go on to recommend modifications to the standard procedure. These modifications include: (a) use of a variable settling time for the test to closely approximate field conditions, (b) use of a variable sediment-water mixing ratio, and (c) use of unfiltered supernatant water for analytical testing.

140. The elutriate test was also evaluated as a predictor by O'Brien and Gere Engineers, Incorporated (1980), in a report on the Upper Hudson River dredging operations. They found that predicted PCB concentrations from elutriate test results were generally lower than those actually measured in the effluent, indicating that the standard elutriate test was not accurate. Discrete settling technique

141. Eichenberger and Chen (1980) proposed a method for predicting effluent contaminant concentrations based on field study results from their previous work (Chen et al. 1978; Lu et al. 1978). The proposed method relies on discrete settling theory (Hazen 1904) as adapted by Fair, Geyer, and Okun (1968).

142. However, there were basic flaws in their theoretical approach. Montgomery (1979) has determined that flocculent or zone settling, not discrete behavior, governs settling behavior for the case of fine-grained dredged material. The pipette analysis employed by Eichenberger and Chen does not account for the settling properties of the particular sediment at concentrations actually present during disposal or for the site-specific retention time during disposal. Furthermore, sediment procedures and operating conditions for the sites used in the verification were not representative of those which would be encountered if one were dredging highly contaminated sediments.\*

# Summary of Literature

143. Existing design criteria for dredged material containment areas deal only with solids retention and do not directly address contaminants. Although present regulatory policy calls for confined disposal of dredged material otherwise unacceptable for open-water disposal, no valid method existed prior to this study for the prediction of contaminant concentrations in disposal area effluents. Such methods are needed so that the potential for contaminant release and subsequent environmental impacts resulting from these activities may be properly predicted and evaluated.

144. Past work related to effluent contaminant concentrations has been mainly limited to monitoring activities for ongoing disposal operations. A wide variety of contaminants has been studied, and it has been determined that retention of contaminants within the disposal area is generally proportional to the retention of particles. There is good evidence that most contaminants, especially heavy metals, are adsorbed on or closely associated with particles; but, contaminants may concentrate in smaller particle-size fractions. Furthermore, these small-size fractions tend to remain in suspension, are the most difficult ones to retain during disposal, and are retained at lower per-

centages than the average-sized solids.

145. Efforts to predict contaminant release have been generally limited to use of the standard elutriate test, which was developed for the evaluation of open-water disposal, not confined disposal. This approach has proven unsatisfactory, and predictive techniques must be developed which are specifically tailored to simulate conditions in confined disposal areas. Sufficient information exists in the literature to support the development of a predictive technique based on laboratory tests and the application of the fundamental physical and chemical principles of dredged material behavior in confined disposal sites.

\* Personal Communication, E. L. Thackston, 1974, Vanderbilt University.

# PART III: SEDIMENT SAMPLING AND CHARACTERIZATION

# Project Descriptions

146. Four projects were used in laboratory and field evaluations for this study. The projects were located along the gulf coast, Atlantic coast, and inland waterways and included both saltwater and freshwater sediments which contained a variety of contaminants (see Figure 8). A brief description of each project is given below.

#### Mobile Harbor

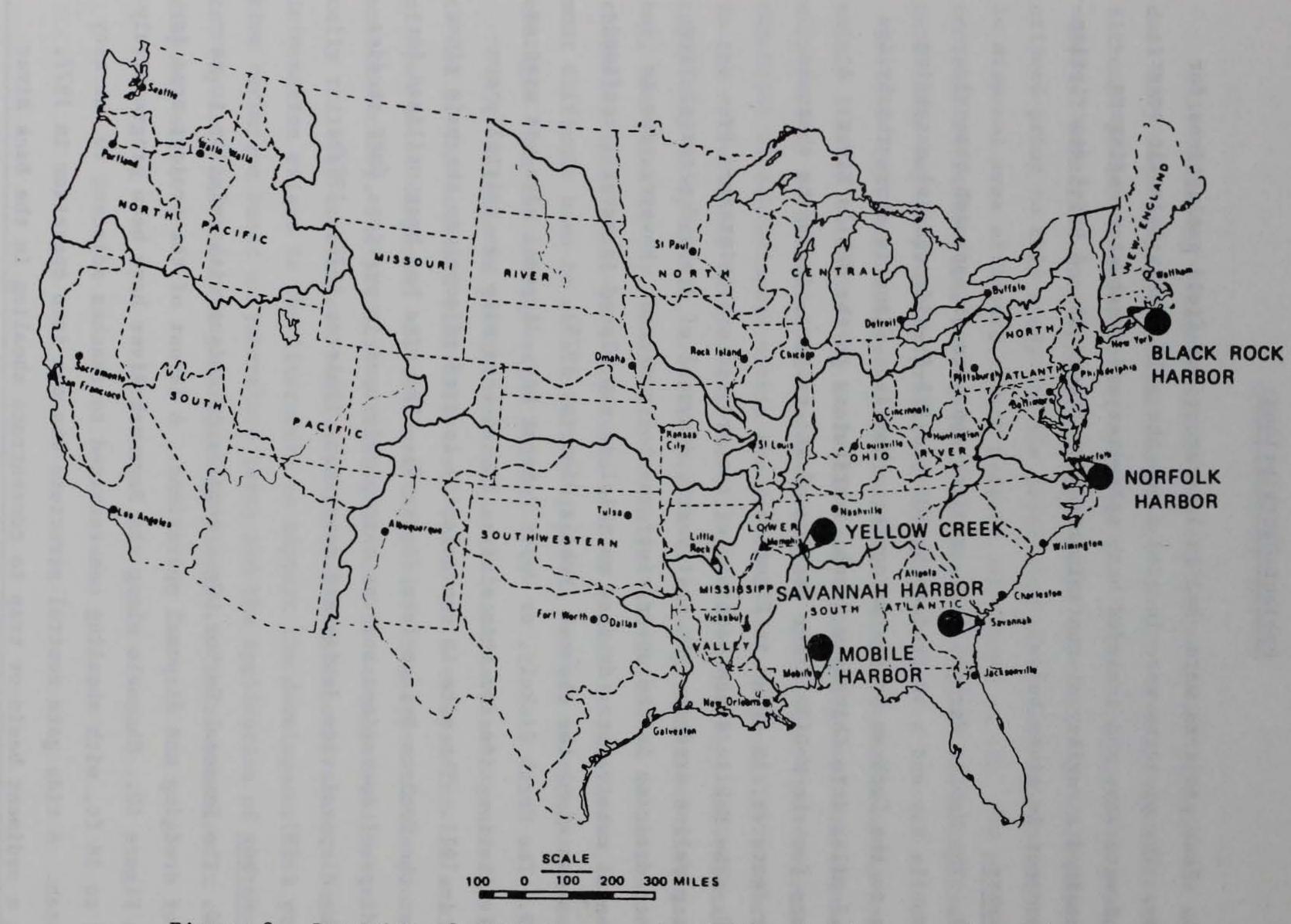
147. The Mobile Harbor, Ala., project consists of approach channels through Mobile Bay and a 40-ft-deep by 500- to 775-ft-wide channel extending 4.6 miles to the Cochran Bridge in northern Mobile. Channels above the bridge extend 2.7 miles into Chickasaw Creek, a tributary to the Mobile River. A project map for the Mobile River section of the project, including channels and other features, is shown in Figure 9.

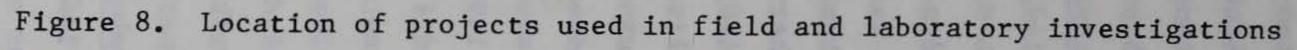
148. The Mobile River sections of the project are maintained by hydraulic pipeline dredges. In past years, disposal of dredged material from maintenance dredging in the upper river was not confined. However, due to environmental constraints, dredged material is now placed in several confined disposal areas along the channel (Mobile District 1975).

149. The North Blakely, or Upper Polecat Bay, disposal site was used as a field evaluation site for this study. The 85-acre site was initially constructed in 1971. The site is conveniently located adjacent to the main river channel at the Cochran Bridge (see Figure 9). The site has been utilized for several disposal operations and was extensively used in previous DMRP studies concerning disposal site design and management (Palermo 1977a, 1977b; Montgomery 1979).

# Savannah Harbor

150. The Savannah Harbor, Ga., complex is unique with relation to management of dredging and disposal operations. A layout of the project area is shown in Figure 10. Channels along the Savannah River have been progressively deepened to 38 ft, with shoaling concentrated to reaches adjacent to the city of Savannah. A tide gate control structure was put into operation in 1977, creating a sediment basin or trap to concentrate shoaling in the Back River channel, thereby reducing shoaling in the navigation channel and reducing





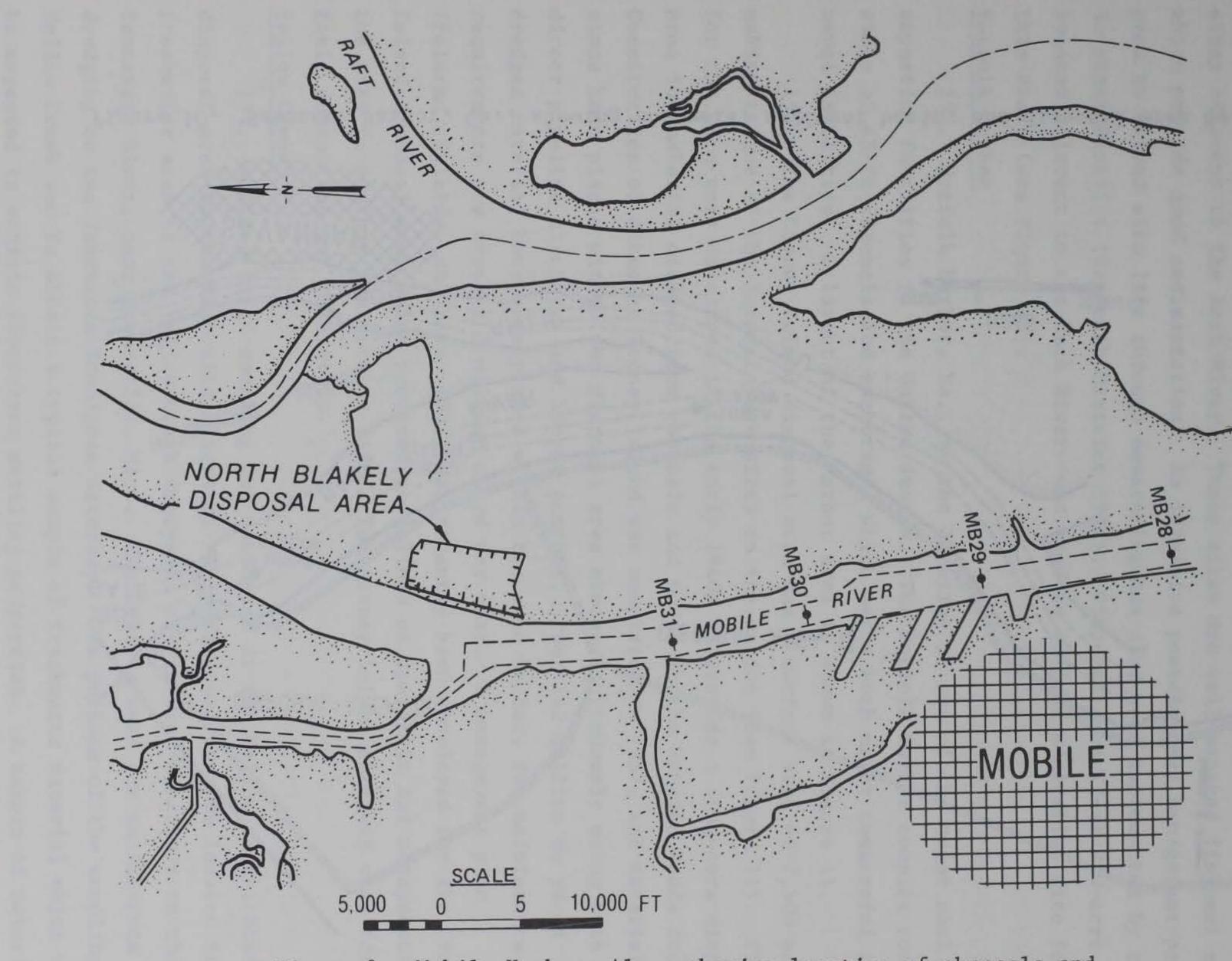


Figure 9. Mobile Harbor, Ala., showing location of channels and North Blakely disposal area

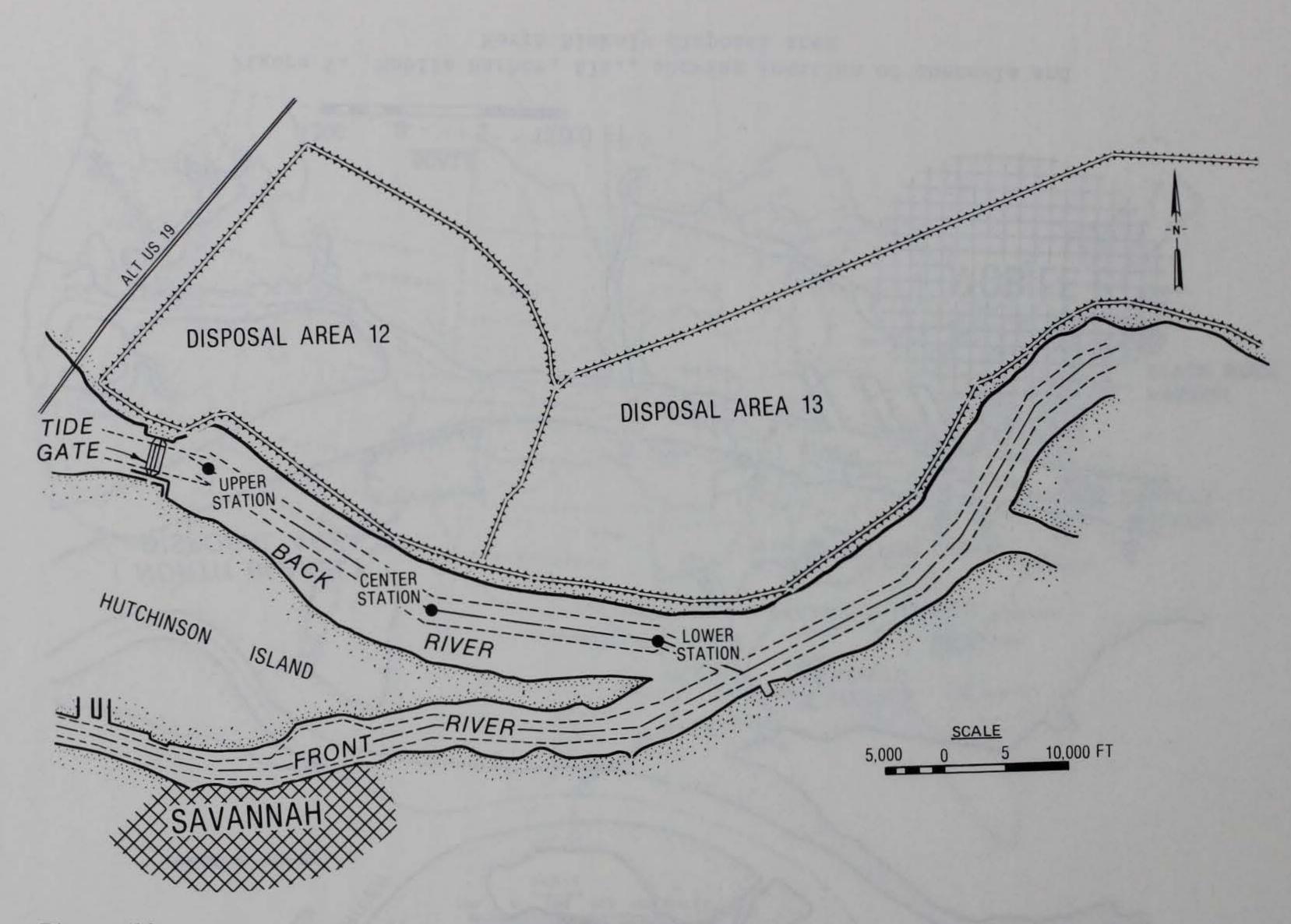
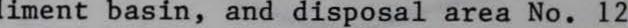


Figure 10. Savannah Harbor, Ga., showing channels, sediment basin, and disposal area No. 12



dredging costs. Approximately 7 million cu yd of material are removed annually from the project area.

151. Dredging in the Savannah Harbor is accomplished using hydraulic pipeline dredges, depositing directly into several large confined disposal sites adjacent to the Back River. These sites are well-managed disposal areas which provide good sedimentation. An intensive postdisposal management program to extend site life through dewatering has also been implemented by the Savannah District (Savannah District 1982). Disposal Area 12--a 900-acre site located adjacent to the Back River--was used as a field evaluation site for this study (see Figure 10).

## Norfolk Harbor

152. Norfolk Harbor, Va., is the location of one of the major coal exporting facilities in the United States. The Norfolk Harbor complex consists of 45-ft channels and anchorages which serve both major commercial and naval facilities. A layout of the harbor area is shown in Figure 11.

153. The Craney Island disposal area has a surface area of 2,500 acres, making it one of the largest such sites in the nation (see Figure 11). Plans for the site were developed in the early 1940s to provide a long-term disposal area for material dredged from channels and ports in the Hampton Roads area. Construction of dikes at Craney Island was completed in 1957, and material has since been placed within the disposal area almost continuously using both direct pipeline discharge and hopper pumpout. Over 142 million cu yd of dredged material have been placed within the area so far, and maintenance requirements now average 5 million cu yd per year. A management plan (Palermo, Shields, and Hayes 1981) has recently been developed for the Craney Island disposal area which provides guidelines on operation and management of the site to prolong its service life. The Craney Island site was used for a field evaluation for this study.

## Yellow Creek

154. Limited field sampling was conducted at the Yellow Creek, Miss., disposal area in the Nashville District. This disposal area is located in a freshwater area at the Yellow Creek Embayment of Pickwick Reservoir on the Tennessee River, near Burnsville, Miss. The area is used for maintenance dredging on the Tennessee-Tombigbee Waterway. The purpose of the sampling at Yellow Creek was to obtain a typical sample of freshwater material which would be expected to exhibit flocculent settling properties. A sample of material

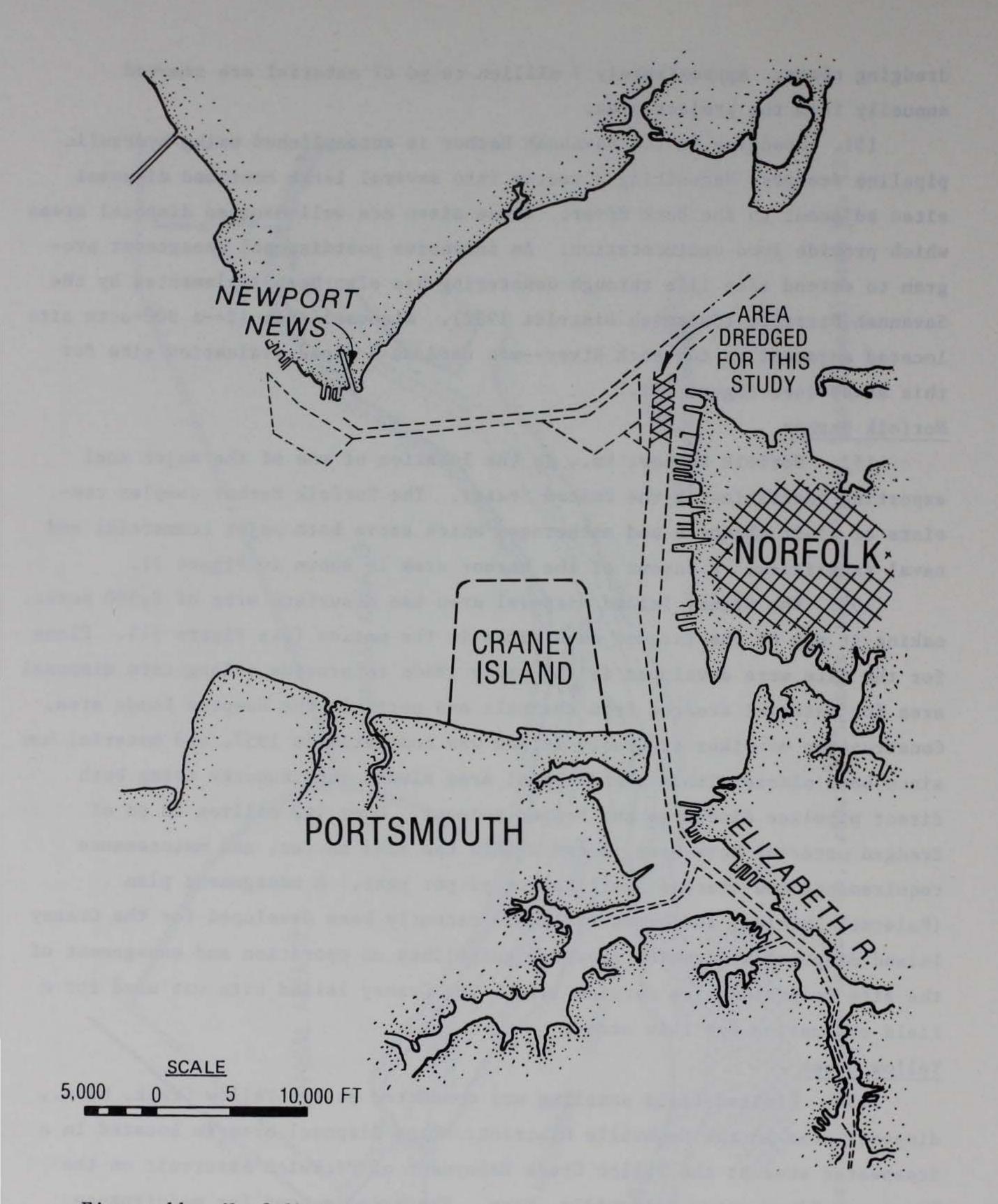


Figure 11. Norfolk Harbor, Va., showing location of channels, areas dredged, and Craney Island disposal area was taken directly from the disposal area immediately in front of the primary weir box. This sample was used in the test vessel selection series described in Part IV. Black Rock Harbor

155. Black Rock Harbor, located near Bridgeport, Conn., is an active harbor serving both commercial and recreational navigation. Approximately 250,000 tons transit the harbor annually (1978 estimate). The principal items of commerce are petroleum, sand, gravel, and scrap iron.

156. The project consists of an 18-ft authorized channel depth with channel widths of 200 ft, 150 ft, and 100 ft, moving upstream. The channel was dredged in 1955 to a depth of 18.0 ft, with 1 ft allowable overdredge. Shoaling has since reduced the channel depth to approximately 13.0 ft, with isolated shoaling to depths as little as 9.0 ft. Approximately 425,000 cu yd of sediment was removed from the channel in late 1983 to restore the authorized channel dimensions.

157. Black Rock Harbor is described as a "flagged" harbor with regard to contaminants (New England River Basin Commission 1981). Current regulatory conditions require that flagged harbors be evaluated for confined disposal before open-water sites can be considered. In the case of Corps projects, the state or local sponsor is responsible for locating and providing the appropriate upland sites. Various permits or certificates may also be required for upland disposal, and a Federal Section 402 discharge permit may be required if the effluent resulting from sediment dewatering (effluent during disposal operations) is collected and discharged into an adjacent body of water.

158. The Black Rock Harbor Project is the selected site for the CE Field Verification Program (FVP), designed as a cooperative effort between the CE and EPA to field verify testing procedures for implementing the requirements of Sections 404 and 103. Through the FVP, promising procedures developed by both the CE and EPA (including the predictive technique developed in this study) will be applied to project conditions at Black Rock Harbor using dredged material from a single maintenance operation. The dredged material was placed in both an aquatic site and a confined disposal site under wetland and upland conditions, thus providing an unusual opportunity for direct comparison of the environmental consequences of the same material under different disposal conditions. Results of the program will provide CE and EPA field elements with documented and verified state-of-the-art techniques and interpretive procedures for complying with the regulatory requirements for dredged material evaluations. Samples from Black Rock Harbor were used in the test vessel selection series and factorial experiments for the modified elutriate test development described in Part IV.

#### Channel Sediment and Water Sampling

#### Purpose and scope

159. The purpose of sediment and water sampling was to obtain adequate volumes of material for sediment characterization and for conducting the laboratory tests described in Part IV. In some cases these sampling operations required collection of unusually large volumes of sediment (approximately 50 gal) and of site water (approximately 100 gal) due to the large variety of laboratory test series to be performed and the need for test replication. Equipment and procedures

160. Channel sediments were sampled using grab-type samplers, except for the Savannah Harbor sediments, which were sampled directly at the sediment-water interface by a diving team. Both Peterson and Shipek samplers were used. These samplers have proven adequate for obtaining surface samples of bottom sediments reflecting the in situ density and water content of the sample (Palermo, Montgomery, and Poindexter 1978). The samples were taken by

repetitive grabs at the desired location until sufficient volume was obtained.

161. Site-water samples were obtained using a positive displacement pump, operating the intake within a few feet of the sediment-water interface. Care was taken to run the pumping apparatus for a sufficient length of time to allow approximately three times the combined tube volume to pass through the system before the sample was collected (Plumb 1981).

## Sampling rationale

162. Procedures for sediment sample collection, handling, and preservation must minimize sample contamination and preserve the physical and chemical integrity of the samples prior to testing. Plumb (1981) states that the value of data obtained from a sampling program is dependent on (a) collecting representative samples, (b) using appropriate sampling techniques, and (c) adequately preserving the samples. The first requirement regarding representative samples is especially difficult for sediments and dredged material because of the usually large variation. Plumb establishes the following criteria to define the representative nature of a sample:

a. The area to be sampled must be clearly defined.

- b. The sampling locations should be randomly distributed within the area.
- <u>c</u>. Replicate samples should be collected from each location unless variability has been established previously.

