



DREDGED MATERIAL RESEARCH PROGRAM



TECHNICAL REPORT D-77-23

HABITAT DEVELOPMENT FIELD INVESTIGATIONS WINDMILL POINT MARSH DEVELOPMENT SITE JAMES RIVER, VIRGINIA

APPENDIX F: ENVIRONMENTAL IMPACTS OF MARSH DEVELOPMENT WITH DREDGED MATERIAL: SEDIMENT AND WATER QUALITY

Volume I: Characteristics Of Channel Sediments Before Dredging And
Effluent Quality During And Shortly After Marsh Habitat Development

by

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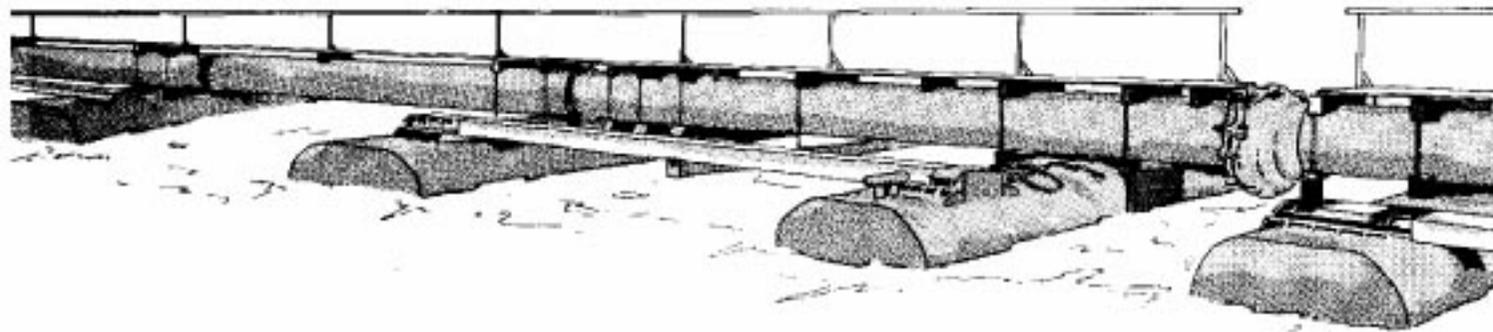
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HABITAT DEVELOPMENT FIELD INVESTIGATIONS, WINDMILL POINT
MARSH DEVELOPMENT SITE, JAMES RIVER, VIRGINIA

- Appendix A: Assessment of Vegetation on Existing Dredged Material Island
- Appendix B: Propagation of Vascular Plants
- Appendix C: Environmental Impacts of Marsh Development with Dredged Material: Acute Impacts on the Macrobenthic Community
- Appendix D: Environmental Impacts of Marsh Development with Dredged Material: Botany, Soils, Aquatic Biology, and Wildlife
- Appendix E: Environmental Impacts of Marsh Development with Dredged Material: Metals and Chlorinated Hydrocarbon Compounds in Marsh Soils and Vascular Plant Tissues
- Appendix F: Environmental Impacts of Marsh Development with Dredged Material: Sediment and Water Quality

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30 September 1978

SUBJECT: Transmittal of Technical Report D-77-23, Appendix F
(Volume I)

TO: All Report Recipients

1. The technical report transmitted herewith represents the results of one of a series of research efforts (work units) undertaken as part of Task 4A (Marsh Development) of the Corps of Engineers' Dredged Material Research Program. Task 4A was part of the Habitat Development Project (HDP) and had as its objective the development and testing of the environmental, economic, and engineering feasibility of using dredged material as a substrate for marsh development.
2. Marsh development using dredged material was investigated by the HDP under both laboratory and field conditions. The study reported herein (comprising Work Units 4A11D, G, and H) was an integral part of a series of research contracts jointly developed to achieve Task 4A objectives at the Windmill Point Marsh Development Site, James River, Virginia, one of six marsh establishment sites located in different geographic regions of the United States. Interpretation of this report's findings and recommendations is best made in context with the other reports in the Windmill Point site series (4A11A-M).
3. This report, "Appendix F: Environmental Impacts of Marsh Development with Dredged Material: Sediment and Water Quality," appears in two volumes and is one of six contractor-prepared appendices published relative to the Waterways Experiment Station's Technical Report D-77-23, entitled "Habitat Development Field Investigations, Windmill Point Marsh Development Site, James River, Virginia; Summary Report" (4A11M). The appendices to the Summary Report are studies that provide technical background and supporting data and may or may not represent discrete research products. Appendices that are largely data tabulations or that clearly have only site-specific relevance were published as microfiche; those with more general application were published as printed reports.

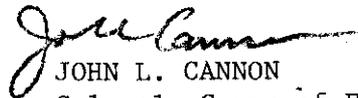
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(Volume I)

4. Volume I, entitled "Characteristics of Channel Sediments Before Dredging and Effluent Quality During and Shortly After Marsh Habitat Development," is forwarded herewith. Research described in this document included a chemical and physical evaluation of channel sediment characteristics before dredging and a chemical and physical evaluation of effluent at the habitat development site during active disposal, dewatering, and 3.5 months after disposal was complete. Volume II is entitled "Substrate and Chemical Flux Characteristics of a Dredged Material Marsh." Research described in Volume II included documentation of changes in the physical and chemical properties of the developed marsh substrate and the longer term tidal flux characteristics of nutrient and metallic substances. The relationship between substrate conditions and chemical flux is discussed and all observations are compared with parallel studies conducted in a nearby natural marsh.

5. Data from this report will be included in the Windmill Point Summary Report (4A11M) and synthesized in Technical Reports DS-78-15 and DS-78-16, entitled "Upland and Wetland Habitat Development with Dredged Material: Ecological Considerations" and "Wetland Habitat Development with Dredged Material: Engineering and Plant Propagation," respectively.



JOHN L. CANNON
Colonel, Corps of Engineers
Commander and Director

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) | | |
| <p>This volume is the first of a two-volume appendix presenting the results of chemical and sedimentological studies conducted at a dredged material marsh development site located near Windmill Point, on the tidal freshwater James River, 16 km below Hopewell, Virginia.</p> <p>Navigation channel sediments were collected in January 1975, before dredging and marsh development, and described according to their temperature, pH, oxidation reduction potential, percent water, percent volatile solids, particle size composition, mineralogy, and cation exchange capacity. Sediment interstitial water and total sediment concentrations of sulfides and various nutrients and metals were also documented. The relationships between channel sediment characteristics and the chemical quality of effluent leaving the diked marsh development site were studied under three different conditions: (a) in January, 1975--during</p> <p style="text-align: right;">(Continued)</p> | | |

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20. ABSTRACT (Continued).

actual dredging and dredged material disposal for marsh substrate development, (b) during dewatering (2-4 days after the completion of dredged material disposal operations), and (c) in May 1975--3.5 months after dredging, before the beginning of marsh vegetation planting operations had begun or any extensive natural vegetation development had occurred.