163. Random locations within the desired channel areas were sampled and composited to ensure a representative material for laboratory testing. Portions of the sediment and water sampling conducted for this study were for purposes of sediment characterization. This sampling was conducted so as to provide an areal representation of the area to be dredged. Samples from such an areal sampling were composited for purposes of some testing, e.g., for column settling tests.

164. Samples taken at the Mobile, Savannah, and Norfolk Harbor projects and used in laboratory studies were taken at locations corresponding to planned positions of the operating dredge during sampling at the confined disposal sites. In this way, sediment samples taken from the channel were more representative of material sampled during the field evaluation studies. Sample handling and preservation

165. Samples of channel sediment and dredging site water were placed in prepared 5-gal, airtight plastic containers. The containers were filled to

the top to prevent any entrapment of air upon sealing. The samples were immediately transported to the cold room and were maintained at 4° C until utilized for testing.

## Sampling operations

166. <u>Mobile Harbor</u>. Samples of channel sediment and water were collected from the Mobile Harbor project on three different occasions. During January 1982, 5-gal samples of channel sediment were taken at several stations. These samples were used for sediment characterization, and portions of the samples were then composited. The composite sample was used for column settling tests and for the test vessel selection test series described in Part IV.

167. Once plans were formulated for conducting the field verification studies at the Upper Blakely site in Mobile, Station MB 28 (see Figure 9) was selected for subsequent sampling. This was the planned location for the dredge during the subsequent field evaluation studies. During May 1982, 20 gal of channel sediment and 20 gal of near-bottom water were taken at Station MB 28. These samples were used in conducting the three-factor experiments described in Part IV. During July 1982, an additional 50 gal of sediment and 100 gal of water were collected at this same station. These samples were used in the column settling test, response surface experiments, and for the replicate set of modified elutriate tests as described in Part IV.

168. <u>Savannah Harbor</u>. Samples of sediment and water were taken at the Savannah Harbor site during August 1982. Samples were taken from the Back River (opposite disposal area No. 12) at the center station, shown in Figure 10. The sediment samples were taken directly at the sediment-water interface by a diving team at a short distance ahead of the operating dredge. This ensured that the sediment sample would be as representative as possible of material sampled during the field evaluation study. These samples were used for conducting the column settling test, response surface experiment, and the set of replicate modified elutriate tests described in Part IV.

169. <u>Norfolk Harbor</u>. Samples of sediment and dredging site water were collected from the Norfolk Harbor 45-ft channel during February 1983. Samples were taken immediately in front of the operating dredge at the time of the field evaluation at the Craney Island disposal area. This assumed that the sample of sediment taken would be as representative as possible of material

sampled at the disposal site. These samples were used in conducting the replicate set of modified elutriate tests described in Part IV.

170. <u>Black Rock Harbor</u>. During March and April 1982, an extensive sediment sampling program was conducted at Black Rock Harbor. The purposes of the sampling program were to physically and chemically characterize the sediments prior to dredging and to provide samples of sediment for all predictive laboratory testing for the FVP. The sediment sampling design was based on providing spatial coverage of the area to be dredged and sufficient sediment volume for all anticipated laboratory testing requirements.

171. During March 1982, samples were taken using a Peterson dredge at 10 evenly spaced center-line stations within the channel study reach for purposes of physical sediment characterization. Approximately 5 gal of sediment was obtained at each station. A composite of these samples was used in the test vessel selection series described in Part IV.

172. The samples for FVP chemical/biological testing were taken during

May 1982. A 45-ft workboat equipped with a large A-frame hydraulic winch and work platform was used for the sampling operation. An 18-in. box corer with 4-ft penetration was used to collect the samples at 26 locations within the channel. Chemical characterization for each location was conducted and the samples were then composited. A portion of the composite sample was used in the three-factor experiments described in Part IV.

# Testing Procedures

# Physical characterization

173. Physical characterization tests for sediments consisted of visual classification, Atterberg limits, and grain-size determinations. In some cases, characterization data were previously available. All characterization tests conducted for this study were performed by the WES Geotechnical Laboratory in accordance with standard soil testing procedures (Office, Chief of Engineers 1970). Samples were then classified according to the Unified Soil Classification System (USCS) (US Army Engineer Waterways Experiment Station 1953).

# Chemical characterization

174. Previous chemical data for sediments were available from baseline studies made in conjunction with environmental impact statements, routine

sediment studies, or similar studies. The bulk chemical composition of the sediments was available in all cases. In some instances these results were supplemented by standard elutriate tests. All chemical analyses were performed according to accepted procedures (American Public Health Association (APHA) 1981; EPA 1974a, 1974b; Plumb 1981), except where noted.

# Characterization Results

# Mobile sediments

175. <u>Physical characterization</u>. Physical characterization tests conducted on Mobile sediment samples included grain-size distribution, Atterberg limits, specific gravity, and in situ water content. All sediment samples were classified as highly plastic clay (CH) under the USCS. The Atterberg limits are shown in the plot of plasticity index versus liquid limit in Figure 12. The composite sample for the station 28 sediment was classified as a

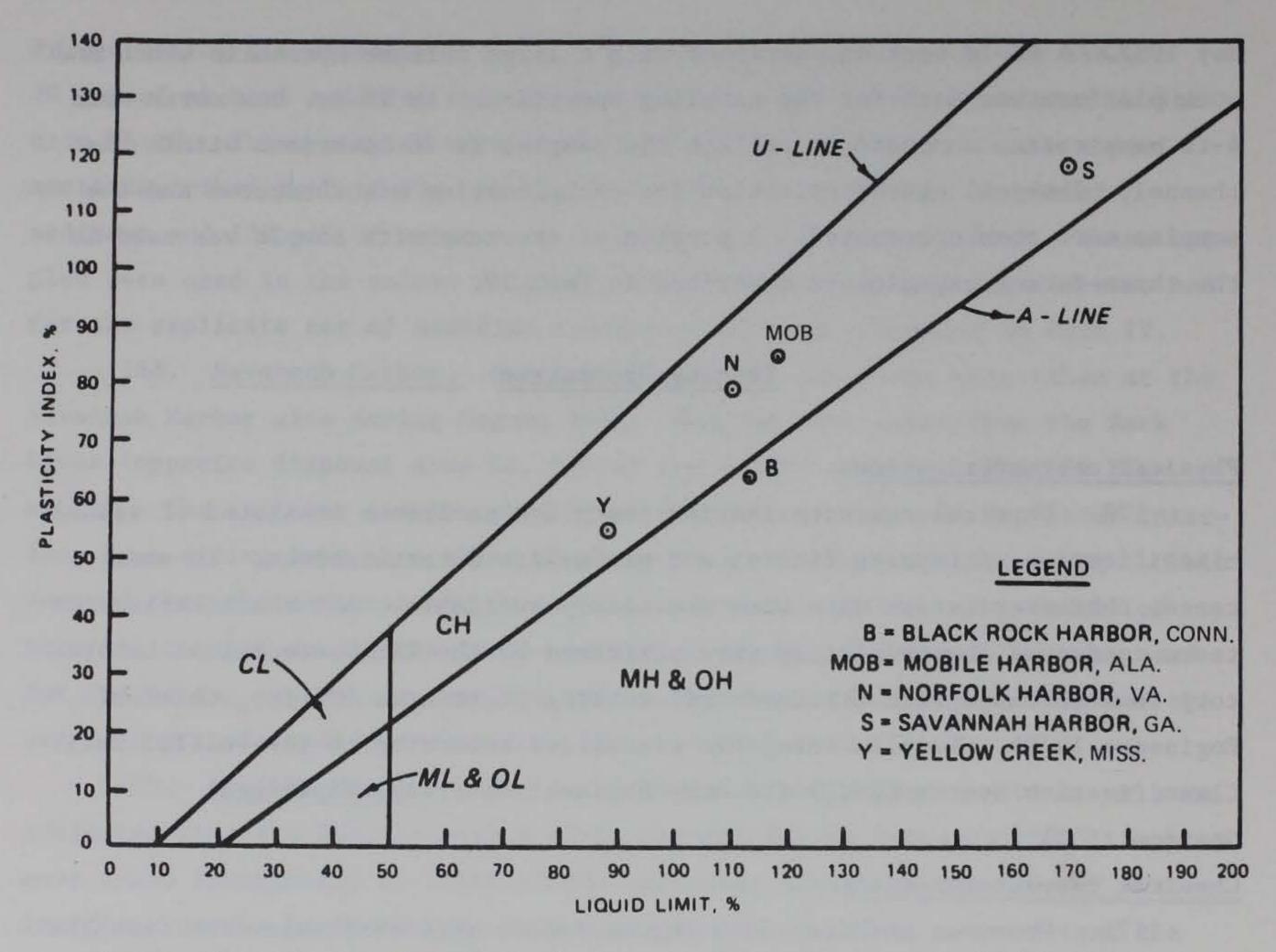


Figure 12. Plasticity chart showing distribution of liquid limits and plasticity indexes for sediment samples

gray highly plastic clay (CH) with less than 5 percent sand (retained on the #200 sieve). The physical characterization of the sediment samples compared closely with previous test results on dredged material samples taken from the same site (Palermo 1977a, 1977b).

176. <u>Chemical characterization</u>. Chemical characterization of the Mobile Bay sediment consisted of bulk sediment analyses and standard elutriate testing. The characterization testing was conducted by the Mobile District through two contracts. The bulk analysis was conducted on samples from stations MB 26 through MB 31, while elutriate testing was performed only on samples from station MB 28 (see Figure 9). The samples were analyzed for all 129 EPA priority pollutants. Results of this testing for selected parameters are summarized in Table 3 (Thompson Engineering Testing 1982, Environmental Protection Systems, Inc. 1982a). Concentrations of the many additional parameters which were measured but are not reported were below the limits of detection.

#### Savannah Harbor

177. <u>Physical characterization</u>. Physical characterization tests conducted on the composited sediment sample from Savannah Harbor included grainsize distribution, Atterberg limits, and specific gravity. The sediment was classified as a brownish gray, highly plastic clay (CH) using the USCS. Less than 5 percent of the material was sand (retained on the #200 sieve). The Atterberg Limits are plotted in Figure 12.

178. <u>Chemical characterization</u>. Chemical characterization of the Savannah Harbor sediments consisted of bulk sediment analysis of samples from the upstream, center, and downstream portions of the sediment basin (Savannah Laboratories and Environmental Services 1982). The results for the three stations were practically identical, as shown in Table 4. Standard elutriate tests were conducted for only one station, and the results are also shown in Table 4.

#### Norfolk Harbor

179. <u>Physical characterization</u>. Detailed physical characterization of Norfolk Harbor sediments was previously performed by Palermo, Shields, and Hayes (1981). The sediment from the area dredged during the field evaluation for this study was classified as a black, highly plastic clay (CH) with less than 5 percent sand. Atterberg limits are plotted in Figure 12.

180. <u>Chemical characterization.</u> A bulk sediment analysis was conducted on a sample collected for this study during the field evaluations (James R. Reed and Associates 1983). The results from the analysis of the bulk sediment and dredging site water are presented in Table 5.

# Other sites

181. Only results of physical characterization tests are presented for additional sediments used for physical testing and analysis of settling characteristics. The Yellow Creek sediments were classified as a brown, highly plastic clay (CH) with less than 3 percent sand. The Black Rock Harbor sediments classified as a black, sandy, organic clay (OH) with approximately 28 percent sand. This material also had a specific gravity of 2.44, unusually low for marine sediments. Atterberg limits for these sediments are plotted in Figure 12. 182. A bulk sediment chemical analysis was performed on the Black Rock Harbor composite sample, and the dredging site water used in the three-factor experiment is described in Part IV. Results are shown in Table 6.

3

# PART IV: DEVELOPMENT OF A MODIFIED ELUTRIATE TEST

## Considerations in Test Development

#### General

183. Prediction of contaminant levels in effluents from confined disposal areas requires the development of a suitable laboratory test to identify which contaminants may be released during a confined disposal operation and to predict the relative magnitude of release. This part describes the development of a modified elutriate test and the experimental design used to determine the influence of the various factors on the results obtained.

184. The modified elutriate test must be designed to simulate contaminant release under conditions of confined disposal--reflecting the (a) settling behavior of the dredged material, (b) retention time of the containment area, and (c) projected chemical environment. Also, practical requirements of a modified elutriate test procedure to be used in a regulatory program dictate that the test be able to be conducted in a reasonable time and at reasonable cost (Lee and Plumb 1974).

185. Gambrell, Khalid, and Patrick (1978) and Lee, Lopez, and Piwoni (1976) indicated that results of the standard elutriate test were influenced by solid-liquid contact time, agitation, oxidation conditions, and method of

solid-liquid separation. The proposed modified elutriate test development described in this chapter investigates the influence of these variables on the proposed test which simulates the confined disposal process.

186. Requirements which were considered to be important may be summarized as follows:

- a. The test must reflect the retention time and sedimentation regime expected to occur within the disposal area.
- b. The test must be adaptable to sediments of varying physical and chemical characteristics.
- <u>c</u>. The test must produce a supernatant with sufficient volume for analysis of contaminants.
- d. The laboratory test must be able to predict both the concentrations of dissolved contaminants and that fraction associated with the total suspended solids remaining in the supernatant under quiescent settling conditions.

e. The test must be such that it can be performed at reasonable cost by nonresearch-level laboratories normally employed by regulatory agencies.

#### Material dependency

187. Contaminant concentrations in effluents from disposal areas will be highly dependent upon the specific sediment dredged. Variations in specific contaminants present, their average concentrations, and the variability present within a given channel bottom area all contribute to a strong influence of the sediment to be dredged for test results.

188. Sediments exhibiting both flocculent and zone settling behavior and containing various classes of contaminants were used in the laboratory developmental work. This ensured that the procedures selected were adaptable to varying types of sediments. Samples used in the test development were obtained from projects in which both moderately and highly contaminated sediments were to be dredged.

## Vessel size

189. Retention times and settling behavior in confined disposal sites can best be simulated by a column settling test. Chen et al. (1978) recommended the use of some type of a column test for prediction of effluent water quality. Montgomery (1979) determined that columns at least 8 in. in diameter and as deep as the expected field depth are needed to describe the settling behavior of dredged material for purposes of disposal site design and evalua-

tion. However, the size of the sample required for such a large column and the associated sample preservation and handling problems make the routine use of this column by analytical laboratories difficult. In addition, the guidelines for evaluation of dredged material disposal normally require replication of tests. This requirement would increase the logistical difficulties of using a large column for modified elutriate tests. Therefore, selection of a smaller test vessel for use in the modified elutriate test was investigated. (It should be noted that no such replication is required for column settling tests performed solely for purposes of predicting effluent suspended solids concentrations.)

# Agitation/oxidation

190. Previous research (Lee, Lopez, and Piwoni 1976) had determined that contaminant release in the standard elutriate test is directly related to both the magnitude of the agitation applied and the level of oxidizing conditions present. The standard elutriate test calls for agitation by shaking for a period of 30 min. If it is known beforehand that dissolved oxygen concentrations may be increased during disposal, compressed air mixing is used. For the modified elutriate test, compressed air mixing was investigated as a preferred method of agitation since the confined disposal process will expose the dredged material to oxidizing conditions--both from the fall and splash of the water during entry and from surface aeration during retention (Gambrell, Khalid, and Patrick 1978). Field evaluations conducted as part of this study confirmed that oxidizing conditions developed in ponded supernatant water.

## Retention time

191. The differences between modified and standard elutriate testing are especially critical with regard to solid-liquid separation. The standard elutriate test is solely designed to obtain a suitable sample for analysis of the constituents released during open-water disposal. It calls for analysis of the soluble fraction obtained by 1 hr of settling, followed by complete separation of solids by centrifugation and/or filtration. Conditions existing in confined disposal areas are not well simulated by such a short retention time or by analysis of the soluble fraction only since it is anticipated that a significant fraction of the contaminants released from the containment area will be discharged as adsorbates on fine particles which do not settle.

192. For modified elutriate testing, an analysis of both the dissolved

constituents and those adsorbed on, or associated with, suspended solids is more appropriate (Lu et al. 1978). Furthermore, since settling time in a confined disposal site is highly variable, a representative supernatant requires a settling time during the test corresponding to the retention time expected in the proposed disposal site under evaluation.

# Sediment concentration

193. The standard elutriate test calls for a 1:4 ratio of sediments to water on a volume basis. This is not representative of influent slurry concentrations for confined disposal areas. Montgomery (1979) determined that the concentration of dredged material slurries has a major effect on their settling behavior. Variation of the sediment concentration in the modified elutriate test was therefore evaluated and its resulting effect on contaminant release determined.

# Test Vessel Selection

# Objective

The objective of this testing was to select a smaller test vessel 194. for the modified elutriate test based on examination of the concentration and grain-size distribution of supernatant particles. Settling tests were performed on several sediments using the 8-in.-diam settling column as a reference and a variety of smaller cylinders and vessels.

# Test vessels

195. Several smaller vessels were selected for testing, including:

- a. A 2-L flask (selected because this is the test vessel now used for the standard elutriate test).
- A 2-l graduated cylinder (selected to compare results using b. the flask and a cylinder of identical volume). This comparison is considered necessary because a column configuration has advantages for bubble aeration due to more efficient air-water contact and more effective agitation of the slurry.
- c. A 4-l graduated cylinder (selected because this is the largest easily obtainable graduated cylinder).
- An 8-in.-diam settling column. d.
- Beakers and glass vessels (approximately 8 in. in diameter; e. used to determine the effect of cylinder diameter).

Determination of total suspended solids

196. Samples were extracted from the supernatant of the test vessels using a syringe and 3/16-in. inside diameter tubing. Small-diameter pipettes were not used because the dredged material flocs could potentially be broken (Gibbs and Konwar 1982). Total suspended solids concentrations were then determined. Generally, it was found that sediments which exhibited gross zone settling behavior left low suspended solids concentrations (on the order of tens of milligrams per litre) in the supernatant, and filtration was required for analysis. Sediments exhibiting gross flocculent settling behavior left much higher concentrations (on the order of tens of grams per litre) in the supernatant, and direct gravimetric means could be used for analysis.

197. Supernatant suspended solids samples were filtered by a vacuum filtration apparatus and cellulose filters with an opening of 0.45 µm. This opening has traditionally been considered as the transition between suspended and dissolved fractions in past dredged material criteria development studies

(Plumb 1981). Sample volumes between 50 and 100 mg were used, with the sample size adjusted according to the estimated levels of solids in the samples. Determination of grain-size distribution

198. The grain-size distributions of supernatant samples were determined using an optical instrument due to the extremely low concentrations of suspended solids in the samples. The samples were analyzed by the US Department of Agriculture Southwest Rangeland Research Center in Tucson, Ariz., using a Leeds and Northrup Microtrac Particle-Size Analyzer. This instrument is capable of detecting particle sizes from approximately 0.8  $\mu$ m to 177  $\mu$ m using the principal of low-angle forward-scattering of laser light in conjunction with optical filtering. Haverland and Cooper (1981) found the Microtrac to be an expedient and reliable technique for determination of grain-size distribution. Samples of approximately 250 mg were required for the analysis because of the low suspended solids concentrations. A 10 percent formaldehyde solution was added to the samples prior to shipment to prevent bacterial growth and subsequent masking of true grain-size distribution. Data analysis

199. The means and variances of total suspended solids concentration and average particle size values for supernatant samples extracted at the same retention time from the 8-in. settling column and small test vessels were compared using a t-test and F test, respectively. The null hypothesis was

assumed, i.e. that there is no significant difference between the means or variances and that the two samples were drawn from the same population. The F test is an indication of whether the variations between data sets are significantly different from variations within data sets. The t-test is an indication of whether the means of data sets are significantly different.

200. The t- and F tests were conducted using a TTEST procedure available on the Statistical Analysis System (SAS) (SAS Institute Inc. 1982a, 1982b). The TTEST procedure computes the t- and F statistics and the probability of obtaining a greater absolute value of the t- or F statistics. Therefore, a calculated significance probability  $\alpha = 0.05$  corresponds to a 95 percent level of confidence that the null hypothesis can be rejected and that the means or variances are significantly different.

## Mobile Harbor test series

201. The initial tests were conducted using sediments from Mobile Harbor (composite). The objectives of this test series were as follows:

- <u>a</u>. Define the basic relationship between initial concentration of slurry (C) and retention time (T) in producing appropriate supernatant volumes for sample extraction for a typical saltwater sediment exhibiting zone settling behavior.
- b. Develop appropriate laboratory techniques for extraction of supernatant samples.
- <u>c</u>. Determine limitations of vessel size in producing acceptable quantities of supernatant for anticipated analytical needs.
- d. Directly compare total suspended solids concentration and grain-size distribution of supernatant particles for small test vessels and the 8-in. reference settling column.
- e. Determine the need for test replication in comparisons of concentrations and grain size of suspended solids in the supernatants.

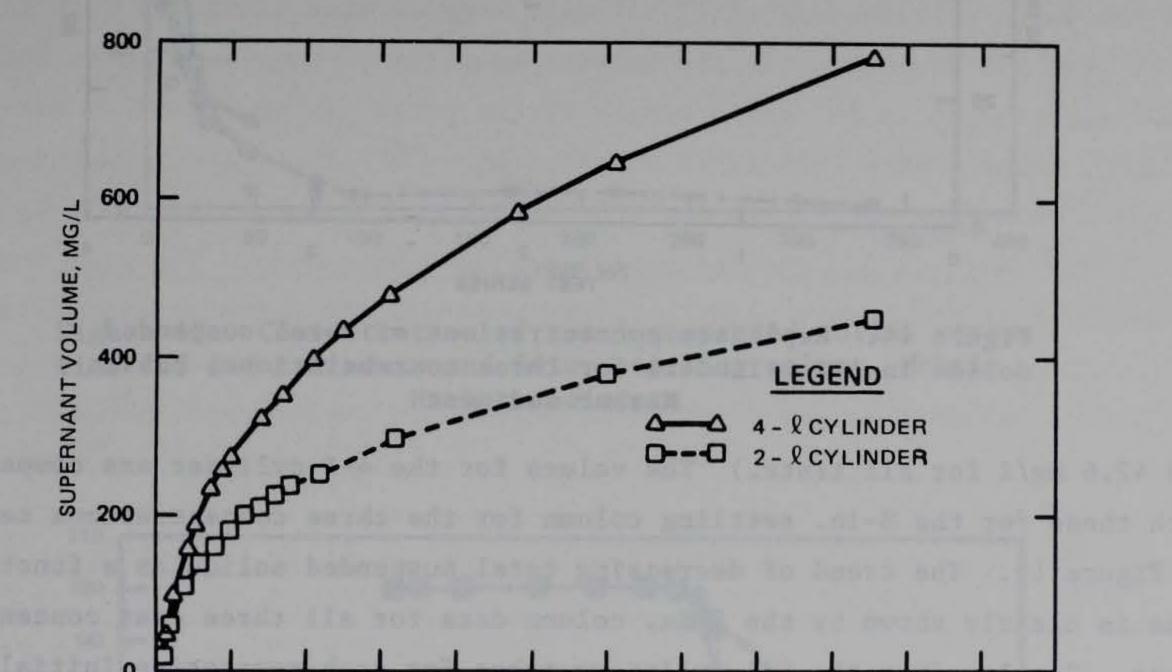
202. Summary of test procedures. Sediments from a saltwater environment generally exhibit zone settling, with settling velocity a function of initial slurry concentration (C). Therefore, column tests were run on slurries at three concentrations, C = 62 g/l, 108 g/l, and 155-g/l. Samples were extracted from the 8-in. settling column from side ports located at heights between 6.0 and 2.4 ft as the interface cleared the ports. The 62-g/land 108-g/l tests were continued for 48 hr. The 155-g/l test was continued for 15 days. The 2-l flasks, 2-l graduated cylinders, and 4-l graduated cylinders were loaded concurrently with the 8-in. column for each concentration. Tests were run in triplicate for each small vessel, yielding a total of

27 small-vessel tests. Samples for a given concentration were extracted simultaneously from the small vessels and the 8-in. settling column at a retention time (T) when sufficient supernatant volume (400 to 500 ml) had developed in all small vessels for analysis of total suspended solids and grain-size distribution.

203. <u>Results of total suspended solids comparisons.</u> A syringe and glass tubing were found to be a satisfactory method of sample extraction from the small test vessels. Decanting was attempted, but resulted in significant resuspension of settled material. Syringe and tubing were therefore used as a sample extraction technique for all subsequent tests. A very low concentration of total suspended solids (in the milligram-per-litre range) was found in all tests.

204. A satisfactory volume of supernatant had not developed until T = 6, 10.5, and 48 hr for the 2-l vessels at C = 62, 107, and 155 g/l, respectively. The rates of supernatant volume development as a function of

time for C = 155 g/l for the 2-l and 4-l cylinders are shown in Figure 13. The required 400-ml volume was developed in approximately 7 hr for the 4-l cylinder, but required 48 hr in the 2-L cylinder. Results for the other concentrations tested were similar. This factor places a severe limitation on the use of 2-L vessels when samples must be extracted at a relatively small T using initial slurry concentrations approaching those normally encountered in the field. It was therefore concluded that the 2-L vessels were unsatisfactory for use in the modified elutriate procedure. These vessels were not used in subsequent total suspended solids and grain-size test series.



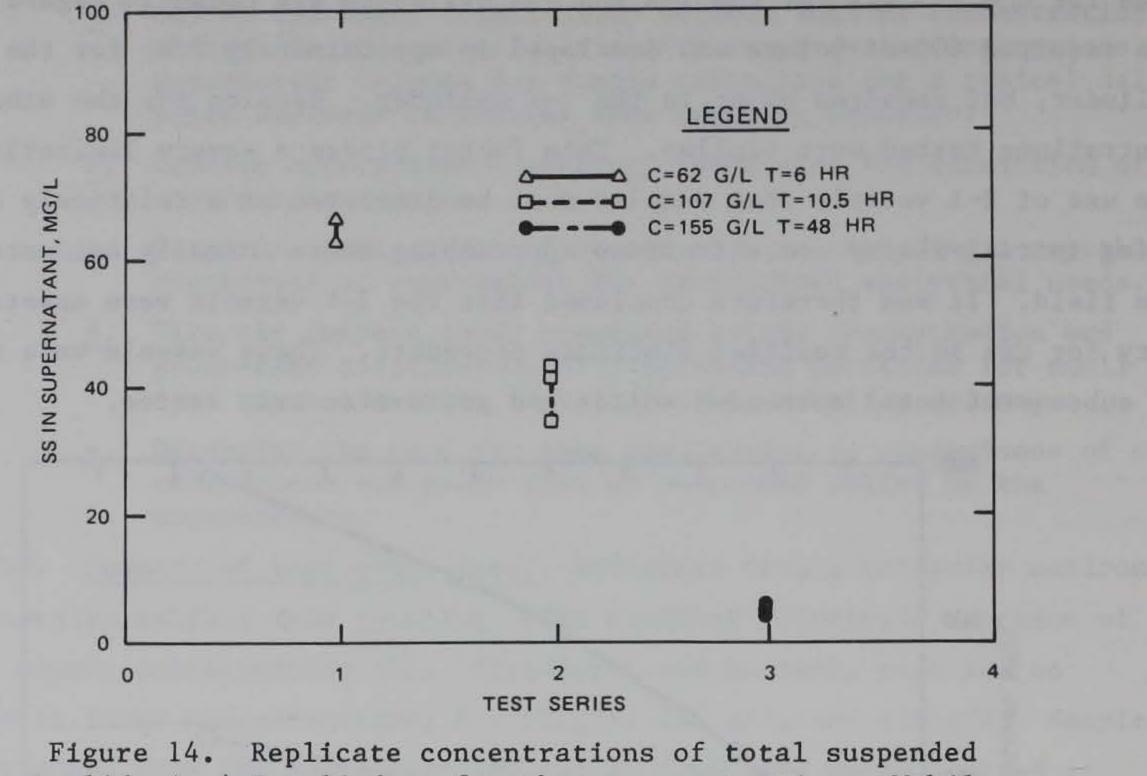
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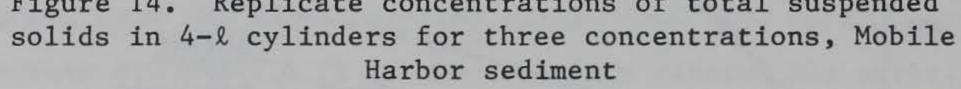
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Supernatant water volume versus retention time for 2-L Figure 13. and 4-1 cylinders at 155 g/l, Mobile Harbor sediment

The total suspended solids concentrations for three replicates at 205. each respective combination of C and T were extremely close for all small vessels tested. A plot of total suspended solids for the three 4-L cylinder replicates at the three concentrations tested is shown in Figure 14. Results for other small vessels tested were similar. Based on these excellent results, no additional replication was used in later small vessel comparison tests.

206. The values of total suspended solids from the 4-L cylinder were significantly different ( $\alpha > 0.05$ ) from values from the 8-in. reference settling column. (The 4-1 cylinder mean was 36.5 mg/1, and the 8-in. column mean





was 42.6 mg/l for all tests.) The values for the 4-l cylinder are compared with those for the 8-in. settling column for the three concentrations tested in Figure 15. The trend of decreasing total suspended solids as a function of time is clearly shown by the 8-in. column data for all three test concentra-

tions. Samples from the 4- $\ell$  cylinders taken for each respective initial concentration show a similar trend with slightly lower values at equivalent times of extraction. In order to define this comparison more fully as a function of time, samples were taken from the 4- $\ell$  cylinders at various time intervals for the subsequent test series with Yellow Creek sediments.

207. <u>Results of grain-size distribution comparisons.</u> The mean particle sizes for all samples extracted from the 4- $\ell$  cylinder and the 8-in. settling column were not significantly different at the 95 percent confidence level for the three C and T combinations tested. The average grain-size distributions for three replicates for the 62-g/ $\ell$  tests are shown in Figure 16. Yellow Creek test series

208. A second test series for purposes of test vessel selection was run using sediment from the Yellow Creek disposal area (a freshwater sediment). The objectives of this test series were the following:

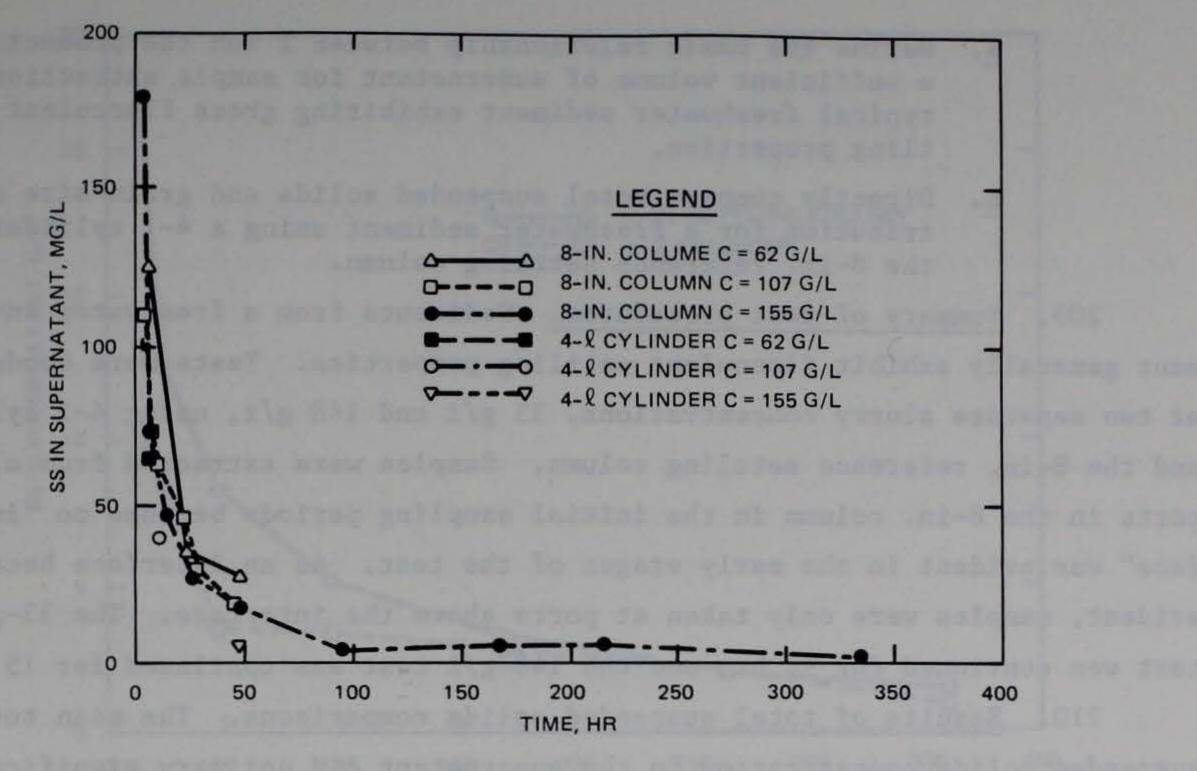


Figure 15. Concentration of total suspended solids versus time for 4-L cylinders and 8-in. settling column, Mobile Harbor sediments

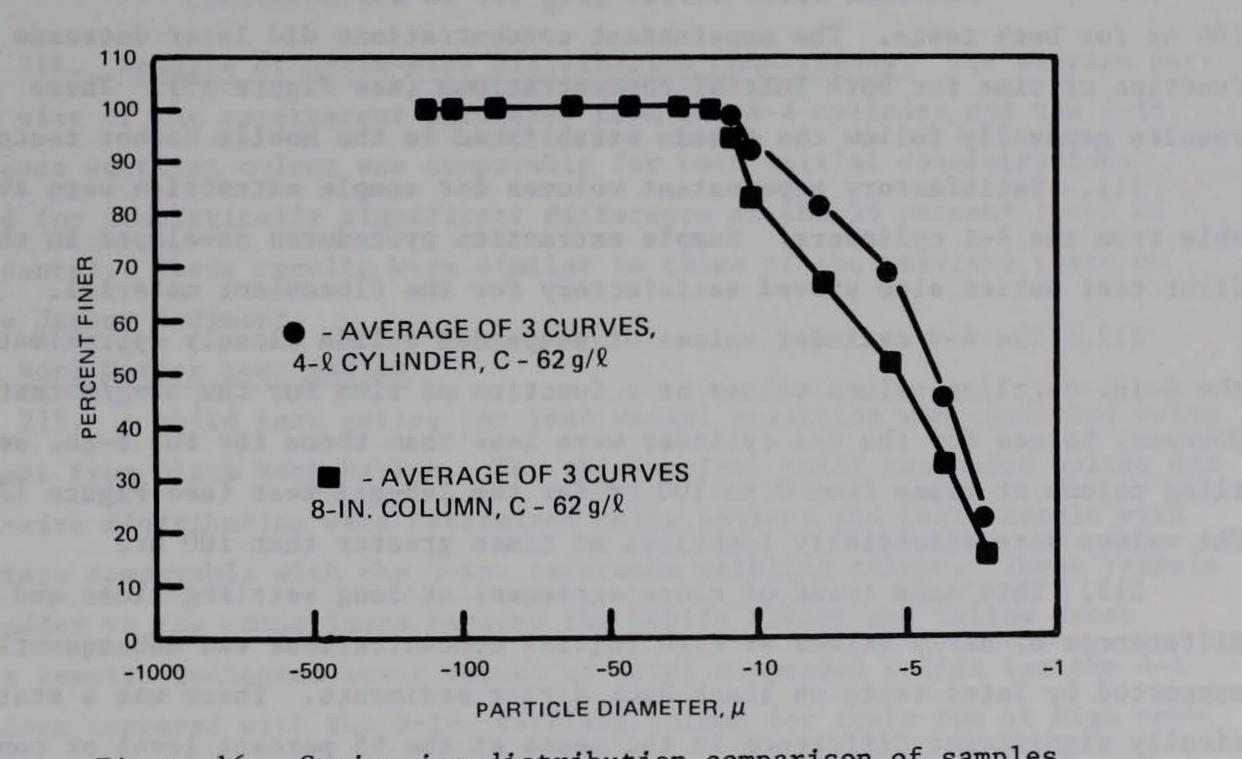


Figure 16. Grain-size distribution comparison of samples from 4-l cylinders and 8-in. settling column for slurry concentrations of 62 g/l, Mobile sediments

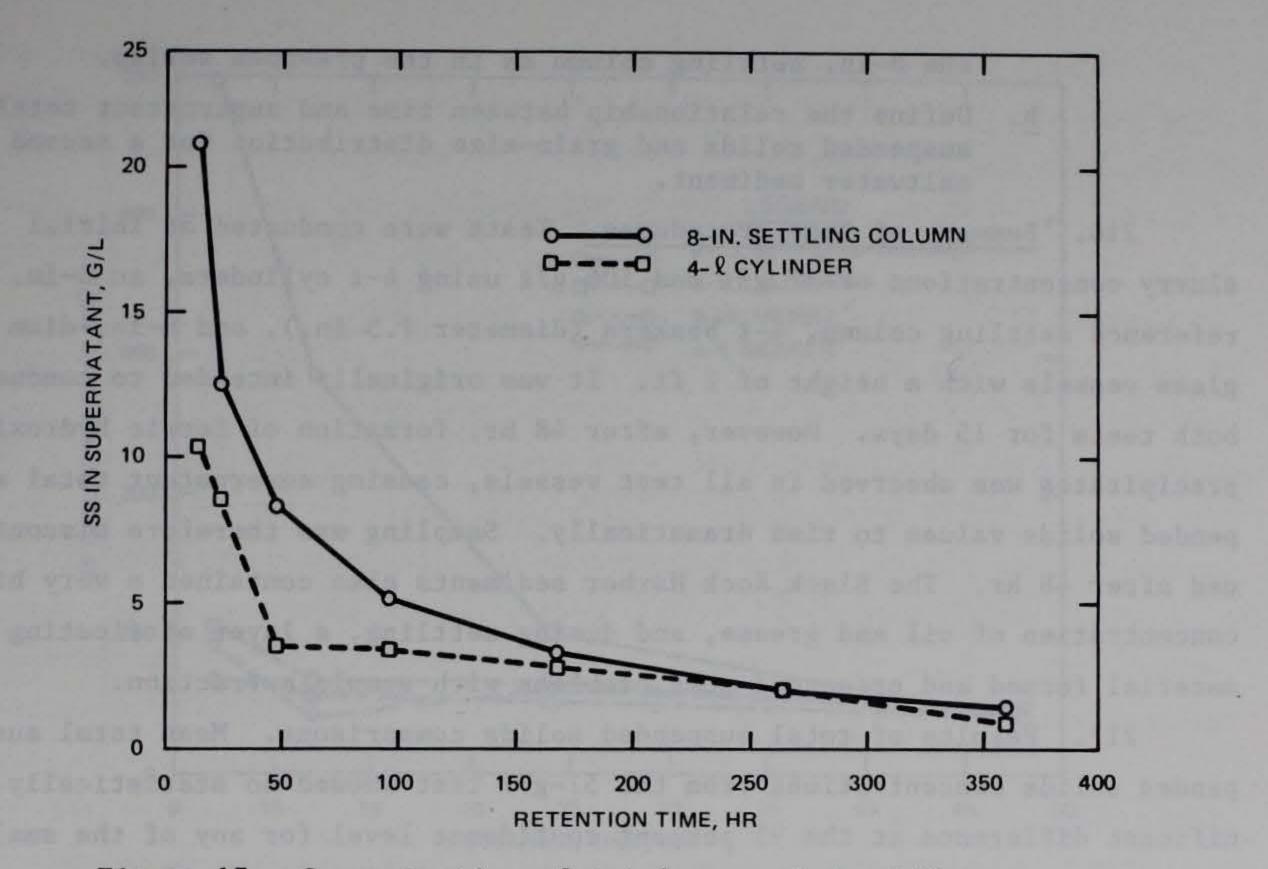
- a. Define the basic relationship between T and the production of a sufficient volume of supernatant for sample extraction for a typical freshwater sediment exhibiting gross flocculent settling properties.
- b. Directly compare total suspended solids and grain-size distribution for a freshwater sediment using a 4-l cylinder and the 8-in. reference settling column.

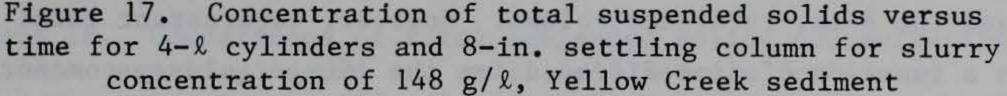
209. Summary of test procedures. Sediments from a freshwater environment generally exhibit flocculent settling properties. Tests were conducted at two separate slurry concentrations, 33 g/l and 148 g/l, using 4-l cylinders and the 8-in. reference settling column. Samples were extracted from all ports in the 8-in. column in the initial sampling periods because no "interface" was evident in the early stages of the test. As an interface became evident, samples were only taken at ports above the interface. The 33-g/ltest was continued for 96 hr, and the 148-g/l test was continued for 15 days.

210. <u>Results of total suspended solids comparisons.</u> The mean total suspended solids concentration in the supernatant did not vary significantly at the 95 percent confidence level for the two initial concentrations tested. The values measured in the 8-in. reference column supernatant had decreased from approximately 20 g/l at 10 hr to approximately 5 g/l after approximately 100 hr for both tests. The supernatant concentrations did later decrease as a function of time for both initial concentrations (see Figure 17). These results generally follow the trends established in the Mobile Harbor tests. 211. Satisfactory supernatant volumes for sample extraction were available from the 4-l cylinders. Sample extraction procedures developed in the first test series also proved satisfactory for the flocculent material.

212. The 4- $\ell$  cylinder values of suspended solids closely approximated the 8-in. settling column values as a function of time for the 33-g/ $\ell$  test. However, values for the 4- $\ell$  cylinder were less than those for the 8-in. settling column at times from 0 to 100 hr for the 148-g/ $\ell$  test (see Figure 17). The values were essentially identical at times greater than 100 hr.

213. This same trend of close agreement at long settling times and differences of early values at high initial concentrations was subsequently supported by later tests on Black Rock Harbor sediments. There was a statistically significant difference in the means at the 95 percent level of confidence for some specific times of extraction for each of these tests. However, the difference in means was not statistically significant for the full test.





214. <u>Results of grain-size distribution comparisons.</u> The average particle size of the supernatant particles from the 4-l cylinder and the 8-in. reference settling column was comparable for both initial concentrations tested (no statistically significant difference at the 95 percent level of confidence). These results were similar to those of the previous tests on Mobile Harbor sediment.

#### Black Rock Harbor test series

215. A third test series for test vessel selection was conducted using sediment from Black Rock Harbor. For this series, total suspended solids and grain-size distribution were determined using beakers and test vessels with diameters comparable with the 8-in. reference settling column. These vessels were added to the comparisons because the Mobile Harbor and Yellow Creek series results indicated lower values of total suspended solids for the 4- $\ell$ cylinders compared with the 8-in. settling column for tests run at high concentrations. The objectives of this series were the following:

a. Directly compare concentration and grain-size distribution of suspended solids for the 4-L cylinder, 8-in. test vessels, and

the 8-in. settling column as in the previous series.

b. Define the relationship between time and supernatant total suspended solids and grain-size distribution for a second saltwater sediment.

216. Summary of test procedures. Tests were conducted at initial slurry concentrations of 57 g/ $\ell$  and 106 g/ $\ell$  using 4- $\ell$  cylinders, an 8-in. reference settling column, 4- $\ell$  beakers (diameter 7.5 in.), and 8-in.-diam glass vessels with a height of 2 ft. It was originally intended to conduct both tests for 15 days. However, after 48 hr, formation of ferric hydroxide precipitates was observed in all test vessels, causing supernatant total suspended solids values to rise dramatically. Sampling was therefore discontinued after 48 hr. The Black Rock Harbor sediments also contained a very high concentration of oil and grease, and during settling, a layer of floating oil material formed and presented some problems with sample extraction.

217. <u>Results of total suspended solids comparisons.</u> Mean total suspended solids concentrations from the  $57-g/\ell$  test showed no statistically significant difference at the 95 percent confidence level for any of the small vessels and the 8-in. reference column. However, supernatant total suspended solids as a function of time differed for the  $106-g/\ell$  slurry concentration in the early hours of the tests (see Figure 18). Mean concentration differences were statistically significant at the earlier retention times. At times greater than 24 hr, the small vessel concentrations showed no significant dif-

ference from the 8-in. column. For both initial concentrations, the total suspended solids reached values of approximately 50 mg/l at times greater than 10 hr for all small vessels.

218. The values from the 4-1 cylinders and 8-in.-diam beaker and vessel were practically identical for both tests. Based on these results, small 8-in.-diam vessels hold no advantage over 4-1 cylinders in producing supernatants with total suspended solids concentrations comparable to those in 8-in. settling columns.

219. <u>Results of grain-size distribution comparisons.</u> The number of  $4-\ell$  columns tested for the Black Rock Harbor sediment allowed determinations of grain-size distributions as functions of time. The change in grain-size distribution from the  $4-\ell$  cylinder for times of 5 to 48 hr is shown in Figure 19. A definite shifting from finer to coarser particle sizes is found. This is likely due to formation of flocs by smaller particles and/or the increase in

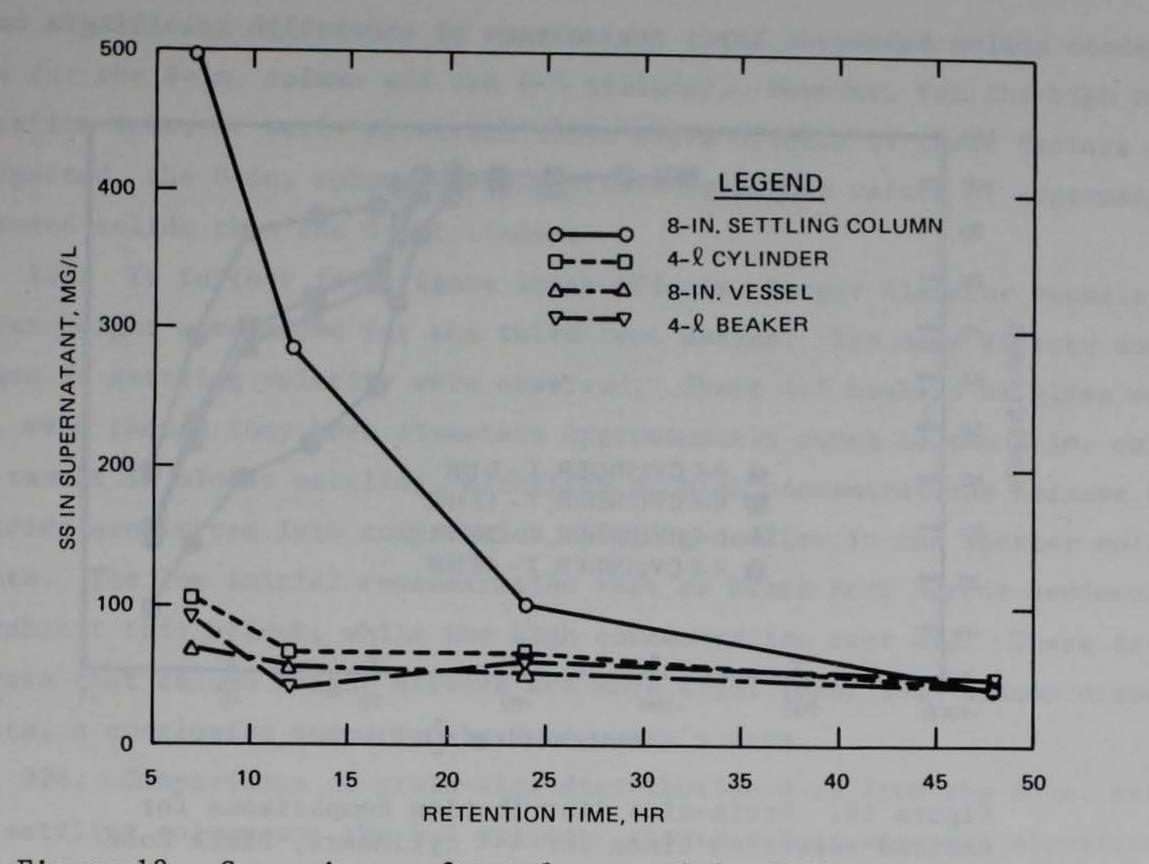


Figure 18. Comparisons of total suspended solids concentration for 8-in. settling column and small test vessels for slurry concentration of 106 g/l, Black Rock Harbor sediment

particle size due to the early stages of ferric hydroxide precipitation. This trend was not observed in the 8-in. settling column. As with the previous

test series, mean particle diameters showed no significant difference at the 95 percent confidence level.

#### Summary and discussion

220. The first test series with Mobile Harbor sediment demonstrated that 2-& vessels were of insufficient volume for sample extraction, and these vessels were therefore eliminated from further testing. The 4-& graduated cylinder was found to yield adequate supernatant volumes of 400 to 500 m& at retention times of approximately 6 hr, and satisfactory techniques of sample extraction were developed using syringe and glass tubing. These findings were also supported by the second test series using freshwater sediment from the Yellow Creek project.

221. In both the Mobile Harbor and Yellow Creek tests, there was a significant difference (95 percent confidence level) in supernatant total suspended solids concentration between those from the 8-in. reference settling

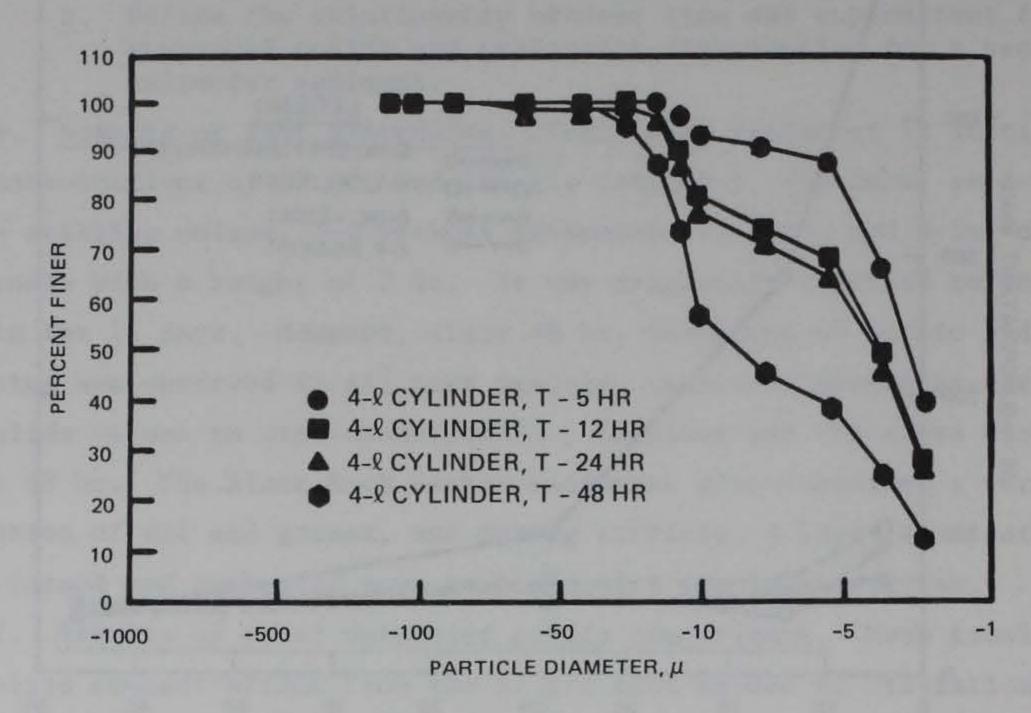


Figure 19. Grain-size distribution comparisons for various retention times for 4-L cylinders, Black Rock Harbor sediment

column and the 4- $\ell$  cylinder for retention times less than 48 hr for those tests conducted at initial slurry concentrations greater than 100 g/ $\ell$ . At longer retention times and for the entire group of data, there was no significant difference. No significant difference in mean total suspended solids was observed for tests conducted at low initial slurry concentrations. This variation in results may be explained by apparent wall and column height effects when conducting settling tests in small diameter columns at relatively high slurry concentrations, confirming the observations of Montgomery (1978).

222. Both the Mobile Harbor and Yellow Creek test series clearly reflected the trends described by Montgomery. Wall and column height effects were not significant in the 8-in. reference settling column because settling velocities were higher, and water was forced to flux through the sediment mass to a greater degree. This resulted in a higher concentration of fine particles expelled into the supernatant. This phenomenon was supported by results of the third test series on Black Rock Harbor sediments, in which settling tests were conducted at a low initial concentration of 57 g/ $\ell$  and a higher initial concentration of 106 g/ $\ell$ . For the low concentration test, in which bridging and column height would not be expected to be a major factor, there was no significant difference in supernatant total suspended solids concentrations for the 8-in. column and the 4- $\ell$  cylinder. However, for the high concentration test, at early retention times where effects of these factors would be expected, the 8-in. column had significantly higher values of supernatant suspended solids than the 4- $\ell$  cylinder.

223. To further investigate these effects, larger diameter vessels of shorter height were added for the third test series. The same effects due to changes in settling velocity were observed. Short 4-l beakers or glass vessels, even though they have diameters approximately equal to the 8-in. column, will result in slower settling velocities at high concentrations because the particles are forced into compression settling earlier in the shorter column heights. The low initial concentration test on Black Rock Harbor sediment did not exhibit this effect, while the high concentration test did. These data indicate that column height effects are more significant than column diameter effects, a conclusion supported by Montgomery's data.

224. Comparisons of grain-size distribution data from the 8-in. reference settling column and the 4-& cylinder showed values were not significantly different for all three sediments tested. This indicates that supernatant particles are essentially of like composition and size, with like affinity for association of contaminants by physical and chemical bonding, regardless of the concentration of total suspended solids in the supernatant. The particles will also be subjected to the same potential physicochemical changes in the field (i.e. changes in dissolved oxygen, pH, temperature, etc.), regardless of the concentration. For these reasons, grain-size distribution is a more important physical factor than total suspended solids concentration when comparing supernatant particles for purposes of test vessel selection. 225. Based on the above findings, the 4-& cylinder was selected as an appropriate test vessel for subsequent laboratory testing. This vessel was subsequently used in all modified elutriate tests.

226. The differences in total suspended solids concentrations of supernatants between the small test vessels and the 8-in. reference column were accounted for in the final development of a technique for predicting water quality of the effluents from confined disposal areas. The 4-& cylinders were used in the modified elutriate test to determine the relative concentration of dissolved parameters (in milligrams per litre) and the contaminant fraction of the total suspended solids (SS) (in milligrams per kilogram SS). The 8-in. settling columns must be used for predicting the effluent suspended solids concentrations as a function of time.

#### Three-Factor Experiments

#### Experimental design

227. The literature indicated that the major factors that will influence the degree of contaminant release for a specific sediment under laboratory conditions are agitation/oxidation, sediment concentration, and retention time. The relative degree of release will be a summation of the effects of these factors. Evaluation of their relative importance and potential interactions can be done by a factorial experiment. Therefore, factorial experiments (three-factor) were conducted on sediments from Mobile Harbor and Black Rock Harbor. The purpose of these experiments was to develop the basic mechanics of conducting modified elutriate tests and to evaluate the significance of the three test factors which could be varied as part of the test procedure.

228. A series of tests was conducted, holding one factor constant in each test series. A schematic of the Mobile Harbor three-factor experiment is shown in Figure 20. All tests were conducted using the 4-1 cylinder that was selected as the standard test vessel as a result of the experiments described

previously.

229. The procedure was a straightforward application of the factorial three-factor experiment described by Kennedy and Neville (1974). The three factors of aeration time, initial sediment concentration, and retention time (designated A, C, and T) were evaluated at two levels each, yielding a total of eight experiments, each with three replicates. Replication was kept to the minimum required for statistical analysis because of the high analytical costs involved. The dependent variable was the concentration or value of a specific parameter. The values for A, C, and T are shown in Table 7. Parameters were selected for analysis based on which contaminants were present in the bulk sediment analyses of the particular sediment. A list of the parameters analyzed is shown in Table 8.

#### Equipment and procedure

230. <u>Apparatus.</u> The following items were used in conducting the threefactor experiments:

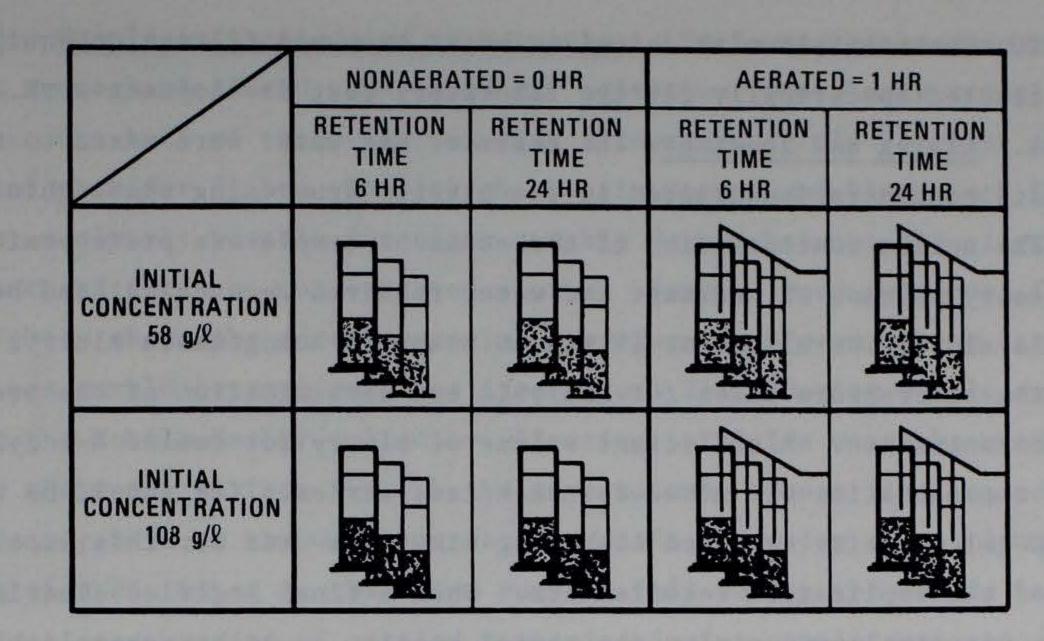


Figure 20. Schematic illustration of three-factor experiment for Mobile Harbor sediment

- a. Plastic drum (40-gal capacity) and Lightning mixer with stainless steel shaft and blades used for mixing sediment and dredging site water.
- b. Box-type laboratory shaker capable of shaking four 1-gal jars

at 100 excursions per minute.

- <u>c</u>. Manifold with deionized water trap and 3/16-in. inside diameter tubing for use in compressed air agitation.
- <u>d</u>. Vacuum filtration equipment consisting of vacuum pump, manifold, and multiple ports for filtration of samples.
- e. Graduated cylinders (4 l) and assorted glassware for sample extraction and handling.
- f. Wide-mouth, 1-gal capacity glass jars with Teflon-lined screwtype lids for holding samples during mechanical agitation.
- g. Sample bottles (200 ml) and reagents for sample preservation.
- h. Instruments for direct determination of temperature, pH, dissolved oxygen, salinity, and conductivity.

231. Prior to use, all glassware, filtration equipment, filters, and equipment to be used in sample preparation were thoroughly cleaned and prepared. After washing with detergent, the apparatus was rinsed four times with tap water, once with reverse osmosis water, and placed in a 20 percent HCl acid bath for a minimum of 1 hr. After soaking in the acid bath, the apparatus was rinsed five times with reverse osmosis water and five times with deionized water. Filters were presoaked for 2 hr in a 5-molar HCl bath and then rinsed 10 times with distilled water. 232. The manifold with deionized water trap and filtration equipment was constructed specifically for the laboratory test development work.

233. <u>Mixing and loading.</u> The sediment and water were mixed to the approximate concentration desired in the plastic drum using the Lightning mixer. The solids concentration of the sediment sample was predetermined and the necessary volumes of sediment and water required were calculated beforehand. The slurry was mixed for 15 min to ensure a homogeneous slurry. Samples of the slurry were taken for analysis and determination of the precise solids concentration. A sufficient volume of slurry for twelve 4-l cylinders of equal concentration was mixed for each test series. (It should be noted that a 40-gal capacity drum and Lightning mixer was used for this experiment because of the replication requirements. Once a final modified elutriate test procedure was developed, mixing for normal testing could be accomplished by a small laboratory mixer.)

234. The cylinders were filled in groups of three. One-gallon jars were filled with the slurry and immediately placed in the box-shaker. The jars were mechanically agitated for 5 min. Following shaking, the slurry was poured into the cylinders. Cylinders which were to be treated with compressed air bubbling were filled first. (It should be noted that mechanical agitation was included as a step in the developmental work because of its use in the standard elutriate test. Observations during the test indicated that bubble aeration would provide sufficient mixing and agitation. Therefore, mechanical agitation was not specified in the final test procedure.)

235. Glass tubing was inserted to the bottom of the cylinders to be bubbled, and agitation was initiated immediately. Air bubbling was continued for 1 hr, at which time the glass tubes used for agitation were raised to the appropriate level for later sample extraction. The slurry was then allowed to settle. In the cylinders not bubbled the slurry was allowed to begin settling immediately after filling and insertion of tubes for sample extraction was completed.

236. The initial slurry mixing and the four filling, shaking, and loading cycles for 12 columns required approximately 45 min. The entire process described above was repeated for two initial slurry concentrations in each experiment. The final Mobile Harbor initial slurry concentrations were 59 g/ $\ell$ and 108 g/ $\ell$ . The final Black Rock Harbor initial slurry concentrations were 39 g/ $\ell$  and 114 g/ $\ell$ .

Sample extraction and preservation. Following either mechanical 237. agitation or mechanical and compressed air agitation, the slurry was allowed to settle. One-half of the cylinders were allowed to settle for 6 hr and one-half of them for 24 hr. In both the Mobile Harbor and Black Rock Harbor cylinders, a clearly visible interface quickly formed between the clarified supernatant and the more concentrated slurry. Samples were extracted from a point slightly above the interface using a syringe and Tygon tubing attached to the glass sample extraction tubes (see Figure 21). During sample extraction from the Mobile Harbor cylinders, floating particles were observed to fall from the water surface through the supernatant. These floating particles were evidently held at the water surface by surface tension as settling began. They were then dislodged as the water surface fell during the sample extraction. Minor resuspension of settled particles during sample extraction was also unavoidable. This problem was also evident with the Black Rock Harbor tests, which also had a layer of floating oil at the surface.

238. Whenever possible, a total of 1,250 ml of sample was extracted. The sample was siphoned into a 2,000-ml beaker, immediately stirred vigorously, and split into aliquots designated AB through G. Each of the aliquots was then processed as shown in the flow diagram in Figure 22.

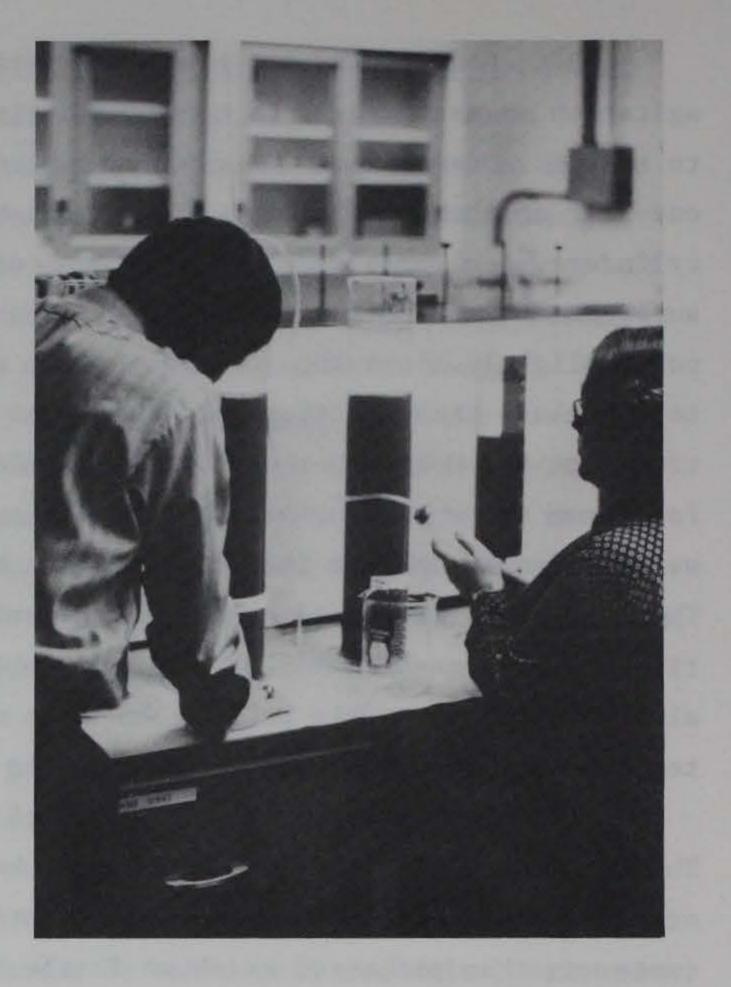
239. The aliquots were used as follows:

a. The AB aliquot (450 ml) was used to obtain samples for analysis of dissolved concentrations of metals and nutrients. The

sample was placed in the filtration apparatus and filtered using a prerinsed 0.45- $\mu$ m filter. The first 50 ml of sample was discarded. The filtered sample was then split into equal aliquots (A and B) for analysis. Samples for analysis of metals were preserved by lowering to pH < 2.0 using ultrapure HNO<sub>3</sub>. Samples for analysis of nutrients were preserved by lowering to pH < 2.0 using ultrapure H<sub>2</sub>SO<sub>4</sub>. All samples were then placed in the cold room to await analysis.

- b. The C aliquot (200 ml) was used for analysis of total metals. The sample was digested using standard procedures (EPA 1974a).
- <u>c</u>. The D aliquot (100 ml) was used for determination of total and dissolved mercury.
- <u>d</u>. The E aliquot (250 ml) was used for analysis of total nutrients.
- e. The F aliquot (200 ml) was used for determination of the physicochemical parameters of temperature, salinity, dissolved oxygen, pH, and conductivity. This aliquot was then preserved with a 10 percent formaldehyde solution and used for

Figure 21. Sample extraction in progress using syringe and tubing



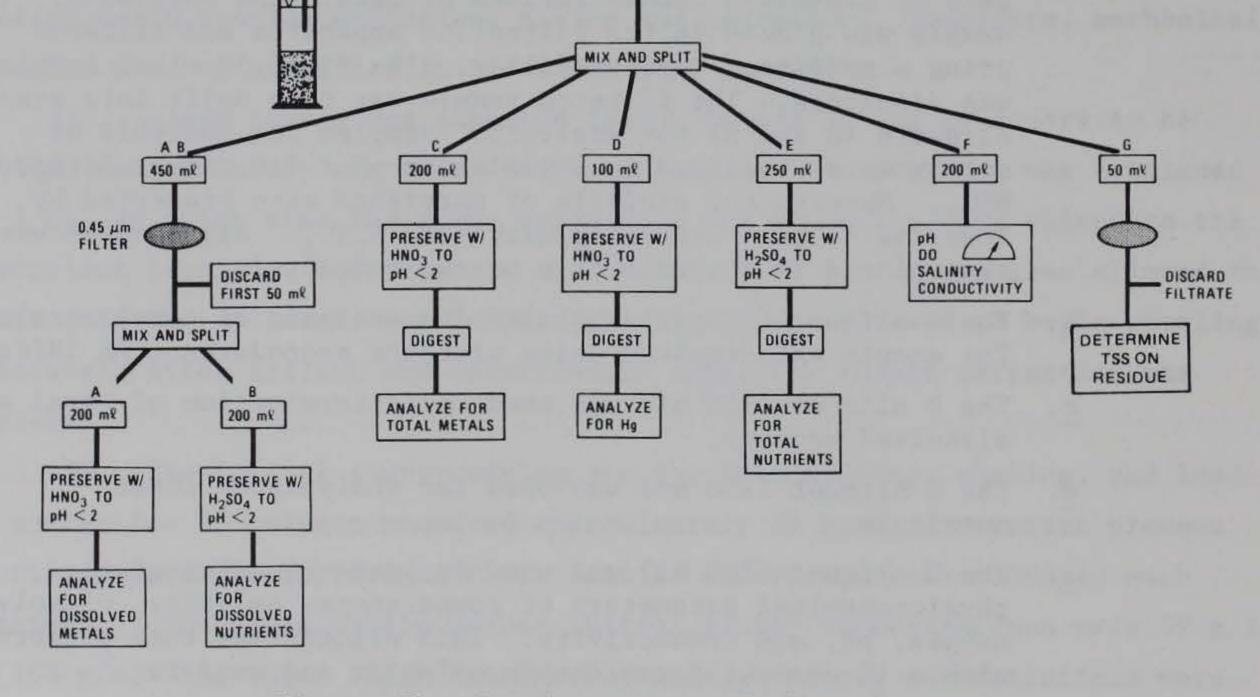


Figure 22. Sample processing flow diagram

determination of grain-size distribution of selected samples as described previously.

<u>f</u>. The G aliquot (50 ml) was used for determination of total suspended solids by filtration.

At the higher concentrations and the extraction time of 6 hr, a supernatant volume of less than 1,250 ml was available for extraction. For this case, the extracted volume was split into the six aliquots of similar proportions and processed as above. This did not raise the detection limits.

240. <u>Measurement of physicochemical parameters.</u> Temperature, salinity, and conductivity were measured using a YSI Model 33 SCT Meter. Dissolved oxygen was measured using a YSI Model 57 oxygen meter. Measurements of pH were made using an Orion Model 601 Digital Ionalyzer. All instrument readings were taken immediately upon sample extraction and processing. These same instruments were used for later analysis of these parameters for the Mobile Harbor field evaluation.

241. <u>Chemical analyses.</u> All chemical analyses for this study were conducted according to standard procedures (APHA 1981; EPA 1974a, 1974b). Metals analyses were performed using an atomic absorption spectrophotometer with heated graphite furnace. Nutrient analyses were performed using a Technicon Auto Analyzer. Organic analyses were performed using a high resolution gas chromatograph/mass spectrometer. The WES Analytical Laboratory performed analyses for the Mobile Harbor and Black Rock Harbor samples.

242. <u>Calculation of contaminant fractions of the total suspended</u> <u>solids.</u> The fraction of the suspended solids represented by each parameter was desired. The chemical analysis provided dissolved and total concentrations of parameters in milligrams per litre, and the total suspended solids was also determined. The contaminant fractions of the total suspended solids (in milligrams per kilogram SS) were then calculated (see Equation A3 Appendix A).

# Data analysis

243. The results from the three-factor experiments were analyzed using an analysis of variance (ANOVA) procedure available on SAS (SAS Institute Inc. 1982a, 1982b). All physicochemical parameters, dissolved metals, dissolved nutrients, and total nutrients were balanced data sets. However, one sample for total metals analysis in the Mobile Harbor test was lost during the digestion procedure. This caused the data set for those parameters to be unbalanced. The analysis of variance for the unbalanced sets was performed using a generalized linear models (GLM) procedure available on SAS. Both the GLM and ANOVA procedures yield a variety of statistics. The main statistic of interest is the significance probability, or level of significance,  $\alpha$ . If the significance probability is small for a given factor or factor interaction, that factor or interaction is significant. Correlations of test results with test factors and interactions were also determined using a correlation procedure (CORR) available on SAS. The CORR procedure calculates correlation coefficients and significance probabilities for the correlations. Results and discussion

244. General. Typical results for the three-factor experiment are shown in Figure 23. Similar data plots for all parameters are shown in Appendix B. Both dissolved concentrations and fractions of the total suspended solids for most parameters showed a high degree of variability, as indicated by the typical ranges plotted in Figure 23. However, the effects of test factors and interactions proved to be statistically significant for many parameters. Results of the three-factor experiment performed on Mobile Harbor and Black Rock Harbor sediments are summarized in Tables 9 and 10, respectively. The parameters for which factors are significant at the 95 percent level of confidence ( $\alpha < 0.05$ ) are indicated in Tables 9 and 10. Further discussion of factor or interaction significance refers to significance at the 95 percent level of confidence. 245. The analysis of variance for the Mobile Harbor experiment indicated main effects C, A, and T were significant in 15, 7, and 11 of the 27 parameters analyzed, respectively. For the Black Rock Harbor experiment, the main effects were significant for 19, 10, and 14 of the 27 parameters analyzed, respectively. For both experiments, initial concentration, C, was significant for the most parameters, followed by retention time, T, and aeration time, A. Fortunately, the C factor is the factor for which field values can be most easily simulated in a laboratory experiment. Retention time, T, can also be anticipated for the field condition, although with more difficulty, and laboratory values of retention time set accordingly. The degree of oxidation which occurs in the field condition is the most difficult factor to determine. Fortunately, this factor proved to be significant for the least number of parameters. This same trend was also evident in the factor interactions.

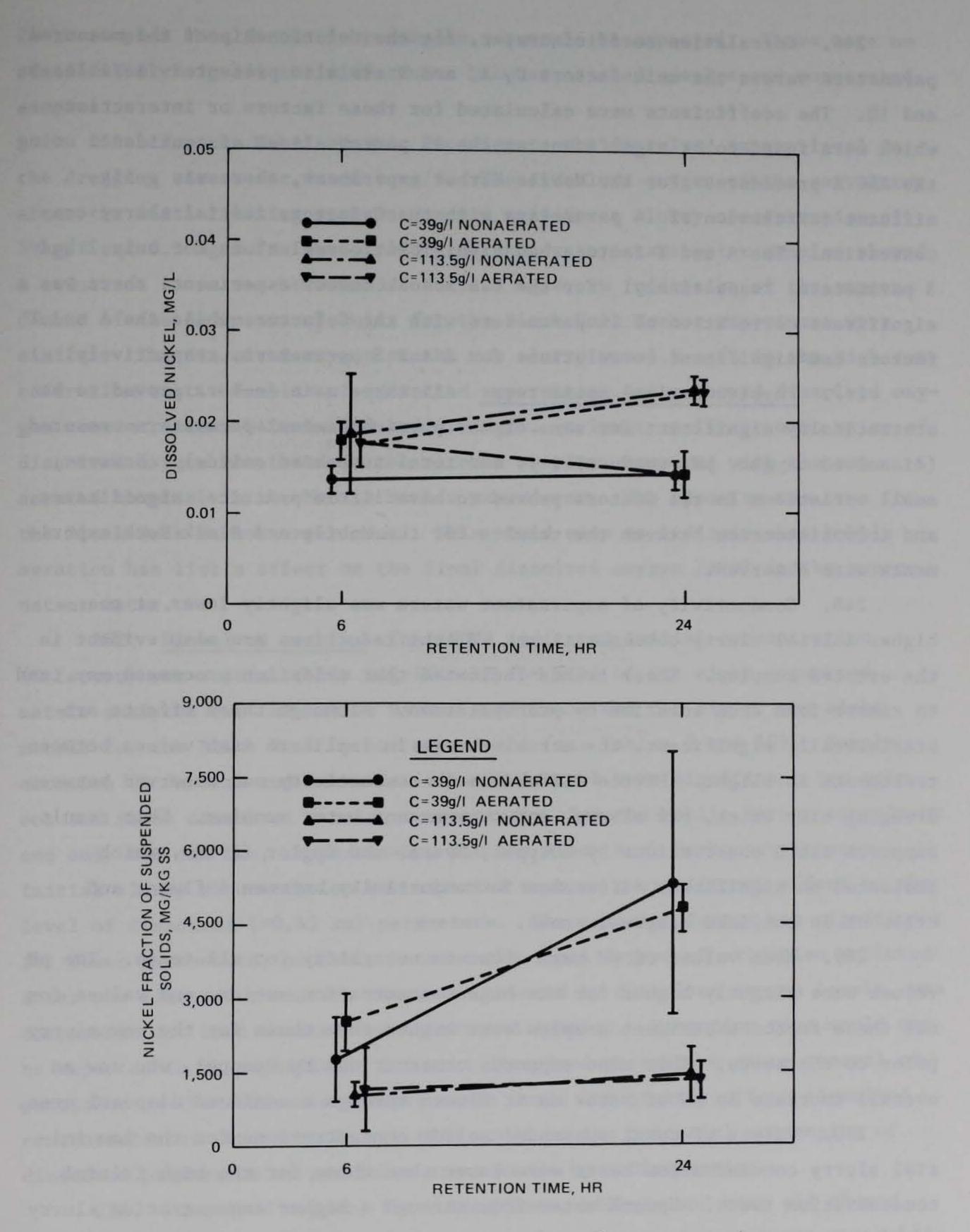


Figure 23. Typical results from three-factor experiment, Black Rock Harbor sediment 246. Correlation coefficients, r, for the relationship of the measured parameters versus the main factors C, A, and T are also presented in Tables 9 and 10. The coefficients were calculated for those factors or interactions which were found to be significant at the 95 percent level of confidence using the ANOVA procedure. For the Mobile Harbor experiment, there was a significant correlation of 14 parameters with the C factor, initial slurry concentration. The A and T factors had significant correlations for only 2 and 3 parameters, respectively. For the Black Rock Harbor experiment, there was a significant correlation of 14 parameters with the C factor, while the A and T factors had significant correlations for 2 and 8 parameters, respectively.

247. <u>Physicochemical parameters.</u> All three main factors proved to be statistically significant for some of the physicochemical parameters measured (dissolved oxygen, pH, conductivity, and total suspended solids). However, small variations in the factors proved to have little practical significance, and inconsistencies between the results for the Mobile and Black Rock experiments were observed.

248. Conductivity of supernatant waters was slightly lower at the higher initial slurry concentrations. Slight reductions are also evident in the aerated samples. These trends indicated that oxidation processes may tend to remove ions from solution by precipitation. Although these effects are statistically significant, the actual change in replicate mean values between

treatments is slight. Little difference in conductivity was observed between dredging site water, raw slurry, and supernatant water samples. This result supports field observations by Hoeppel, Myers, and Engler (1978), which indicated no significant difference in conductivity between influent and effluent in confined disposal areas.

249. Mean values of pH were close to neutrality for all tests. The pH values were slightly higher for the high concentration series, and values for all three-factor experiment samples were higher than those for the raw slurry prior to the tests. This also supports observations by Hoeppel, who saw an overall increase in pH of water as it flowed through a confined disposal area.

250. Values of total suspended solids concentrations for the low initial slurry concentration tests were lower than those for the high initial concentration tests. Upward water flux through a higher concentration slurry would be expected to carry a higher particle load into the supernatant. The total suspended solids concentrations in the supernatant were lower in the 24-hr samples than in the 6-hr samples, as would be expected. There were no statistically significant differences between aerated samples and nonaerated samples.

251. For the Mobile Harbor experiment, the dissolved oxygen level in the dredging site water was 8.5 mg/l. The dissolved oxygen of the raw slurry after the initial mixing process was 6.4 mg/l for a slurry concentration of 59 g/l and 0.3 mg/l for one of 108 g/l. All supernatant water samples showed a reduction to values between 3.4 and 4.9 mg/l, an indication of the oxygen demand of the sediment. Results for the Black Rock Harbor experiment were similar. The dissolved oxygen of the raw slurry was 1.0 mg/l in the high concentration test. Samples of extracted supernatant water showed dissolved oxygen concentrations between 1.0 and 4.0 mg/l. A lower replicate mean value of dissolved oxygen was found in the aerated samples, compared with the nonaerated samples, in the Mobile Harbor experiment. The opposite was true for the Black Rock Harbor experiment. This would seem to indicate that bubble aeration has little effect on the final dissolved oxygen level in the supernatant water.

252. Dissolved metals. The ANOVA indicated initial concentration (C factor) was statistically significant for five of the eight dissolved metals analyzed for the Mobile Harbor experiment and for six of the eight metals for the Black Rock Harbor experiment (see Tables 9 and 10). Sample aeration (A factor) and retention time (T factor) were significant for only one and three dissolved metals, respectively, for the Mobile Harbor experiment and only two and two, respectively, for the Black Rock Harbor experiment. Initial slurry concentration was expected to have a significant effect on the level of dissolved (<0.45 µm) parameters. The aeration factor was significant for fewer parameters, probably because the final degree of oxidation achieved after the allotted retention time, as measured by dissolved oxygen levels, was comparable for both aerated and nonaerated samples. Retention time would not be expected to be significant for most dissolved parameters since removal of particles by the sedimentation processes would not greatly affect dissolved concentrations. An exception to this would be the potential scavenging of dissolved parameters as particles are removed by sedimentation.

253. Dissolved copper, iron, manganese, nickel, and zinc all showed significant increases for the higher initial concentration tests in the Mobile Harbor experiment, as expected. As an example, dissolved manganese concentrations were 4.56 to 7.12 mg/l for the 108-g/l test, as compared with 1.54 to 3.67 mg/l for the 59-g/l test. Lee, Lopez, and Piwoni (1976) observed similar results for manganese and iron in evaluating factors affecting standard elutriate test results. Cadmium concentrations were higher for the low initial slurry concentration in the Mobile Harbor tests, indicating scavenging of dissolved cadmium by higher particle concentrations in the tests with higher initial slurry concentration. For the Black Rock Harbor tests, this same scavenging behavior was observed for dissolved copper.

254. Few definite trends for dissolved metals were observed for either the aeration or retention factors. Aeration was statistically significant only for dissolved manganese, which showed decreases in concentration for the aerated samples. The results for manganese are somewhat contradictory to those of Lee, who showed release of manganese under oxidizing conditions. However, Lee also showed release of manganese under reducing conditions. It should be noted that significant oxidation also occurred in the nonaerated samples during the mixing process because of oxygen absorbed from the atmosphere.

255. The overall results for dissolved metals are generally supported by Lee's data. He observed that release of some metals to the soluble phase is increased, while that for others is decreased under any given set of test conditions. The differences between dissolved metal results in the Mobile

Harbor and Black Rock Harbor experiments can possibly be attributed to the low concentrations in the Mobile Harbor tests (at or below detection limits) and the relatively high concentrations in the Black Rock Harbor tests. This is further discussed in the summary for the three-factor experiments.

256. <u>Dissolved nutrients.</u> As with the dissolved metals, the results varied for individual parameters. The initial slurry concentration was a significant factor for total phosphorus, nitrate-nitrogen, ammonia nitrogen, and total organic carbon in the Black Rock Harbor experiment, and was significant for three of the four parameters in the Mobile Harbor experiment. The significance of this factor was especially apparent for ammonia nitrogen in the Mobile experiment, where the concentrations in the 59-g/ $\ell$  tests ranged from 4.57 to 4.89 mg/ $\ell$ , while the concentrations in the 108-g/ $\ell$  tests ranged from 10.50 to 11.65 mg/ $\ell$  (see Appendix B).

257. The aeration and retention time factors had no significant correlations with any dissolved nutrients. It is apparent from the data that these effects were completely overridden by the initial concentration factor.

258. <u>Metals fractions of the total suspended solids.</u> The retention time factor was statistically significant for only two of the eight metal fractions analyzed in the Mobile Harbor experiments (see Table 9). However, the Black Rock Harbor results showed significant correlations for four of the eight metal fractions. The retention time factor would be expected to be significant for most parameters associated with the total suspended solids. As sedimentation removes particles from the supernatant, only the finest particle sizes remain in suspension. Previous research (Dossis and Warren 1981; Hoeppel, Myers, and Engler 1978) has shown that certain metals have a greater relative affinity for smaller particles due to their higher specific surface. The metal fractions of the total suspended solids (milligrams per kilogram SS) would therefore be expected to show an increase with increased retention time.

259. The great difference between the Mobile Harbor and Black Rock Harbor results regarding the metals fraction of the total suspended solids can be attributed to the very low metal concentrations in the Mobile Harbor supernatant samples. The concentrations of both the dissolved and total metals were at, or below, the detection limit in many of the samples. The fractions calculated as described previously would in some case have no meaning if either dissolved and total concentration, or both, were below the detection limit. The Black Rock Harbor samples showed higher total and dissolved metal concentrations, and the calculated metals fractions in the total suspended solids are more indicative of the processes actually occurring in the test.

260. The replicate mean values for the metals fractions of the total suspended solids generally indicate increases for all metals fractions with increased retention time, except for manganese. However, the retention time factor was statistically significant in only a few cases.

# Summary and conclusions

261. The three-factor experiments conducted on Mobile Harbor and Black Rock Harbor sediments served as an initial trial of the modified elutriate testing apparatus and procedure. Replicate samples were mixed at two initial slurry concentrations, given either an aerated or nonaerated treatment, and allowed to settle for two retention times. The test procedure proved workable, and no problems was encountered in the mixing, aeration, and sedimentation phases of the tests. However, some difficulty was experienced with particle resuspension during extraction of the supernatant samples. A total of 27 parameters were analyzed in each experiment, including physicochemical parameters and dissolved and total nutrients and metals.

262. The effects of the variable test factors of initial slurry concentration (C), aeration (A), and retention time (T) were evaluated by determining the significance of factors and factor interactions using an analysis of variance procedure. Of the 27 parameters analyzed in the Mobile Harbor tests, the C factor was statistically significant for 15 parameters, the A factor for 7, and the T factor for 11. For the Black Rock Harbor tests, the C factor was significant for 19 parameters, the A factor for 10, and the T factor for 14. However, few definite trends of practical significance were observed for any of the factors. This indicates that the results of the test are relatively insensitive to small variations in the test factors. The differences between bulk concentration of contaminants in the Mobile Harbor and Black Rock Harbor sediments may account for the relatively low number of parameters with significant differences in the Mobile Harbor tests compared with the Black Rock Harbor tests. For the Mobile Harbor experiment, dissolved and total concentrations of cadmium, chromium, lead, and nickel were near or below the detection limits for some of the samples. Subsequent analysis of the field data for the Mobile Harbor test also showed concentrations of these parameters at or below the detection limits. Subsequent calculation of the fraction of contaminants in the total suspended solids would be artificially This fact would mask the results of the analysis of variance and callower. culation of correlation coefficients. For this reason, these metals were not considered in the analysis of response surface data for Mobile Harbor sediments described below. 263. Based on these results, none of the three factors could be eliminated from consideration and ignored in subsequent development of a modified elutriate test procedure. Since initial slurry concentration (C factor) can be estimated for given field conditions, this factor can be directly simulated in the laboratory. However, the nature of the disposal area hydraulics and the level of aeration due to initial impact and mixing, wind action, and shear-generated atmospheric reaeration make the A and T factors more difficult to estimate and simulate. Therefore, appropriate A and T factors were selected by comparing laboratory test results for a broader combination of these factors with actual field data.

# Response Surface Experiments

## General

264. As mentioned above, a more extensive test series was used to define recommended aeration levels and settling times for the final modified elutriate test procedure. The later design was developed as a response surface analysis, which considered all significant factors determined by the initial three-factor experiment. Response surface experiments were conducted on sediments from Mobile Harbor and Savannah Harbor. The purpose of the response surface experiments was to determine the combination of aeration level (A factor) and the retention time (T factor) which would produce laboratory results closest to the results available from preliminary field studies.

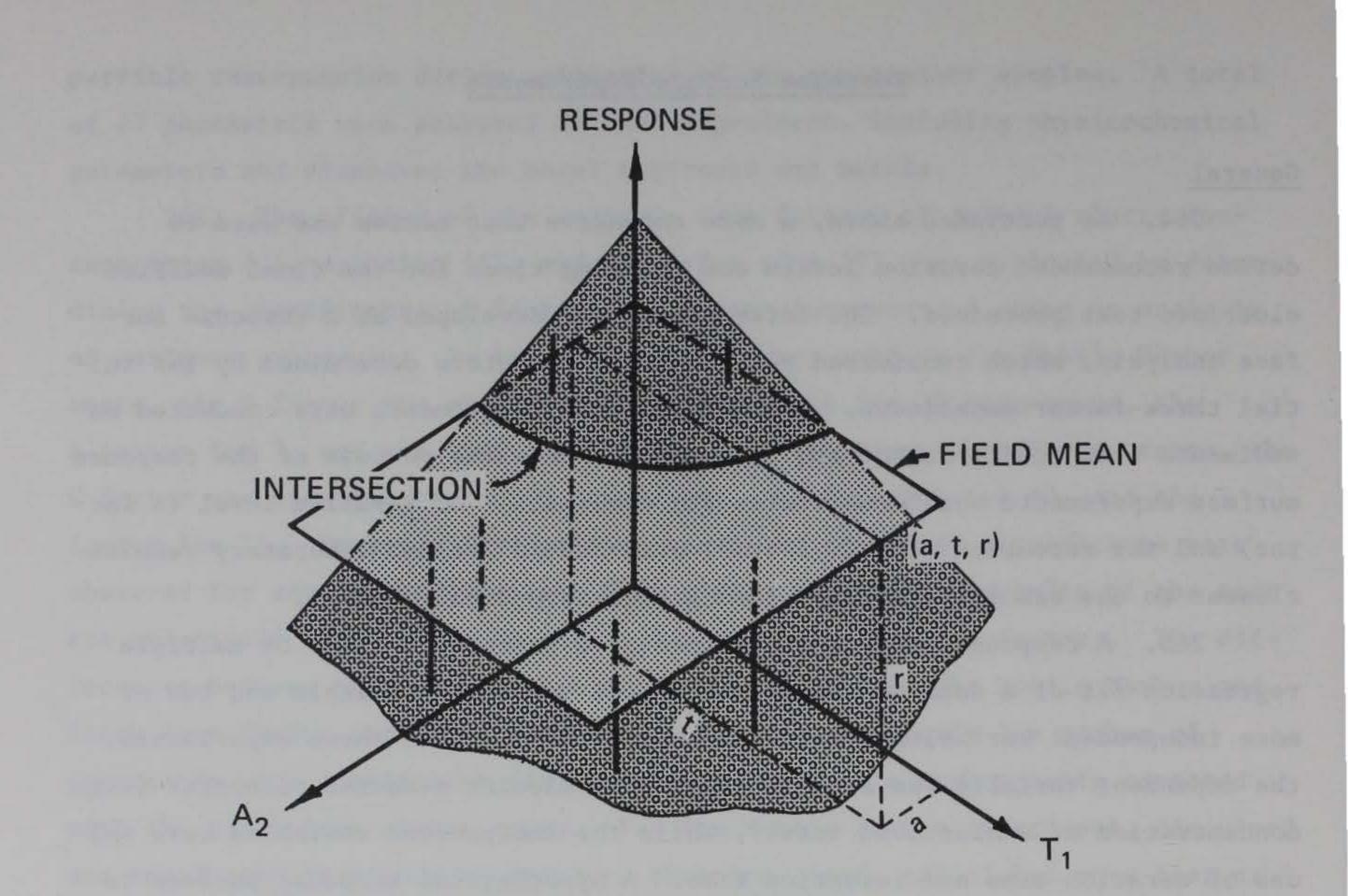
265. A response surface is defined as a regression plane or multiple regression fit of a data set comprised of one dependent variable and two or more independent variables (Freund and Miller 1977). For these experiments, the dependent variable was a response of a particular measured parameter (e.g. concentration of a dissolved metal), while the independent variables were values of aeration time and retention time. A hypothetical response surface is shown in Figure 24.

266. Preliminary field data had been collected at both the Mobile Harbor and Savannah Harbor field sites prior to conducting the response surface experiments. A detailed description of the field evaluations was given by Palermo (1984). The field results could therefore be used directly in determining the best A and T factor combinations for the laboratory tests. The intersection of the response surface with the field mean for each parameter allows sets of laboratory A and T values which best simulate the field results to be determined. Such a hypothetical intersection is also shown in Figure 24.

#### Experimental design

267. Levels for the aeration (A factor) were selected based on the practical range of bubbling times suitable for a production-run laboratory procedure. An upper limit of 6 hr of bubbling time was selected as the maximum which would allow for completion of a test during a typical working day. Bubbling times of 0, 1, 3, and 6 hr gave four levels for the A factor.

268. The levels for retention time (T factor) were selected based on results of the dye tracer studies conducted at the Mobile Harbor and Savannah



# RESPONSE SURFACE

Figure 24. Hypothetical response surface (regression plane) showing intersection of the field mean

Harbor field sites. Upper limits for the T factor were selected as approximately twice the actual mean retention time measured in the field. For the Mobile Harbor tests, five T factor levels of 3, 6, 12, 24, and 48 hr were selected. For the Savannah Harbor tests, four T factor levels of 12, 24, 48, and 96 hr were selected. A schematic of the Savannah Harbor test is shown in Figure 25. Response surface test factors for both tests are listed in Table 11.

269. In the interest of cost, replication for these experiments was kept to a minimum. Replication of each factor combination was not necessary because an analysis of variance was not planned for these test series. Limited replication does aid in developing the response surface by providing a smoother multiple regression fit to the data. One replicate sample for each of the two factors at each level was selected for the Savannah Harbor experiment, as shown in Table 12.

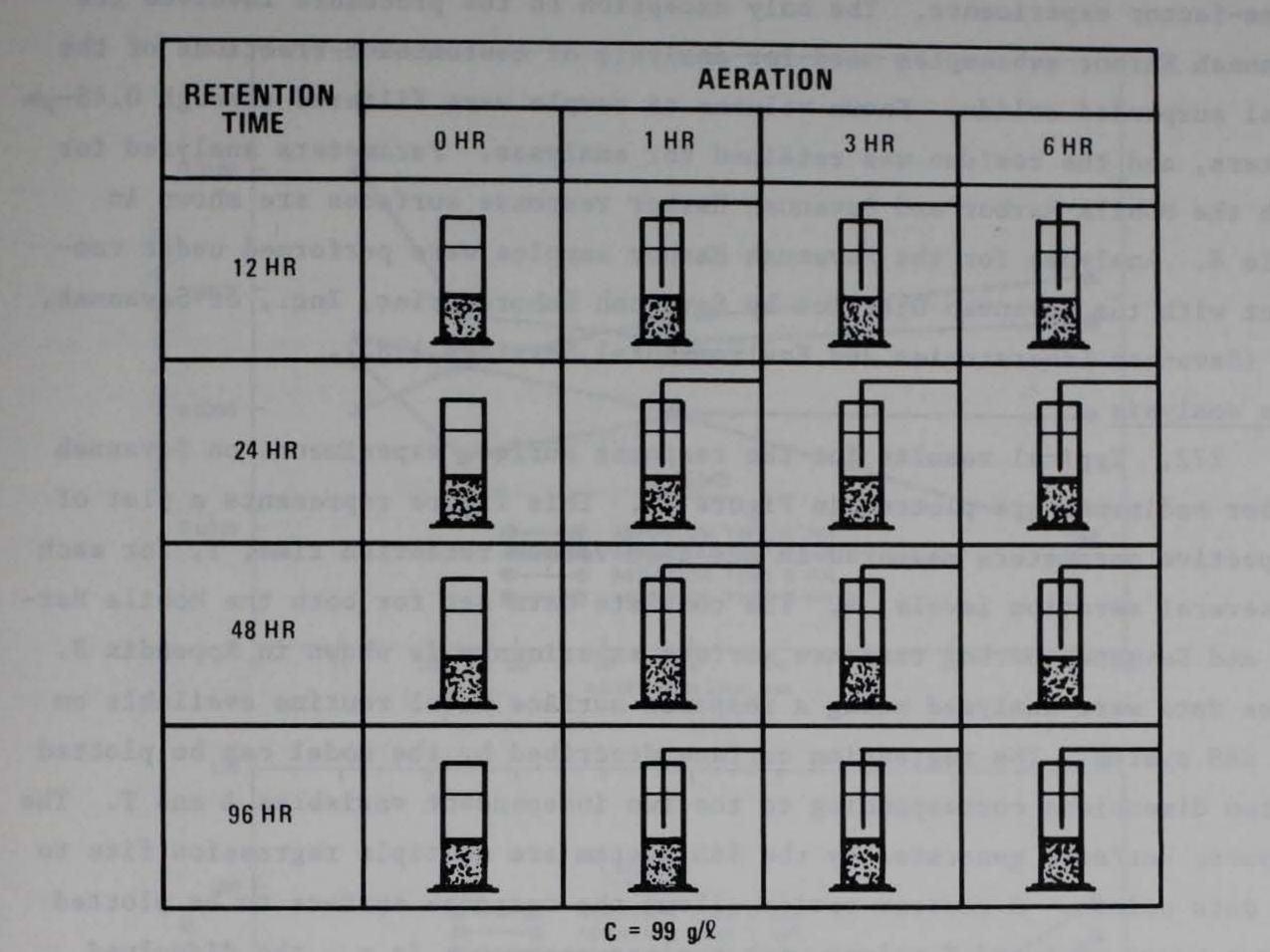


Figure 25. Schematic of response surface experiment, Savannah Harbor sediment

#### Equipment and procedures

270. The equipment and procedures used in the response surface experiments were practically identical to those previously described for the three-factor experiments. Slurry was mixed and loaded into the 4- $\ell$  cylinders at initial concentrations matching as closely as possible those measured during the preliminary field studies. This would make the initial test concentration (C factor) closely approximate the expected mean field value. The mean field influent concentration for the Mobile Harbor site was 87 g/ $\ell$ , and the final concentration for the Mobile Harbor response surface experiment was 92 g/ $\ell$ . For the Savannah Harbor site, the field mean was 107 g/ $\ell$ , while the response surface experiment concentration was 99 g/ $\ell$ .

271. Samples were aerated for various times and allowed to settle for various times according to the experimental design described above. Samples were then extracted, split, processed, and analyzed as described for the three-factor experiments. The only exception to the procedure involved the Savannah Harbor subsamples used for analysis of contaminant fractions of the total suspended solids. Known volumes of sample were filtered through  $0.45-\mu m$ filters, and the residue was retained for analyses. Parameters analyzed for both the Mobile Harbor and Savannah Harbor response surfaces are shown in Table 8. Analyses for the Savannah Harbor samples were performed under contract with the Savannah District by Savannah Laboratories, Inc., of Savannah, Ga. (Savannah Laboratories and Environmental Services 1982).

#### Data analysis

272. Typical results for the response surface experiments on Savannah Harbor sediments are plotted in Figure 26. This figure represents a plot of respective parameters measured in the test versus retention time, T, for each of several aeration levels, A. The complete data set for both the Mobile Harbor and Savannah Harbor response surface experiments is shown in Appendix B. These data were analyzed using a response surface model routine available on the SAS system. The regression surface described by the model can be plotted in two dimensions corresponding to the two independent variables A and T. The response surfaces generated by the SAS system are multiple regression fits to the data points. A contour option allows the response surface to be plotted over a range of A and T values with a given parameter (e.g., the dissolved concentration of a metal) as the contour variable. A typical response surface contour plot is shown in Figure 27. The complete set of response surfaces is shown in Appendix B. The response surface model routine also calculates an  $\alpha$  value for the total regression, indicating the goodness-of-fit of the response surface to the data set. Response surfaces with  $\alpha$  values <0.05 (95 percent level of confidence) were considered significant fits. The response surface contours were used in comparisons of the laboratory data with mean field values. The SAS CORR procedure was also run to evaluate correlation coefficients of measured parameters with levels of aeration effort and retention time.

### Results and discussion

273. <u>General.</u> For both the Mobile Harbor and Savannah Harbor experiments, the response surface data show few definite trends with either T or A for most of the parameters measured. The resulting response surfaces are relatively flat, as shown by the typical data in Figure 26. The significant

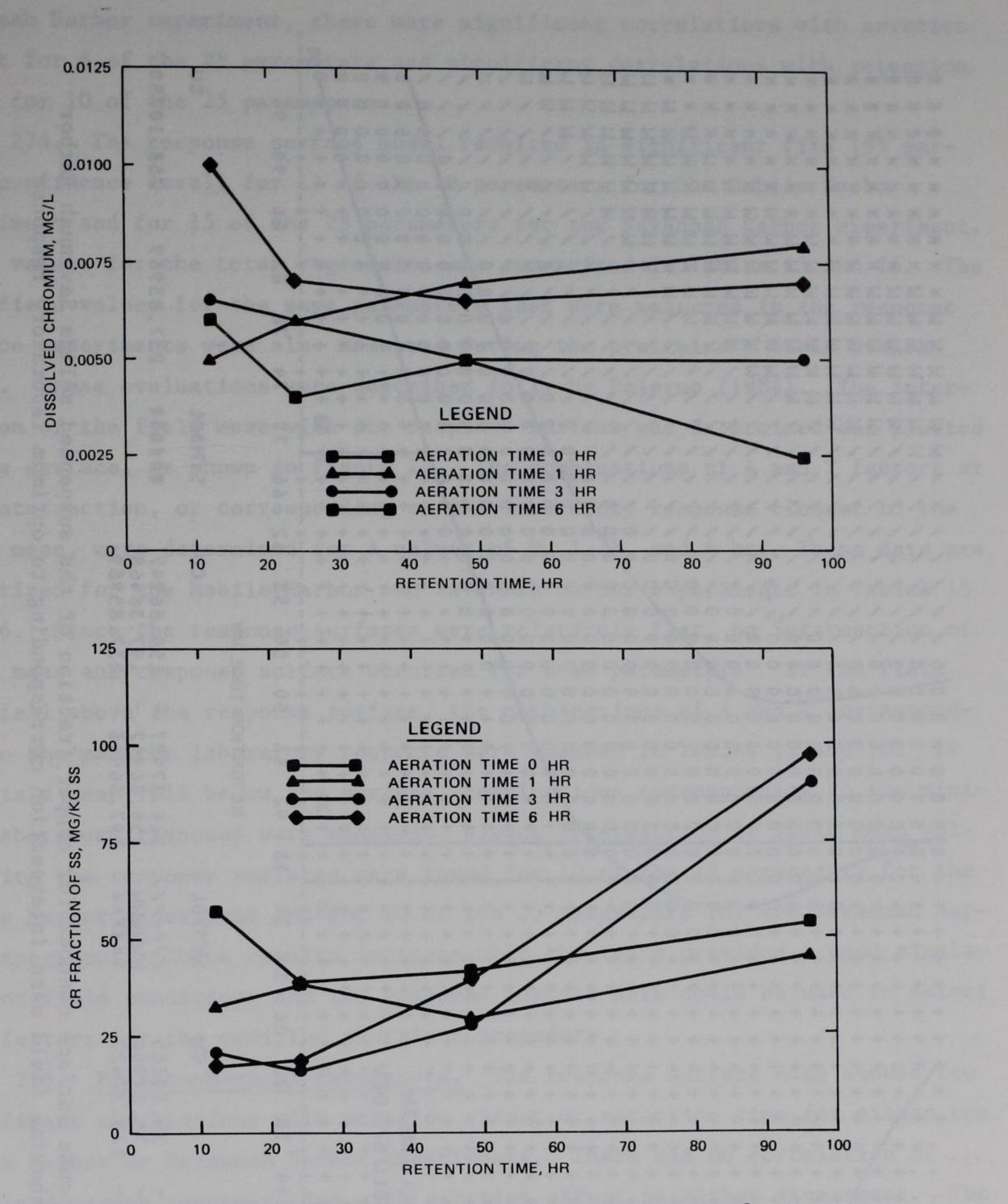


Figure 26. Typical results for response surface experiment, Savannah Harbor sediment

correlations of response surface results with aeration effort and retention time are summarized in Tables 13 and 14 for the Mobile Harbor and Savannah Harbor experiments, respectively. For the Mobile Harbor experiment, there were significant correlations with aeration effort for 5 of 19 parameters and significant correlations with retention time for 7 of 19 parameters. For the

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Figure 27. Response surface contour for copper fraction of the suspended solids Savannah Harbor sediment, showing field mean intersection corresponding to optimum laboratory response

AERATION TIME, HR

CU SYMBOL CU
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197.36468
237.85989

Savannah Harbor experiment, there were significant correlations with aeration effort for 6 of the 25 parameters and significant correlations with retention times for 10 of the 25 parameters.

274. The response surface model resulted in significant fits (95 percent confidence level) for 11 of the 19 parameters for the Mobile Harbor experiment and for 15 of the 25 parameters for the Savannah Harbor experiment. The a values for the total regression are summarized in Tables 15 and 16. The mean field values for the same parameters that were measured in the response surface experiments were also measured during the preliminary field evaluations. These evaluations were described fully by Palermo (1984). The intersection of the field mean with the response surface was determined and plotted on the surface, as shown in Figure 27. The combinations of A and T factors at the intersection, or corresponding to the laboratory response closest to the field mean, were determined for A values of 0, 1, 3, and 6 hr. These data are summarized for the Mobile Harbor and Savannah Harbor experiments in Tables 15 and 16. Since the response surfaces were relatively flat, no intersection of field mean and response surface occurred for some parameters. If the field mean fell above the response surface, the combinations of A and T corresponding to the maximum laboratory response were assumed in Tables 15 and 16. If the field mean fell below the surface, combinations corresponding to the minimum laboratory response were assumed. Direct intersection of field mean values with the response surfaces were found for 10 of the 19 parameters for the Mobile Harbor experiment and for 20 of the 25 parameters for the Savannah Harbor experiment. These results indicate that the tests provided a good simulation of field conditions and the response surface data could be used to select test factors for the modified elutriate procedure.

275. <u>Physicochemical parameters.</u> The response surface data showed few significant correlations with aeration effort or retention time for either the Mobile Harbor or Savannah Harbor experiments. There was no correlation of dissolved oxygen concentration with aeration effort in either experiment. The dissolved oxygen concentrations averaged 5.8 mg/ $\ell$  for the Mobile Harbor tests and 7.5 mg/ $\ell$  for the Savannah Harbor tests. There was a positive correlation of dissolved oxygen with retention time for the Mobile Harbor tests. The presence of relatively high concentrations of dissolved oxygen in all tests indicates that sufficient oxygen was introduced into the system by the mixing process and subsequent surface aeration to achieve oxidizing conditions, even with no bubble aeration.

276. Essentially constant pH conditions were maintained for all tests in both the Mobile Harbor and Savannah Harbor experiments. Both experiments resulted in slightly alkaline conditions (pH approximately 8). There was a statistically significant positive correlation of pH with aeration effort for both experiments. This supports field data collected both by previous investigators and in this study showing increasing pH following confined disposal in which oxidizing conditions were present. Conductivity in both experiments was generally constant for all tests with the values of conductivity proportional to the salinity.

277. As would be expected, the total suspended solids concentration in the supernatant showed a negative correlation with retention time for the Mobile Harbor experiment. Examination of the SS data for the Mobile Harbor tests indicates a sharp reduction in SS between 3 and 12 hr but practically constant values for times from 12 through 48 hr. The Savannah Harbor experiment resulted in practically identical values of SS for all tests, probably because the first extraction time for the experiment was 12 hr. Only colloidal particles would remain in suspension by this time, and further removal would be negligible.

278. The total regression (goodness-of-fit) of response surfaces for

physicochemical parameters was significant for dissolved oxygen, pH, and SS for the Mobile Harbor experiment and for pH and conductivity for the Savannah Harbor experiment. Intersections of the field mean values for physicochemical parameters were generally at higher retention times than the average of all parameters measured in the experiments.

279. <u>Dissolved metals.</u> The Mobile Harbor three-factor experiment results for dissolved metals showed concentrations of dissolved cadmium, chromium, lead, and nickel near or below the detection limits. These parameters were also at or below the detection limits for the response surface experiments and the Mobile Harbor field samples. Although these similar results indicate that the modified elutriate procedure is a good simulation of field behavior for these parameters, any comparison of response surface data for purposes of selecting optimum laboratory aeration time and retention time is impossible. Cadmium, chromium, lead, and nickel were therefore not considered in the analysis of response surface data for the Mobile Harbor experiments.

280. There was generally little correlation of dissolved metal concentrations with either aeration effort or retention time for both the Mobile Harbor and Savannah Harbor response surface experiments. There was a negative correlation of dissolved iron and lead with aeration effort for the Savannah Harbor tests and a negative correlation of dissolved manganese for the Mobile Harbor tests. These results suggest some scavenging of dissolved metals from solution by settling particles and possible precipitation of iron. This same process has been well documented in the standard elutriate test (Lee, Lopez, and Piwoni 1976). The total regression of the response surfaces was significant for only a few dissolved metals: manganese for the Mobile Harbor experiment, and iron and zinc for the Savannah Harbor experiment. This is an indication of the flatness of the surfaces and the difficulty of fitting a response surface to data in which experimental error is the overriding source of variation.

281. <u>Dissolved nutrients.</u> There was generally little correlation of dissolved nitrate or ammonia nitrogen, total phosphorus, or total organic carbon with either test factor in either experiment. As with the dissolved metals, the oxidation processes occurred regardless of the level of aeration effort. The concentrations of nitrate nitrogen showed a significant positive

correlation with aeration effort for both the Mobile Harbor and Savannah Harbor experiments.

282. All the total regressions for the response surfaces were significant with the exception of ammonia nitrogen in both experiments and total phosphorus in the Mobile Harbor experiment. Direct intersections of field mean values with the calculated response surfaces were found for most of the dissolved nutrients.

283. <u>Metals fractions of the total suspended solids.</u> The metals fractions of the total suspended solids were the parameters which most consistently correlated with retention time. There was moderate positive correlation of the copper and zinc fractions with retention time for the Mobile Harbor experiment (two of four metals), while moderate positive correlations were found for the chromium, copper, iron, lead, nickel, and zinc fractions for the Savannah Harbor experiment (six of seven metals). This phenomenon was certainly due to the greater contaminant adsorptive affinity of small-sized particles with large relative surface areas. As retention times progressed, all but the smallest colloidal particles were removed from suspension. Although some of the adsorbed metals were also removed, this process tended to increase the metal fraction in those particles remaining.

284. The manganese fraction was the only metal which showed a negative correlation with retention time (for the Mobile Harbor experiment), indicating that manganese remained largely dissolved even under oxidizing conditions. This exception for manganese supports the findings of previous studies (Lee, Lopez, and Piwoni 1976), which showed manganese released from sediments in dissolved form under all environmental conditions. The precipitation of manganese under oxidizing conditions would be expected, but this occurs slower than precipitation of iron, which is preferentially oxidized.

285. There were few correlations of metal fractions with aeration effort, further supporting the concept that oxidizing conditions were achieved in all tests, and geochemical equilibrium between dissolved and suspended solids fractions was achieved early.

286. The total regressions for the metal fractions response surfaces were significant for all parameters in both experiments with the exception of iron in the Mobile Harbor experiment. This indicates the ease of the response surface model in fitting data in which variation due to experimental error is small in comparison to variation due to the test factors.

287. <u>Nutrient fractions of the total suspended solids.</u> The total phosphorus fraction of the suspended solids showed a positive correlation with retention time for both the Mobile Harbor and Savannah Harbor experiments. The ammonia nitrogen fraction also showed positive correlation with retention time for the Mobile Harbor experiment. The total organic carbon fraction showed the only correlation with aeration effort.

288. The total regressions for nutrient fractions were significant for ammonia nitrogen and total organic carbon in the Mobile Harbor experiment and for total phosphorus in the Savannah Harbor experiments. Significant total regressions were generally found for those parameters which had significant correlations. The nutrient fractions generally showed results similar to those of the metals.

### Summary of response surface experiments

289. The response surface experiments conducted on Mobile Harbor and Savannah Harbor sediments provided data for direct comparison of modified elutriate test results with field data and provided data over a wider range of aeration efforts and retention times.

290. There was little correlation of response surface results with aeration effort. The average retention time for all parameters yielding the laboratory response closest to field means was nearly the same for 0, 1, 3, and 6 hr aeration time for both Mobile Harbor and Savannah Harbor experiments (see Tables 15 and 16). This further supports the findings of the threefactor experiments that aeration effort has little effect on results of the modified elutriate test. The variability exhibited in the data as a function of the A factor can therefore be attributed primarily to experimental error.

291. Even the tests run with no bubble aeration showed measurable dissolved oxygen at the end of the test for both the Savannah Harbor and Mobile Harbor sediments. This indicates that the modified elutriate procedure resulted in oxidizing conditions for the Mobile and Savannah sediments due to the physical mixing of sediment and water, the turbulent air-water contact which occurs while pouring the mixture into the test cylinder, and subsequent atmospheric reaeration.

292. Concentrations of dissolved constituents in the response surface experiments showed little correlation with retention time. However, the contaminant fractions of the total suspended solids did show positive correlations with retention times, with four of the seven parameters having sig-

nificant correlations for the Mobile Harbor experiment, and seven of the ten parameters for the Savannah Harbor experiment (see Tables 13 and 14).

293. The Mobile Harbor and Savannah Harbor field sites were quite different with regard to flow and ponding conditions. The laboratory retention time which gave results closest to those of the field data (Tables 15 and 16) was 20 and 37 hr for the Mobile Harbor and Savannah Harbor experiments, respectively. These values are compared with the mean field retention times for the Mobile and Savannah sites as determined by dye tracer tests in Table 17. The ratio of the time for closest laboratory response to the field mean retention time was 1.6 and 0.7 for the Mobile Harbor and Savannah Harbor sites, respectively.

# Selection of Procedures for Modified Elutriate Test

294. The selection of procedures for the modified elutriate test, based

on the results of the laboratory test development experiments presented in part, is given below. A step-by-step description of the procedure is presented in Appendix A.

#### Test vessel

295. The test vessel selection test series indicated that a 4-L cylinder was generally satisfactory in simulating the supernatant suspended solids concentrations and grain-size distributions produced by the 8-in.-diam settling column used as a standard. The total suspended solids removals by settling occurred faster in the 4-2 cylinder than in the 8-in. column for some sediments tested. However, the grain-size distributions in the two vessels showed no statistically significant difference for any of the sediments tested. Since the particle size is the overriding factor in the affinity of given particles for adsorption of contaminants, samples of suspended particles extracted in the modified elutriate test from 4-L cylinders will give a true indication of the contaminant fraction of the total suspended solids. Since the sedimentation rates are more accurately determined by the 8-in. column, it should be used for a separate prediction of effluent suspended solids concentrations. Values of suspended solids concentrations from the large column test can then be used with the values of dissolved contaminants and contaminant fraction of the suspended solids from the modified elutriate test in predicting total concentrations of contaminants in the effluent. Initial slurry concentration

296. The three-factor experiments showed that initial slurry concentration was the most significant factor influencing test results. Since this factor can be easily set in the laboratory, an initial slurry concentration equal to the expected field mean influent concentration should be used for the modified elutriate test.

### Solid-liquid separation

297. The three-factor experiments and response surface experiments suggest that test results are relatively insensitive to small variations in the procedures for mixing, subsequent sedimentation, and extraction of supernatant water. The replication necessary for the three-factor and response surface experiments called for the preparation of slurry in bulk quantity, with water and sediment from the dredging site mixed with a Lightning mixer. Either this procedure or preparation of smaller slurry volumes with smaller mixers would

prove satisfactory, depending upon the sample volume or replication requirements of the testing program.

298. Extraction of supernatant samples using syringe and tubing proved satisfactory. However, care must be taken to avoid resuspension of settled material. The depth of extraction should be midway between the surface and the interface, but can be adjusted, depending upon the sample volume required to be extracted.

299. Processing of extracted samples should be accomplished immediately. Separation of subsamples for analysis of total and dissolved parameters can be accomplished using 0.45-µm filtration. Determination of the total suspended solids concentration in the supernatant sample using a separate subsample is also required for subsequent computation of the contaminant fraction of the total suspended solids.

#### Aeration effort

300. Results of both the three-factor experiments and the response surface experiments showed that comparable oxidizing conditions were achieved in the test, regardless of the aeration effort. It is conceivable that no bubbling effort would be necessary to achieve the desired oxidizing conditions in the supernatant water for most sediments tested. However, a low-level bubbling effort would ensure consistency in the test procedure and would ensure that sufficient oxygen was always available during the test. A bubbling time

of 1 hr is therefore recommended.

#### Retention time

301. The results for both three-factor and response surface experiments showed significant correlations with time as retention time increased from 6 to 12 hr to 24 hr, or more. A settling period of 24 hr is sufficient for removal of all but colloidal-sized particles, assuming Stoke's Law and the settling depths observed for the  $4-\ell$  cylinders. Settling column studies conducted as a part of this study indicated that dredged material supernatant particles undergo flocculent settling. Therefore, particles comprising the flocs remaining in suspension after 24 hr would certainly all be colloidal size or smaller. As larger particles settle, the smaller particles remain in suspension. They have a higher specific surface (defined as surface area divided by volume). Therefore, for a given particle group with like mineralogical composition, the only characteristic of the particles which influence how much contaminant is adsorbed is the specific surface. All particles (taken as a composite group) in this size range with like mineralogical composition would therefore likely have the same affinity for adsorption of contaminants.

302. The comparisons of the results of the response surface experiments with field means show that the average retention time of the laboratory response which yielded the closest comparison with field data was within this same time range, 20 and 37 hr for the Mobile Harbor and Savannah Harbor experiments, respectively. These retention times correspond to 1.6 and 0.7 times the mean field retention times, respectively (see Table 17). Based on these data, it is recommended that the retention time for the modified elutriate test be set at the estimated mean field retention time, up to a maximum of 24 hr. The 24-hr maximum is desirable since no appreciable change in laboratory test results was evident at longer retention times, and such a maximum would make it convenient for routine testing by production laboratories.

#### Comparison of Modified Elutriate and Field Data

#### Field data

303. Results from the modified elutriate tests were compared with the data collected in the field evaluations conducted at the Mobile Harbor, Savannah Harbor, and Norfolk Harbor sites. The field studies included determina-

tion of mean residence time in the disposal area ponds by dye tracer and collection of influent and effluent samples during a 24- to 48-hr sampling period. Each sample was analyzed for a variety of parameters including dissolved and total concentrations of nutrients, and trace metals. The contaminant fractions of the total suspended solids were computed using Equation A3 (Appendix A). Values for the mean residence time and average influent suspended solids concentrations are presented in Table 18. The effluent quality data are plotted in Figures 28-30.

304. The field data from the Mobile Harbor and Savannah Harbor sites allowed a preliminary assessment of the accuracy of the test. This assessment was used in setting the test factors using results from the response surface experiments described previously. The tests and field evaluations were then conducted for Norfolk Harbor. The field mean data for the Mobile Harbor, Savannah Harbor, and Norfolk Harbor field evaluations were determined from sample sizes of 37, 48, and 18, respectively. Detailed descriptions of the field studies will be presented in a forthcoming report.

#### Modified elutriate testing

305. Once the recommended procedure for conducting modified elutriate tests was finalized, replicate tests were conducted on sediments from Mobile Harbor, Savannah Harbor, and Norfolk Harbor. Sediments for the tests were collected from the areas dredged, as described in Part III. In all cases, the modified elutriate testing was conducted after the field evaluations, so field data on influent concentrations and mean retention times determined by dye tracer tests were available. These data were used to set the modified elutriate test factors for slurry concentration and laboratory retention time. A sufficient number of replicates was performed to establish variability. A summary of the test factors is presented in Table 18. Results of the replicate tests are summarized in Table 19.

#### Comparison of results

306. Ratios of predicted values to field values are summarized in Table 20. The accuracy of the modified elutriate test as a predictor varies among the parameters analyzed. For both the dissolved concentrations and contaminant fractions of the total suspended solids, the predictions are within a factor of two to three of the field data. The results for both the modified elutriate tests and the field data are also shown plotted along with the

associated standard deviations in Figures 28-30. In most cases, the predicted results are within the standard deviations for field results. The predicted results are also on the conservative side for most parameters, i.e., the predicted concentrations are higher than the observed field concentrations, which is a useful safety factor. This is especially true for contaminant fractions of the total suspended solids and can be explained by the fact that, under quiescent laboratory testing conditions, only the fine colloidal particles will remain in suspension. For the field results, resuspension by wind currents can cause coarser particles with relatively low levels of adsorbed contaminants to be discharged in the effluent. Since finer particles have a greater relative affinity for contaminants, it is reasonable to expect the modified elutriate test to predict a higher contaminant fraction of the total suspended solids.

307. The data summarized in Table 20 show that the average ratio of predicted concentration or contaminant fraction to field concentration or

DADAMETERS	LINUTO				RELA	TIVE VA	LUE				
PARAMETERS	UNITS	0 1	2	3	4	5	6	7	8	9	10
DISSOLVED OXYGEN	mg/ <b>L</b>		1								
рН	N. Salar	no test		-		112		0		Tester .	
CONDUCTIVITY	mmhos/cm × 10 <sup>4</sup>	121 201 200 1 21 21 20						240		12	
DISSOLVED: OTAL ORGANIC CARBON	mg/ <b>l</b> × 10	0	•	1000					1	- Shar	
AMMONIA NITROGEN	mg/ <b>L</b> × 10				Ser al	1		en lin	11-11	1000	1000
NITRATE NITROGEN	mg/ <b>L</b> × 10 <sup>-2</sup>				•	1.2.4.3			e shi bulk		ALC: NO
COPPER	mg/ <b>L</b> × 10 <sup>-2</sup>			"Seine					100	in the	
IRON	mg/ <b>L</b> × 10 <sup>-1</sup>							11100	1 10		1
MANGANESE	mg/ <b>L</b>		•	1 Bri			lo ini	( interes	- 17	Tas.	12.0
FRACTION OF SUSPENDED SOLIDS:	animor English		1 - 40 1 - 10	Nace.	30% -	- Seator	Canada I			the re-	LOC .
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		-			-	-				422.00	

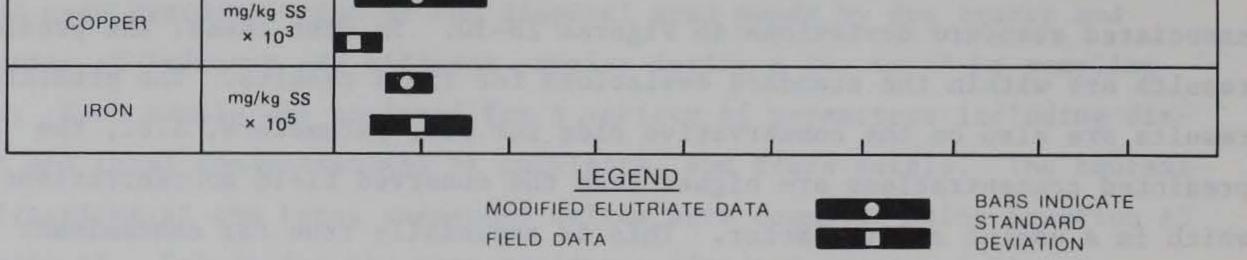


Figure 28. Plot of means and standard deviations for modified elutriate and field data, Mobile Harbor

contaminant fraction for all measured parameters was 1.37, 1.18, and 1.68 for the Mobile Harbor, Savannah Harbor, and Norfolk Harbor sites, respectively. Since overall accuracy within a factor of two for such predictions was considered good, no changes to the test procedure were considered necessary. The recommended procedure for conducting modified elutriate tests is described in Appendix A.

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CONDUCTIVITY	mmhos/cm × 10 <sup>4</sup>					-					The second	
DISSOLVED: TOTAL ORGANIC CARBON	mg/L × 10		The second							The second	No.	
AMMONIA NITROGEN	mg/ <b>£</b> × 10				Tendo	N.S.S.			162	Starter H		
NITRATE NITROGEN	mg/ <b>l</b> × 10 <sup>-2</sup>									-		
TOTAL PHOSPHOROUS	mg/ l × 10 <sup>-1</sup>				•				-			
COPPER	mg/ <b>l</b> × 10 <sup>-3</sup>		10			•				2		
IRON	mg/ <b>L</b> × 10 <sup>-1</sup>						2.50					
LEAD	mg/ <b>L</b> × 10 <sup>-3</sup>	1					-					
NICKEL	mg/ L × 10 <sup>-3</sup>							0				
ZINC	mg/ £ × 10 <sup>-2</sup>				in the second							
FRACTION OF SUSPENDED SOLIDS:							2 4 5 3 4	æ				

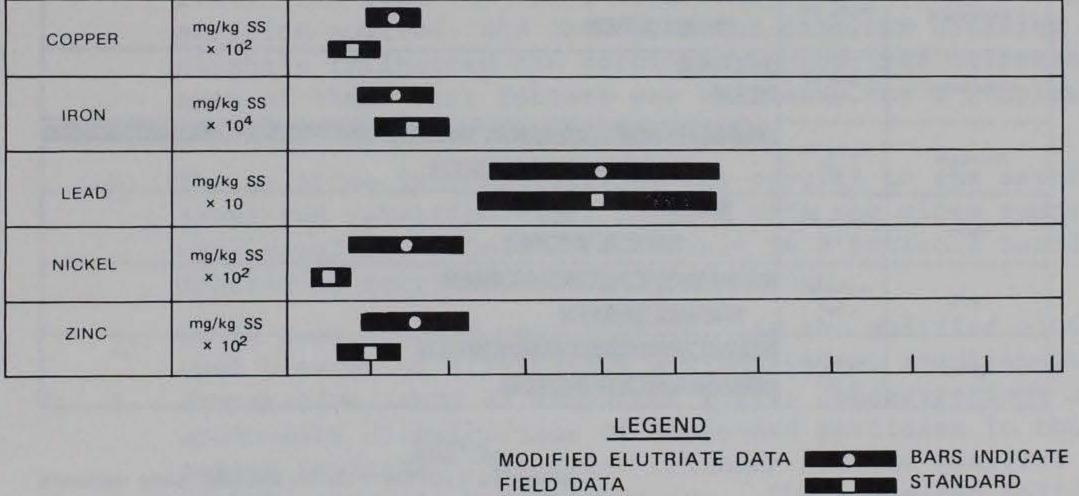


Figure 29. Plot of means and standard deviations for modified elutriate and field data, Savannah Harbor

DEVIATION

PARAMETER	UNITS (		2	3	RELA	TIVE VA	LUE 6	7	8	9	10
DISSOLVED OXYGEN	mg/ <b>L</b> × 10		Ť	Ť	Ť	1	Ĭ	1	Ĭ	Ť	
рН									D	-	
CONDUCTIVITY	mmhos/cm × 10 <sup>4</sup>		٥		1		n				
DISSOLVED: TOTAL ORGANIC CARBON	mg/ <b>L</b>		-					-			
CADMIUM	mg/ <b>L</b> × 10 <sup>-2</sup>	0			•						
CHROMIUM	mg/L × 10 <sup>-2</sup>		0								
COPPER	mg/ <b>£</b> × 10 <sup>-2</sup>					-					
IRON	mg/l × 10 <sup>-1</sup>			X	ACCREDING NO.						
LEAD	mg/ <b>L</b> × 10 <sup>-1</sup>		•		-		-				
MANGANESE	mg/ <b>£</b> × 10 <sup>-1</sup>		-		-	15.70					
ZINC	mg/L × 10 <sup>-2</sup>	-	2000		Fie	ELD DA	TA ME	AN < C	).2		
FRACTION OF SUSPENDED SOLIDS:											
TOTAL ORGANIC CARBON	mg/kg SS × 10 <sup>5</sup>	•									
CADMIUM	mg/kg SS		-	•							

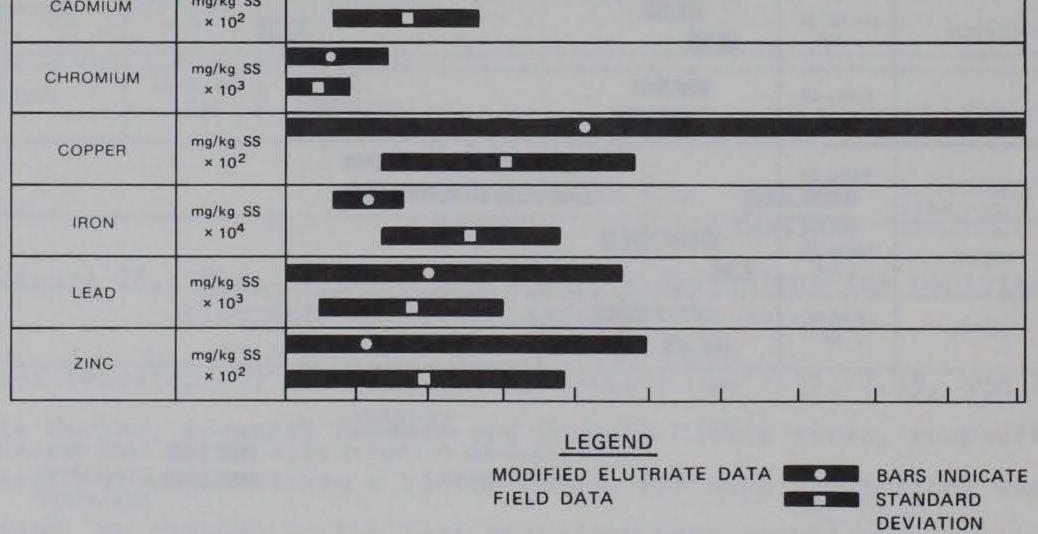


Figure 30. Plot of means and standard deviations for modified elutriate and field data, Norfolk Harbor

# PART V: CONCLUSIONS AND RECOMMENDATIONS

#### Conclusions

#### Literature review

308. A review of the literature discloses:

- a. No reliable method existed prior to this study for prediction of the quality of the effluent from confined dredged material disposal areas. However, proposed testing requirements for obtaining permits for Section 404 of the Clean Water Act mandated the development of a workable method for predicting the quality of the effluent and specified that modified elutriate test results and estimates of sedimentation performance be used as a basis for predictions.
- b. Significant data on standard elutriate test results identified which factors were pertinent in modifying the test for use in evaluating the quality of confined disposal effluents. The main factors included slurry concentration, time of contact, oxidizing conditions, and method of solid-liquid separation.

Modified elutriate test development

309. The following conclusions are drawn concerning the development of a modified elutriate test:

- a. The results of modified elutriate tests are strongly influenced by the type of sediment tested (both physical and chemical characteristics) and the slurry concentration used in the test. The type of vessel used for the settling, the level of aeration applied, and the retention time for settling only slightly influenced the results. Appropriate selection of each of these test factors was necessary for a complete test procedure.
- b. The relative insensitivity of the results to the aeration level and retention time, coupled with the close comparison of test results to field data, result in a protocol easily applied by routine testing laboratories.
- C. Small test columns were required for the modified elutriate test because of replication and analytical requirements. A comparative study of suspended solids concentrations and grain-size distributions of suspended particles in the supernatant indicated that a 4-l cylinder was the smallest test vessel practical for routine use. The suspended solids concentration in the supernatant as a function of retention time was not adequately simulated in the small cylinder. Therefore, suspended solids removal results from a large column test must be used in combination with the modified elutriate test for the prediction.

- d. The recommended modified elutriate test should be conducted with the anticipated average field influent suspended solids concentration, 1 hr of bubble aeration, and settling for the anticipated mean field retention time (up to a maximum of 24 hr), followed by analysis of the supernatant.
- e. Comparison of replicate test results with field data indicated that the modified elutriate test was a generally conservative predictor, and the average predicted results were within a factor of two of the field data.

#### Recommendations

#### 310. The following recommendations are made:

- a. The procedure for conducting modified elutriate tests described in this report should be used on an interim basis for the evaluation of Category 3 (contained or confined disposal with potential for contamination of the receiving water column) material under Section 404 of the Clean Water Act.
- b. Comparisons of predictions using the technique with field data should be made under a wider variety of operating conditions. The testing procedures may then be modified, if appropriate, to improve accuracy and/or precision. This is currently an ongoing effort under the CE Long-Term Effects of Dredging Operations research program.

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and the second second	and the second		Fr	esh Water		and the second second
Paramet	er	Guideline	96-hr LC <sub>50</sub>	Chronic Toxicity	Algal Toxicity	Maximum
Cadmium	Hardness					
	50 mg/l	0.012 µg/l		-	-	1.5 µg/l
	100 mg/L	0.025 µg/l			-	3.0 µg/l
	200 mg/l	0.051 g/l		-	-	6.3 µg/l
Chromium						
Hexavalent		0.29 µg/2	-	-	-	21 µg/l
Trivalent	Hardness			44 µg/l		-
	50 mg/l	-			-	2,200 µg/l
	100 mg/l		김 씨는 영상		-	4,700 µg/l
	200 mg/l			-	-	9,900 µg/l
Copper	Hardness	5.6 µg/l	-	-	-	-
	50 mg/l		1940 <del>-</del> 1949	-		12 µg/l
	100 mg/l		-	-	-	22 µg/l
	200 mg/l		-		-	43 µg/l
Lead	Hardness					
	50 mg/l	0.75 µg/l		-		74 µg/l
	100 mg/l	3.8 µg/l	<b>-</b>		-	170 µg/l
	200 mg/l	20 µg/l	-	-	-	400 µg/l
Mercury	the second second	0.00057 µg/l	-		50 400.02	0.0017 µg/

### EPA Water Quality Criteria For Selected Toxic Chemicals, 1980

Table 1

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Nickel	Hardness					
	50 mg/l	56 µg/l	-	-	-	1,100 µg/l
	100 mg/l	96 µg/l	-	-	-	1,800 µg/l
	200 mg/l	160 µg/l	-	-	-	3,100 µg/l
Polychlorin biphenyls	ated	0.014 µg/l	- 740	-		· ····································
Polynuclear		-	-	-	-	
Selenium		35 µg/l	760 µg/l		-	260 µg/l
Silver	Hardness	_		0.12 µg/l	-	-
SILVEI	50 mg/l	_			-	1.2 µg/l
	100 mg/l		-		-	4.1 µg/l
	200 mg/l		-	-	-	
Zinc	Hardness	47 µg/l		-	-	-
	50 mg/l			-	-	
	100 mg/l			-	-	320 µg/l
		_	-	_	-	570 µg/l
	200 mg/l	(0	Continued)			(Sheet 1 of 3)

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		Saltwater Algal								
Parame	ter	Guideline	96-hr LC <sub>50</sub>	Chronic Toxicity	Algal Toxicity	Maximum				
Cadmium	Hardness	4.5 g/2	1 x 4 - 4 - 4			59 µg/				
	50 mg/l		-	-	-					
	100 mg/l	-			-	and here				
	200 mg/l	-	-		- 5 20	- 117				
Chromium										
Hexavalen	t	18 g/l	-	All antenin	-	1,260 µg/				
Trivalent	Hardness	-	10,300 µg/l	-	-	-				
	50 mg/l	-		-	-	TANLANA PAR				
	100 mg/l	-		-	_	203.000				
	200 mg/l	-	-	-	-					
Copper	Hardness	4.0 g/l	_	-	-	23 µg/				
	50 mg/L	_		- 10 - 10 - 10 - 10 - 10 - 10 - 10 - 10	100 mg 300	_				
	100 mg/L		_		See 1988	-				
	200 mg/l				1014 <u>1</u> 92	_				
Lead	Hardness		410 µg/l	25 µg/l						
	50 mg/l				200					
	100 mg/l		_		Sparity Sale	bas				
	200 mg/l		- Alar	E1.0_	1192 02	_				
Mercury		0.025 g/l			100 -4.4	3.7 µg/				
Nickel	Hardness	7.1 g/l				140 µg/				
	50 mg/l			12000-0						
	100 mg/L			<u> </u>		d <u>e</u> dal				
	200 mg/L			6 P <u> </u>	Alam Piles					
Polychlorina biphenyls		0.030 g/l		-	2 100 000	-				
Polynuclear hydrocarbo			300 µg/l	_	- 1999	aly Marta				
Selenium		54 g/l			1 1 <u>2</u> 1 1 1 1 1	410 µg/				
Silver	Hardness	-				2.3 µg/				
	50 mg/l		an 1937 #1.4	128	_					
	100 mg/L	영상 위원 <u>은</u> 100 년 11			Bardners	and a				
	200 mg/2	_			Sign CL	걸음 물문				
Zinc	Hardness	58 µg/l			1.00 00.1	170 µg/				
	50 mg/L	- 100			13328 105	110 481				
	100 mg/L			174	Annapart					
	200 mg/L				- 1102 05					
	200 mg/t	_	-		Line out					
		(	Continued)							

Table 1 (Continued)

15 30 T 28-843

			Human Health and Safety	
Paramet	ter	Water	Bioaccumulation	Taste & Odor
Cadmium	Hardness	10 g/l		-
	50 mg/l			
	100 mg/L	-	-	and the second
	200 mg/l	-		-
Chromium				
Hexavalen	t	50 µg/l		
Trivalent	Hardness	170 µg/L	3,433 µg/l	-
	50 mg/l			in the states
	100 mg/l	- 1000.1 -	000,12	Anterin Toka I.
	200 mg/l	-	- Co	
Copper	Hardness			1.0 mg/L
	50 mg/l	-		-
	100 mg/l	-		-
	200 mg/l			
Lead	Hardness	50 g/l		
	50 mg/l			-
	100 mg/l	- 000,11 -		
	200 mg/l			- 10
Mercury		144 ng/l	146 ng/L	a Turner
Nickel	Hardness	13.4 µg/l	100 µg/l	
	50 mg/l			-
	100 mg/l			
	200 mg/l			
Polychlorin biphenyls		0.0029 ng/l -C	0.0079 ng/l	-
Polynuclear		0.28 ng/l -C	3.11 ng/l	
Selenium		10 µg/l		
Silver	Hardness	50 µg/l		
	50 mg/l	-		
	100 mg/l			-
	200 mg/l			- /0
Zinc	Hardness			5 mg/2
	50 mg/l			-
	100 mg/l			
	200 mg/l			

#### Table 1 (Concluded)

#### Guidelines for Pollutional Classification of Great Lakes Harbor

Sediments\* (Concentrations Shown are in mg/kg Dry Weight)

Parameter	Nonpolluted	Moderately Polluted	Heavily Polluted
Volatile solids, %	< 5	5 - 8	> 8
Chemical oxygen demand	< 40,000	40,000 - 80,000	> 80,000
Total Kjeldahl nitrogen	< 1,000	1,000 - 2,000	> 2,000
Ammonia	< 75	75 - 200	> 200
Phosphorus	< 420	420 - 650	> 650
Oil and grease	<1,000	1,000 - 2,000	>2,000
Arsenic	< 3	3 - 8	> 8
Barium	< 20	20 - 60	> 60
Cadmium			> 6
Chromium	< 25	25 - 75	> 75
Copper	< 25	25 - 50	> 50
Cyanide	<0.10	0.10 - 0.25	>0.25
Iron	<17,000	17,000 - 25,000	> 25,000
Lead	< 40	40 - 60	> 60
langanese	< 300	300 - 500	> 500
Nickel	< 20	20 - 50	> 50
Zinc	< 90	90 - 200	> 200

Zinc

< 90

90 - 200

> 200

Parameter Mercury	Polluted > 1	
Total PCBs	> 10	

\* US Environmental Protection Agency, Region V, Chicago, Illinois, April 1977.

### Results of Bulk Sediment Analysis and Standard Elutriate Testing

for Mobile Bay Sediments

		Sediment C	oncentrati	on, mg/kg*		MB 28** Standard Elutriate Concentration	MB 28 Water** Concentration
Parameter	MB 26	MB 27	MB 28	MB 30	MB 31	mg/l	mg/l
Cadmium, mg/kg	2	2	2	3	2	<0.002	<0.002
Chromium, mg/kg	47	50	52	59	36	<0.01	<0.01
Copper, mg/kg	27	27	21	18	14	<0.01	<0.01
Iron, mg/kg	27,000	24,000	27,000	26,000	18,000	0.019	<0.1
Lead, mg/kg	27	28	26	15	0.2	<0.01	<0.1
Manganese, mg/kg				Not analyz	ed		
Nickel, mg/kg	27	25	26	35	22	<0.1	<0.1
Zinc, mg/kg	160	160	160	170	150	<0.1	0.012
Total phosphorus mg/kg	4.1	57.4	51.1	11.5 19	.0	0.067	0.030
Ammonia nitrogen mg/kg	190	149	184	192	104	4.5	0.36
Total organic carbon, mg/kg	9,340	11,500	10,500	16,200	7,000	7.5	4.4

Thompson Engineering Testing (1982). \*

\*\* Environmental Protection Systems, Inc. (1982a).

#### Results of Bulk Sediment Analysis and Standard Elutriate

#### Testing for Savannah Harbor Sediments

ParameterUpstrArsenic-Cadmium2Chromium71	<u>eam</u> <u>Center</u> - 1	Downstream - 1	mg/l 0.0028	Water, mg/l <0.001
Cadmium 2	- 1	-	0.0028	<0.001
	1	1		
Chromium 71			0.00015	<0.0001
	72	74	0.0010	<0.001
Copper 21	19	20	0.0036	0.001
Lead 21.	0 20.5	22.4	0.00026	0.00024
Nickel 13	12	13	0.0011	<0.001
Silver 33	3	3	0.00010	<0.00005
Zinc 80	· 79	86	0.0120	0.009

Environmental Protection Systems Inc. (1982b). \*

Savannah Laboratories (1982a). \*\*

#### Table 5

Results of Bulk Sediment and Dredging Site Water Analysis,

#### Norfolk Harbor

Parameter	Bulk Sediment mg/kg	Dredging Site Water Concentration mg/l
Total organic carbon	38,000	4.69
Total phosphorous		0.01
Cadmium	24.7	0.032
Chromium	6.8	0.06
Copper	6.8	0.04
Iron	1,530	0.33
Lead	67	0.22
Manganese	106	0.004
Zinc	77	0.05

## Results of Bulk Sediment Analysis and Standard Elutriate

## Testing for Black Rock Sediment

Parameter	Sediment Concentration mg/kg	Standard Elutriate Concentration mg/l	Dredging Site Water Concentration mg/l
Cadmium .	20	<0.002	0.002
Chromium	1,450	<0.02	<0.05
Copper	2,800	0.02	0.07
Iron	27,600	0.03	0.55
Lead	392	<0.05	0.06
Manganese	304	0.15	0.28
Nickel	197	0.02	0.14
Zinc	1,230	0.02	0.12
Total phosphorus	a (reak) <u>-</u>		0.15
Ammonia nitrogen		43	82
Total organic carbon	53,300	15.0	2.8

#### Table 7

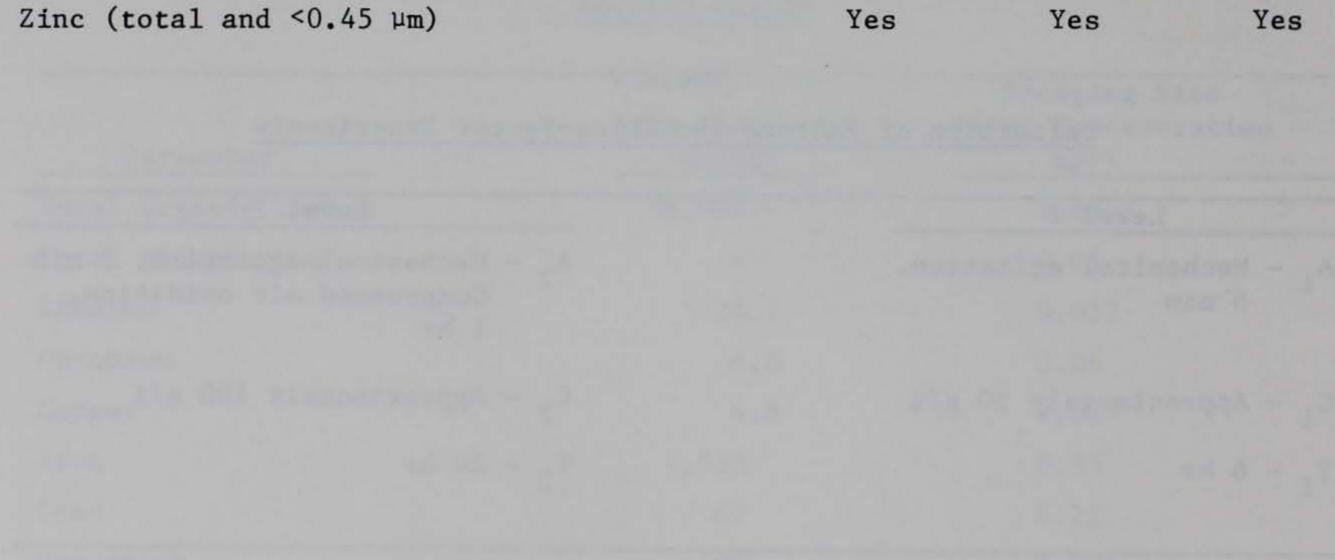
Definition of Factors for Three-Factor Experiments

Level 1	Level 2
A <sub>1</sub> - Mechanical agitation, 5 min	A <sub>2</sub> - Mechanical agitation, 5 min Compressed air oxidation, 1 hr
C <sub>1</sub> - Approximately 50 g/l	C <sub>2</sub> - Approximately 100 g/l
$T_{1} - 6 hr$	T <sub>2</sub> - 24 hr

#### Parameters Evaluated in Three-Factor Tests and

#### Response Surface Tests

Parameter	Mobile	Black Rock	Savannah
Total suspended solids (>0.45 µm)*	Yes	Yes	Yes
Conductivity, mmhos/cm	Yes	Yes	Yes
Dissolved oxygen, mg/l	Yes	Yes	Yes
pH	Yes	Yes	Yes
Total organic carbon (total and <0.45 $\mu\text{m})$	Yes	Yes	Yes
Ammonium nitrogen (total and <0.45 $\mu\text{m})$	Yes	Yes	Yes
$NO_3 + NO_2$ nitrogen (<0.45 µm)	Yes	Yes	Yes
Total phosphorus (total and <0.45 µm)	Yes	Yes	Yes
Cadmium (total and <0.45 µm)	Yes	Yes	No
Chromium (total and <0.45 µm)	Yes	Yes	Yes
Copper (total and <0.45 µm)	Yes	Yes	Yes
Iron (total and <0.45 $\mu$ m)	Yes	Yes	Yes
Lead (total and <0.45 µm)	Yes	Yes	Yes
Manganese (total and <0.45 µm)	Yes	Yes	No
Mercury (total and <0.45 µm)	Yes	Yes	Yes
Nickel (total and <0.45 µm)	Yes	Yes	Yes
Silver (total and <0.45 µm)	No	No	Yes
$7inc$ (total and $\leq 0.45$ lm)	Vec	Vac	Vac



\* Filtration using 0.45-µm filter has been commonly used as the method to separate suspended solids and dissolved fractions in the area of dredged material disposal criteria (Plumb 1981).

#### Summary of Correlation Coefficients\* and Results of

Analysis of Variance, \*\* Three-Factor Experiment,

Mobile Harbor Sediment

The state of the s	T	est Factor	
Parameter	Concentration (C)	Aeration (A)	Retention (T)
Dissolved oxygen	-0.6468*	-0.5120*	**
pH	0.7239*	**	**
Conductivity	-0.5644*		
Total suspended solids	0.6049*	**	**
Dissolved metals			
Cadmium	-0.4769*		-0.6162*
Chromium			
Copper	0.4496*		-0.4196*
Iron	0.8174*		
Lead			
Manganese	0.8319*	-0.5413*	**
Nickel	0.5967*		
Zinc			
Dissolved nutrients			
Total phosphorus	-0.8289*	**	**
Nitrate	0.9979*	**	**
Ammonia Tetel emeric carbon	0.9835*	**	
Total organic carbon	0.9035		
Metal fraction of			
total suspended solids			
Cadmium	-0.7078*		**
Chromium	-0.7070**		
Copper			
Iron			**
Lead			
Manganese	0 6071*		
Nickel	-0.6971*		
Zinc			
Nutrient fraction of			
total suspended solids	4.4		
Total phosphorus	**		0.4478*
Ammonia			0.4470
Total organic carbon			
Total number of signifi-			To redmin Laro
cant correlations	14	2	3
Total number of signifi-			10. 336-01 2010
cant** parameters	15	7	panal in a li se se s
Canter parameters			

 \* Correlation coefficient significant at the 95 percent level of confidence.
 \*\* Analysis of variance indicated factor to be significant at the 95 percent level of confidence.

#### Summary of Correlation Coefficients\* and Results of

Analysis of Variance, \*\* Three-Factor Experiment,

Black Rock Harbor Sediment

The second	Test Factor				
Parameter	Concentration (C)	Aeration (A)	Retention (T)		
Dissolved oxygen	**	**	**		
pH	**	0.5348*	-0.7200*		
Conductivity	-0.9957*				
Total suspended solids	0.7461*		-0.4204*		
Dissolved metals					
Cadmium					
Chromium	0.6227*				
Copper	-0.6065*				
Iron	0.4262*	-0.6485*			
Lead					
Manganese	-0.7228*	**	-0.4048*		
Nickel	0.6588*		a state water		
Zinc	0.9321*		**		
Dissolved nutrients					
Total phosphorus	0.5343*	**	**		
Nitrate	-0.4884*				
Ammonia	0.9994*	**	**		
Total organic carbon	0.9779*	**			
Metal fraction of					
total suspended solids					
Cadmium		See 1	**		
Chromium					
Copper					
Iron	**		0.4125*		
Lead			-0.4771*		
Manganese	0.7490*	**	0.3606*		
Nickel	-0.6440*		0.4798*		
Zinc	**				
Nutrient fraction of					
total suspended solids					
Total phosphorus		**	0.5430*		
Ammonia	**	**			
Total organic carbon			0.4245*		
iotal organic carbon			0.4245**		
Total number of signifi-			to the first first		
cant correlations	14	2	8		
Total number of signifi-			to a long long		
cant** parameters	19	10	14		
F					

 Correlation coefficient significant at the 95 percent level of confidence.
 \*\* Analysis of variance indicated factor to be significant at the 95 percent level of confidence.

### Definition of Test Factors for Response

#### Surface Experiments

MCC.	ention
Mobile	Savannah
$T_1 - 3 hr$	$T_1 - 12 hr$
$T_2 - 6 hr$	$T_2 - 24 hr$
	aladam heylosolt
$T_3 - 12 hr$	$T_3 - 48 hr$
2-9-9-79 E 12-17-12-12-12-12-12-12-12-12-12-12-12-12-12-	
$T_4 - 24 hr$	T <sub>4</sub> - 96 hr
	Enguarda Luiat
$T_{5} - 48 hr$	
Carthon	
	RENT PERCELON OF
12	
for Response Surface	
E	$T_1 - 3 hr$ $T_2 - 6 hr$ $T_3 - 12 hr$ $T_4 - 24 hr$ $T_5 - 48 hr$

T THE PROPERTY AND IN	A factor			the standard
T factor	0 hr	<u>1 hr</u>	<u>3 hr</u>	<u>6 hr</u>
12 hr	1	1	2	1
24 hr	1	2	1	1
48 hr	1	1	1	2
96 hr	2	1	1	1
		Total to	ests = 20	

#### Correlation Coefficients,\* Response Surface

#### Experiment, Mobile Harbor Sediment

Parameter	Aeration Effort	Retention Tim
Dissolved oxygen		0.6847
pH	0.7727	
Conductivity	-0.5421	
Total suspended solids		-0.5256
Dissolved metals		
Copper		
Iron		
Manganese	-0.6177	
Zinc		
Dissolved nutrients		
Total phosphorus	and the second s	
Nitrate	0.6798	
Ammonia		
Total organic carbon		
Metal fraction of		
total suspended solids		
Copper		0.7476
Iron		
Manganese		-0.5753
Zinc		0.5686
Nutrient fraction of		
total suspended solids		
Total phosphorus		0.4838
Ammonia		0.5601
Total organic carbon	0.6276	

 Total number of significant correlations
 5
 7

\* Coefficients with 95 percent confidence level.

#### Correlation Coefficients,\* Response Surface

#### Experiment, Savannah Harbor Sediment

Parameter	Aeration Effort	Retention Time
Dissolved oxygen		
pH	0.4921	
Conductivity		0.7114
Total suspended solids		
Dissolved metals		
Chromium		
Copper		
Iron	-0.6970	
Lead	-0.4411	
Silver		
Zinc		
Dissolved nutrients		
Total phosphorus		
Nitrate	0.5438	
Ammonia		-0.5060
Total organic carbon		0.4654
Metal fraction of		
total suspended solids		0 (007
Chromium		0.6987
Copper		0.6106
Iron	-0.4646	0.6334
Lead		0.4994
Silver		0 5661
Nickel		0.5661
Zinc	0.4519	0.5306

6

Nutrient fraction of total suspended solids Total phosphorus Ammonia Total organic carbon

Total number of significant correlations 0.4484

10

\* Coefficients with 95 percent confidence level.

Retention Time in Hours for Response Surface Experiment

#### Yielding Closest Comparison\*\* With Field

#### Mean, Mobile Harbor Sediments

CANCELLA DE LA COMPANY	α Value		Aeratio	n Effort	122253022
	Total	Non-	Aerated	Aerated	Aerated
Parameter	Regression	Aerated	<u> </u>	<u>3 hr</u>	6 hr
Dissolved oxygen	0.0155*	46	42	35	32
pH	0.0001*	48	48	48	48
Conductivity	0.1919	0	0	0	0
Suspended solids	0.0261*	6	10	15	8
Dissolved metals					
Copper	0.2141	0	0	0	0
Iron	0.6703	22	22	26	26
Manganese	0.0042*	48	48	36	28
Zinc	0.8291	18	22	24	24
Dissolved nutrients					
Total phosphorus	0.1948	0	0	8	20
Nitrate	0.0242*	26	26	32	48
Ammonia	0.2053	26	26	26	26
Total organic carbon	0.0268*	48	48	48	48
Metal fraction of					
total suspended solids					
Copper	0.0021*	0	5	7	0
Iron	0.1604	46	44	32	22
Manganese	0.0032*	14	20	28	48
Zinc	0.0548	6	10	10	4
Nutrient fraction of					
total suspended solids					
Total phosphorus	0.1063*	0	12	34	0
Ammonia	0.0001*	0	6	12	3
Total organic carbon	0.0002*	$\frac{30}{19}$	$\frac{24}{21}$	$\frac{12}{22}$	0
Avg for all parameters		19	21	22	19

Avg all levels = 20

\* Total regression significant at the 95 percent level of confidence.
 \*\* If no intersection of field mean with response surface occurred, the retention time corresponding to the maximum laboratory response for the respective aeration level was assumed when the field mean was above the surface, and the minimum was assumed if the field mean was below the surface.

#### Retention Time in Hours for Response Surface Experiment

#### Yielding Closest Comparison\*\* With Field

#### Mean, Mobile Harbor Sediments

	α Value	100	Aeration Effort		
	Total	Non-			
Parameter	Regression	aerated	<u> </u>	<u>3 hr</u>	6 hr
Dissolved oxygen	0.2348	82	26	77	58
pH	0.0459*	62	23	7	7
Conductivity	0.0012*	96	96	96	96
Suspended solids	0.2261	38	20	4	0
Dissolved metals					
Chromium	0.1266	14	22	46	82
Copper	0.8492	0	3	0	0
Iron	0.0004*	6	0	0	0 0
Lead	0.5156	10	0	0	0
Nickel	0.6188	18	6	54	70
Silver	0.8452	8	8	2	0
Zinc	0.0230*	21	15	0	0
Dissolved nutrients					
Total phosphorus	0.0030*	32	32	27	30
NH3-N	0.2021	51	37	17	7
$NO_3 + NO_2 - N$	0.0438*	34	13	0	0
Total organic carbon	0.0231*	0	30	44	36
Metal fraction of					
total suspended solids					07
Chromium	0.0001*	96	96	96	96
Copper	0.0002*	96			0.0
Iron	0.0017*	67	96	96	96
Lead	0.0010*	0	0	95	65
Nickel	0.0230*	22	60	26	19
Silver	0.0003*	35	32	0	0
Zinc	0.0247*	82	72	49	18
Nutrient fraction of					
total suspended solids					- /
Total organic carbon	0.5538	54	54	54	54
Ammonia	0.2886	12	22	96	96
Total phosphorus	0.0006*	58	46	<u>16</u>	23
Avg for all parameters		40	35	37	36
my for and parameters	Avg a	11 levels :	= 37 hr		

\* Total regression significant at the 95 percent level of confidence.
\*\* If no intersection of field mean with response surface occurred, the retention time corresponding to the maximum laboratory response for the respective aeration level was assumed when the field mean was above the surface, and the minimum was assumed if the field mean was below the surface.

#### Summary of Laboratory and Field Retention Times

Optimum Laboratory		Mean Field Retention**		
Site	Retention, hr*	Hr	Ratiot	
Mobile	20	12	1.6	
Savannah	37	53	0.7	

\* Average optimum laboratory retention for all parameters, Tables 15 and 16.
 \*\* Determined by field survey and dye tracer results.

† Ratio of laboratory retention time with closest comparison with field data to field mean retention.

Table 18

Modified Elutriate Test Factors

Site	<u>n</u>	Field Influent Concentration g/l	Test Slurry Concentration g/l	Mean Field Retention Time, hr	Test Retention Time, hr
Mobile	13	87	106	12	12
Savannah	11	107	99	51	24
Norfolk	24	88	89	41	24

Parameter*	Mobile		Savan	Savannah		Norfolk	
	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	
Dissolved oxygen mg/l	7.17	0.72	7.39	0.42	6.85	0.33	
pН	7.91	0.06	7.91	0.12	7.99	0.03	
Conductivity mmhos/cm	24,000	4,700	18,700	289	25,300	286	
Dissolved metals, mg/l							
Cadmium	<0.002				0.036	0.0042	
Chromium	<0.02				0.063	0.0064	
Copper	0.006	0.0035	0.0038	0.0023	0.042	0.0044	
Iron	0.026	0.023	0.040	0.017	0.153	0.0087	
Lead	<0.05		0.0017	0.0012	0.241	0.020	
Manganese	2.2	0.59			0.82	0.070	
Nickel	<0.02		0.0059	0.0043			
Zinc	<0.05		0.0069	0.0038	0.031	0.0045	
Dissolved nutrients, mg/l							
Total organic carbon	17.5	2.86	31.27	5.12	7.08	0.48	
			(Continued)				

Means and Standard Deviations for Replicate Modified Elutriate Tests

(Continued)

\* n = 13 for Mobile Harbor; n = 11 for Savannah Harbor; n = 24 for Norfolk Harbor. \*\* The notation BD indicates either dissolved or total concentrations were below detection limits, and fractions of the total suspended solids could not be calculated.

Parameter*	Mobile		Savannah		Norfolk	
	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Ammonia	12.71	1.13	11.38	1.40		
Nitrate	0.04	0.019	0.045	0.021	2 2 2 CR-	
Total phosphorus	<0.10		0.25	0.27	0.010	0.002
Metal fraction of						
the total sus- pended solids, mg/kg SS						
Cadmium	BD**		<u></u>	Cott	323	303
Chromium	BD		<u></u> 040	<u></u>	618	745
Copper	993	740	124	32.4	405	606
Iron	84,800	25,100	13,200	4590	11,300	4,570
Lead	BD		40	14.9	1,957	2,570
Manganese	224,000	67,400			2,507	261
Nickel	BD		147	74.7		
Zinc	BD		156	79.9	110	376
Nutrient fraction of the total suspended sol-						
ids, mg/kg ss						
Total organic carbon	152,000	83,600			87,900	93,100
Ammonia	BD					
Total phosphorus	BD		for ser-These	AND THE REPORT	1,874	2,590

#### Ratios of Mean Values from Modified Elutriate

#### Tests to Mean Field Values

Mobile	Savannah	Non-F-11
		Norfolk
1.09	0.91	0.59
1.05	0.99	1.27
0.65		3.75
	The straight linguist	5.75
BD		3.17
BD	BD	2.67
0.95		3.40
0.53		0.62
BD		0.73
0.54*	the second s	12.5**
BD	2.22	
BD		1.16
	and a the heat and have	
BD	0.42	BD
2.30		
0.93		
1.92		2.23
BD		2.35
BD	0.71	2.46
3.53		1.53
0.84		0.46
BD		1.27
BD		
BD		0.66
BD		0.86
BD		
2.12	1 C HE - P possible bill	0.97
1 27	1 10	1.68
	0.65 BD BD 0.95 0.53 BD 0.54* BD BD 2.30 0.93 1.92 BD BD 3.53 0.84 BD BD BD BD BD BD BD BD BD BD	0.65       0.89         BD          BD       BD         0.95       1.03         0.53       0.45         BD       1.13         0.54*          BD       2.22         BD       0.63         BD       0.63         BD       0.42         2.30       0.82         0.93       1.78         1.92       1.19         BD          BD       0.71         3.53       1.63         0.84       0.87         BD       1.02         BD       3.04         BD       1.52         BD       1.52

\* The measured concentrations of total manganese were below measured concentrations for dissolved manganese for the field effluent samples at the Mobile Harbor site (presumably due to analytical error). Therefore, values for the manganese fraction of the total suspended solids could not be compared with the results from the modified elutriate tests.
\*\* The high ratio of laboratory to field value for manganese at the Norfolk Harbor site was due to abnormally high precipitation which occurred during the field sampling period. This ratio was not included in computing the average of the ratios for this site.

APPENDIX A: RECOMMENDED PROCEDURE FOR CONDUCTING MODIFIED ELUTRIATE TESTS

1. This appendix describes a modified elutriate test procedure which may be used to predict both the dissolved and particle-associated concentrations of contaminants in confined disposal area effluents (water discharged during active disposal operations). The laboratory test simulates contaminant release under confined disposal conditions, reflecting the sedimentation behavior of dredged material, retention time of the containment, and the chemical environment in ponded water during active disposal. A schematic of the test is shown in Figure Al.

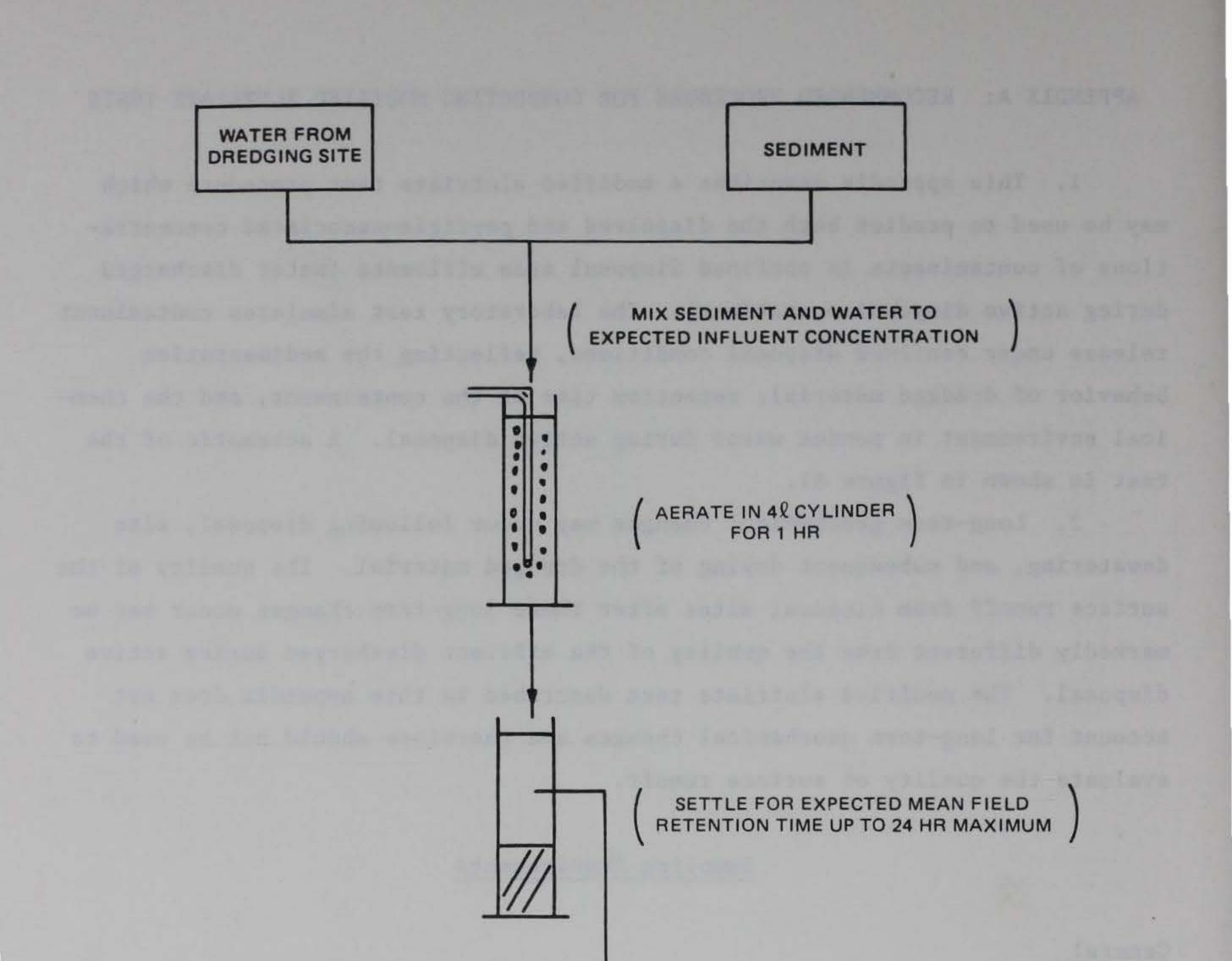
Long-term geochemical changes may occur following disposal, site 2. dewatering, and subsequent drying of the dredged material. The quality of the surface runoff from disposal sites after these long-term changes occur may be markedly different from the quality of the effluent discharged during active disposal. The modified elutriate test described in this appendix does not account for long-term geochemical changes and therefore should not be used to evaluate the quality of surface runoff.

#### Sampling Requirements

#### **General**

Samples of channel sediment and dredging site water are required for conducting modified elutriate tests and column settling tests, and for characterizing the sediment to be dredged. The level of effort, including the number of sampling stations, the quantity of material, and any schemes used for compositing samples is highly project-specific. If at all possible, the sampling operations required for (a) sediment characterization (both physical and chemical), (b) design and evaluation of the disposal site, and (c) the modified elutriate testing should be conducted simultaneously to avoid duplication of effort.

Normally, sediments from maintenance dredging are those for which 4. the quality of the effluent from the disposal site will be of concern. Grab samples of such sediments are satisfactory for obtaining the quantities needed for all testing requirements. General guidance on sampling for chemical



EXTRACT SAMPLE AND SPILT

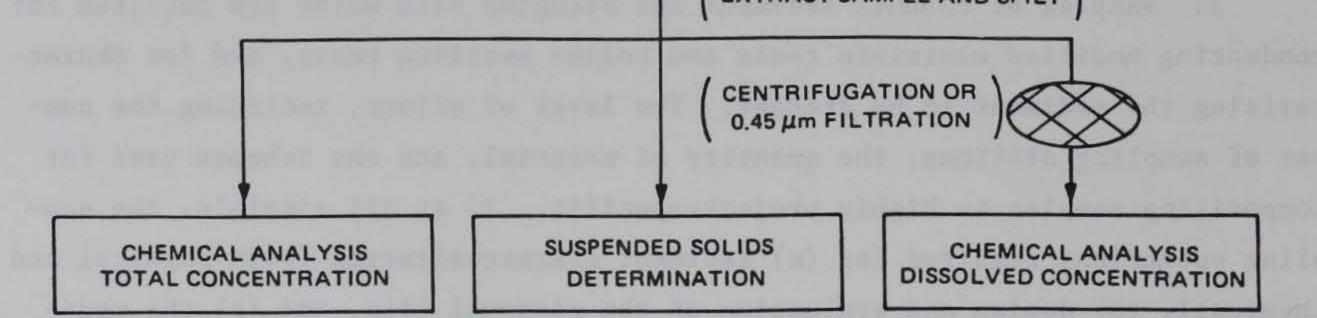


Figure Al. Schematic of modified elutriate test procedure

characterization purposes was given by Plumb (1981).\* Sampling guidance for purposes of disposal site design and evaluation was given by Palermo, Montgomery, and Poindexter (1978).

\* A list of references can be found at the end of the main text.

#### Sample collection and preservation

5. Procedures for sample collection and preservation given below are largely patterned after similar guidance for evaluation of proposed discharges into ocean waters (Environmental Protection Agency/Corps of Engineers (EPA/CE) 1977, Plumb 1981). Samples that are improperly collected, preserved, or prepared will totally invalidate any testing conducted and will lead to erroneous conclusions regarding the potential impact of the proposed discharge. Meticulous attention must therefore be given to all phases of water and sediment sampling, storage, and preparation. The procedures described herein specify the apparatus and procedures to use for sampling water and sediments and for preparing the water and sediments for chemical analysis. The procedures are designed to minimize sample contamination and alteration of the physical or chemical properties of the samples due to freezing, air oxidation, or drying.

6. <u>Number of samples.</u> The number of sediment and water samples to be taken for processing from the dredging or excavation site must be carefully considered because of the extremely heterogeneous nature of samples of this type. The largest source of variation between sediment samples taken at a dredging site has been shown to be the vertical and horizontal distribution of the samples (Brannon et al. 1976). With this in mind, sediment should be collected from a minimum of three sampling stations within the dredging area. The sampling stations should be located throughout the area to be dredged and

should be selected to characterize obviously contaminated as well as noncontaminated areas. The amount of sediment and water collected should be limited to the amount that can be used in the testing program within 2 weeks after sampling.

7. <u>Apparatus.</u> The following items are required for water and dredged material sampling and storage:

- a. Noncontaminating sediment grab or core sampler (Smith-McIntyre or Van Veen grab, K. B. Corer, etc.).
- b. Noncontaminating water sampler (Van Dorn water sampler, etc.).
- <u>c</u>. Acid-rinsed linear polyethylene bottles for water samples to be analyzed for metals and nutrients.
- d. Solvent-rinsed glass bottles with Teflon-lined screw-type lids for water samples to be analyzed for pesticide materials.
- e. Plastic jars or bags for collection of sediment samples.

f. Ice chests for preservation and shipping of dredged material and water samples.

8. <u>Water sampling.</u> A collection of water samples should be made with appropriate noncontaminating water-sampling devices. Special care must be taken to avoid the introduction of contaminants from the sampling devices and containers. To avoid trace metal contamination, sampling devices should be constructed of plastic materials. Prior to use, the sampling devices and containers should be thoroughly cleaned with a detergent solution, rinsed with tap water, soaked in 10-percent hydrochloric acid (HCl) for 4 hr, and then thoroughly rinsed with metal-free water. Water samples taken for trace organic analyses should be taken with glass or stainless steel devices. If plastic devices must be used, they must be cleaned, aged, and characterized as to the material that may leach from them into the samples. The sampling devices should be thoroughly cleaned, following the procedures outlined by EPA (1974a), and then rinsed just before using with the same solvent to be used in the analysis, probably hexane.

9. A representative dredging site water sample is obtained by collecting the sample volume from approximately 1 m above the sediment surface. The portion of the samples to be used for pesticide material analyses must be stored in glass or aluminum containers.

10. The samples should be stored immediately at 2 to 4° C, <u>never</u> <u>frozen</u>. The storage period should be as short as possible to minimize changes in the characteristics of the water. It is recommended that samples be processed within 2 weeks of collection.

11. <u>Sediment sampling</u>. Sediment samples should be taken with a corer or a grab sampler in a manner designed to ensure that their characteristics are representative of the proposed dredging site. Sampling stations should include known or suspected areas of high contamination as well as more representative areas. The larger the proposed dredging site, the more samples will be required for adequate coverage and characterization. The samples should be placed in airtight linear polyethylene containers. If organic materials are of primary concern, airtight glass storage containers should be used. Care should be taken to ensure that the containers are completely filled by the samples and that air bubbles are not trapped in the containers. The samples should be stored immediately at 2 to 4° C. <u>The samples must never be frozen</u> or dried. The storage period should be as short as possible to minimize changes in the characteristics of the dredged material. It is recommended that the samples be processed within 2 weeks of collection.

#### Modified Elutriate Test Procedure

The modified elutriate tests should be conducted and appropriate 12. chemical analyses should be performed as soon as possible after sample collection. The volume of elutriate sample needed for chemical analyses will vary depending upon the number and types of analyses to be conducted. Both dissolved and total concentrations of contaminants must be determined. The volume required for each analysis, the number of parameters measured, and the desired analytical replication will influence the total elutriate sample volume required. A 4-L cylinder is normally used for the test, and the supernatant volume available for sample extraction will vary from approximately 500 to 1,000 ml, depending on the sediment properties, settling times, and initial concentration of the slurry. It may be necessary to composite several extracted sample volumes or use large diameter cylinders to obtain the total required volume.

#### Apparatus

- The following items are required: 13.
  - Laboratory mixer, with stainless steel or Teflon shaft and a. blades.
  - Graduated cylinders (Four-litre cylinders are normally used. ь. Larger cylinders may be used if large sample volumes are required. Nalgene cylinders are acceptable for testing involving analysis of metals and nutrients. Glass cylinders are required for testing involving analysis of organics.)
  - Assorted glassware for sample extraction and handling. c.
  - Compressed air source with deionized water trap and 3/16-in. d. inside diameter tubing for bubble aeration of slurry.
  - Vacuum or pressure filtration equipment, including vacuum pump e. or compressed air source and an appropriate filter holder capable of accommodating 47-, 105-, or 155-mm-diam filters.
  - Presoaked filters with a  $0.45-\mu m$  pore-size diameter. f.
  - Plastic sample bottles, 250-ml capacity for storage of water g. and liquid phase samples for metal and nutrient analyses.
  - Wide-mouth, 1-gal capacity glass jars with Teflon-lined screwh. type lids for sample mixing. These jars should also be used for sample containers when samples are to be analyzed for pesticide materials.

14. Prior to use, all glassware, filtration equipment, and filters should be thoroughly cleaned. Wash all glassware with detergent, rinse five times with tap water, place in a clean 10-percent (or stronger) HCl acid bath for a minimum of 4 hr, rinse five times with tap water, and then rinse five times with distilled or deionized water. Soak filters for a minimum of 2 hr in a 5-M HCl bath and then rinse 10 times with distilled water. It is also a good practice to discard the first 50 ml of water or liquid phase filtered. Wash all glassware to be used in preparation and analysis of pesticide residues using the eight-step procedure given by EPA (1974a).

#### Test procedure

15. The step-by-step procedure for conducting the modified elutriate test is outlined below. An example calculation procedure is also given in the following pages.

16. Step 1 - Slurry preparation. The sediment and dredging site water should be mixed to approximately equal the expected average field influent concentration. If estimates of the average field influent concentration cannot be made based on past data, a slurry concentration of 150 g/l (dry-weight basis) should be used. Predetermine the concentration of the well-mixed sediment in grams per litre (dry-weight basis) by oven drying a small subsample of known volume. Each 4-l cylinder to be filled will require a mixed slurry volume of 3-3/4 l. The volumes of sediment and dredging site water to be mixed for a 3-3/4-l slurry volume may be calculated using the following expressions:

$$V_{\text{sediment}} = 3.75 \frac{C_{\text{slurry}}}{C_{\text{sediment}}}$$

(A1)

(A2)

and

Vwater = 3.75 - Vsediment

where

V sediment = volume of sediment, &

3.75 = volume of slurry for 4-l cylinder, l

C<sub>slurry</sub> = desired concentration of slurry, g/l (dry-weight basis)

sediment = predetermined concentration of sediment, g/l
(dry-weight basis)

V = volume of dredging site water, l

17. Step 2 - Mixing. Mix the 3-3/4  $\ell$  of slurry by placing appropriate volumes of sediment and dredging site water in a 1-gal glass jar and mixing for 5 min with the laboratory mixer. The slurry should be mixed to a uniform consistency with no unmixed agglomerations of sediment.

18. <u>Step 3 - Aeration</u>. The prepared slurry must be aerated to ensure that oxidizing conditions will be present in the supernatant water during the subsequent settling phase. Bubble aeration is therefore used as a method of sample agitation. Pour the mixed slurry into a  $4-\ell$  graduated cylinder. Attach glass tubing to the aeration source and insert the tubing to the bottom of the cylinder. The tubing can be held in place by insertion through a predrilled No. 4 stopper placed in the top of the cylinder. Compressed air should be passed through a deionized water trap, through the tubing, and bubbled through the slurry. The flow rate should be adjusted to agitate the mixture vigorously for 1 hr.

19. <u>Step 4 - Settling</u>. Remove the tubing and allow the aerated slurry to undergo quiescent settling for a time period equal to the anticipated field mean retention time, up to a maximum of 24 hr. If the field mean retention

time is not known, allow settling for 24 hr. Guidance for estimating the field mean retention is given in the following paragraphs.

20. <u>Step 5 - Sample extraction.</u> After the period of quiescent settling, an interface will usually be evident between the supernatant water with a low concentration of suspended solids and the more concentrated settled material. Samples of the supernatant water should be extracted from the cylinder at a point midway between the water surface and interface using a syringe and tubing. Care should be taken not to resuspend the settled material.

21. <u>Step 6 - Sample preservation and analyses.</u> The sample should be analyzed as soon as possible after extraction. Total suspended solids in milligrams per litre, and dissolved and total concentrations of desired analytes in milligrams per litre should be determined. The analyte fraction of the total suspended solids in milligrams per kilogram of suspended solids (SS) can then be calculated for appropriate analytes. Filtration using 0.45-µm filters should be used to obtain subsamples for analysis of dissolved concentrations. Samples to be analyzed for dissolved pesticide or polychlorinated biphenyl (PCB) materials must be free of particles but should not be filtered, due to the tendency for these materials to adsorb on the filter. However, particles can be removed before analysis by high-speed centrifugation at 10,000 times gravity using Teflon, glass, or aluminum centrifuge tubes (Fulk et al. 1975). The total suspended solids concentration can also be determined by filtration  $(0.45 \ \mu m)$ . The analyte fraction of the total suspended solids may be calculated in terms of milligrams per kilogram of SS as follows:

$$F_{SS} = (1 \times 10^6) \frac{C_{total} - C_{diss}}{SS}$$
(A3)

#### where

F<sub>SS</sub> = analyte fraction of the total suspended solids, mg analyte/kg of suspended solids (1 × 10<sup>6</sup>) = conversion factor, milligram/milligram to milligram/ kilogram C<sub>total</sub> = total concentration, mg analyte/l of sample C<sub>diss</sub> = dissolved concentration, mg analyte/l of sample

#### SS = suspended solids concentration, mg solids/l of sample

22. Subsamples for analyses of total concentrations should undergo appropriate digestion prior to analysis. All digestion and chemical analyses should be performed using accepted procedures (American Public Health Association (APHA) 1981; EPA 1974a, 1974b).

23. Samples to be analyzed for pesticide or PCB materials should immediately undergo solvent extraction. The extract may then be held in clean uncontaminating containers for periods up to 3 or 4 weeks at -15 to -20° C before the analyses are performed.

24. Samples for metals analysis should be preserved immediately by lowering the pH to <2 with 3 to 5 ml of concentrated HNO<sub>3</sub> per litre (EPA 1979). High purity acid, either purchased commercially or prepared by a subboiling unit, must be used. 25. Nutrient analyses should be conducted as soon as possible. Acidification with  $H_2SO_4$  to pH <2 and storage at 4° C may allow the sample to be held for a maximum of 24 hr for ammonia nitrogen, Kjeldahl nitrogen, and nitrate nitrogen analyses (EPA 1979). Storage at 4° C will allow holding of samples to be analyzed for dissolved orthophosphate and total dissolved phosphorus for up to 24 hr. Subsamples to be analyzed for cyanide should be preserved with 2 ml of 10 N sodium hydroxide per litre of sample (pH >12) (EPA 1979).

#### Prediction of Effluent Quality

26. Concentrations of contaminants discharged in the effluent will be the sum of the dissolved fraction and that fraction associated with suspended particulates which are discharged. Prediction of effluent quality in terms of total contaminant concentrations must therefore be based on both the modified elutriate test results and estimates of the total suspended solids concentration in the effluent. Procedures for confined disposal site design and operation (Palermo, Montgomery, and Poindexter 1978; Montgomery, Thackston, and Parker 1983; Palermo 1985) must therefore be applied to evaluate sedimentation performance for the containment area. These procedures provide estimates of effluent suspended solids concentrations based on results of settling column tests. The standard column settling test for site design is now being modified to allow a refined prediction of effluent suspended solids concentrations. These modifications will be documented in a forthcoming report.

27. The modified elutriate test procedure defines dissolved contaminant concentrations in milligrams per litre and particulate-associated concentrations in milligrams per kilogram under quiescent settling conditions and accounts for geochemical changes occurring in the disposal area during active disposal operations. Using these test results, the total contaminant concentration in milligrams per litre in the effluent may be determined for the estimated sedimentation performance as follows:

$$C_{total} = C_{diss} + \frac{C_{part} \times TSS_{eff}}{1 \times 10^6}$$
(A4)

where

- C<sub>total</sub> = estimated total concentration in effluent, mg analyte/l of water
  - C<sub>diss</sub> = dissolved concentration, as determined by modified elutriate tests, mg analyte/l of sample
  - C<sub>part</sub> = particulate concentration, as calculated from modified elutriate results, mg analyte/kg of suspended solids
- TSS<sub>eff</sub> = suspended solids concentration of effluent, as estimated from evaluation of sedimentation performance in 8-in. column, mg suspended solids/l of water

The acceptability of the proposed confined disposal operation can then be evaluated by comparing the predicted total contaminant concentrations with applicable water quality standards, considering an appropriate mixing zone.

A10