During dredging, about two-thirds of the channel sediments' organic material was lost, probably by flotation or as organic surface scums. The volatile solids concentration in the confined dredged material substrate, when compared with values in the navigation channel sediment, decreased from 14.5 to 4.9 percent. The average concentration of suspended solids leaving the dike during dredging was 16 percent. Mean particle size of the material in suspension was 3.7 μm compared with the mean value of 4.8 μm for the channel sediments. Clay/silt ratios of unity or higher in the suspended material leaving the dike indicated that suspension transport was largely colloidal or clay size materials. Dissolved chemical concentrations in the effluent from the dike during dredging were monitored and compared with predicted values calculated assuming a 1:5 mixture of channel sediment interstitial water to James River water. Measured dissolved concentrations of zinc, copper, and cadmium exceeded predicted values by 7700, 1000, and 630 percent, respectively. Predicted concentrations for lead were exceeded by 250 percent, nickel and mercury by 150 percent, and ammonium-N by 40 percent. Concentrations of dissolved iron and orthophosphate were below predicted values by 50 and 60 percent, respectively, probably as a result of precipitation of iron oxy-hydroxides and phosphates. Cadmium was the only dissolved metal that remained at elevated concentrations during the dredging (0.019 mg/l) and dewatering (0.018 mg/l) periods. The other eight dissolved metals either decreased substantially during dewatering or, as was the case for dissolved mercury and nickel, were represented by low values during both the dredging and dewatering periods. Measured decreases ranged from the large change in dissolved zinc from 5.31 to 0.10 mg/l to the smaller change in dissolved calcium from 63 to 38 mg/l; dissolved lead decreased during dewatering to less than the minimum detection level of 0.05 mg/l. Ebb tide concentrations of dissolved iron (0.52 mg/l) and ammonium (2 mg/l) were higher 3.5 months after dredging, suggesting an export of these components from the development site. Dissolved nitrates and nitrites were similar (0.26 mg/l) to their elevated concentrations during the dewatering period. Dissolved cadmium decreased substantially to 0.003 mg/l while dissolved copper (0.006 mg/l) and nickel (0.02 mg/l) remained at levels similar to those observed during dewatering. Dissolved mercury was slightly higher (0.001 mg/l) during ebb tide than James River background water (0.0002 mg/l) during flood tide.

Particulate concentrations of chemical substances in the dike effluent during dredging were apparently influenced by oxidation and reduction reactions and solubilization from exchangeable or organic sediment phases. Effluent concentrations were compared with channel sediment concentrations. The oxidation of interstitial dissolved iron and possibly manganese was probably responsible for an increase in particulate iron from 41,000 to 43,000 $\mu\text{g/g}$ and particulate manganese from 1,100 to 1,300 $\mu\text{g/g}$. Particulate zinc decreased from 240 $\mu\text{g/g}$ in the channel sediments to 210 $\mu\text{g/g}$ in the effluent. Because of the greater concentration of suspended material leaving the development site 3.5 months after dredging (ebb tide = 1,400 mg/l; flood tide = 100 mg/l), there was a net loss of particulate iron, copper, manganese, zinc, and lead.

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PREFACE

This report contains the results of investigations of the chemical and sedimentological characteristics of the James River Artificial Habitat Development Site and a reference marsh near Windmill Point, Virginia. Studies were conducted in the channel before dredging and during site construction as well as at specific time intervals after marsh development. This study forms a part of the Dredged Material Research Program (DMRP), Environmental Laboratory (EL), U. S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi, and was conducted under contracts DACW65-75-C-0051 and DACW65-76-C-0039 with the Old Dominion University Research Foundation, Old Dominion University (ODU), Norfolk, Virginia. Contracting was handled by the U. S. Army Engineer District, Norfolk (NAO); LTC R. H. Routh, CE, NAO, was the Contracting Officer.

Dr. Donald D. Adams^{*}, Institute of Oceanography, ODU, was the principal investigator and supervised the field program and chemical studies. Dr. Dennis A. Darby, Department of Physics and Geophysical Sciences, conducted the geological and sedimentological studies, while Randolph J. Young, Institute of Oceanography, was responsible for the metals program. Research assistants for this study were A. S. Katsaounis, W. T. Nivens, D. L. Stealey, C. L. (Poméroy) Young, and D. T. Walsh. Part-time help was provided by G. Adams and P. Crowley. Computer programs were developed by P. J. Anninos, J. A. Menchhoff, and L. E. Whitlock. Numerous students participated in both the field operations and laboratory analysis. The utilization of laboratory and cold room facilities at the Department of Chemistry, ODU, was greatly appreciated. Close cooperation with NAO, especially with Mr. E. E. Whitehurst, was especially helpful. The cooperation of the captain and crew of NAO's vessel ADAMS is gratefully acknowledged. Mr. David Harrison, Flowerdew Hundred Farm and Windmill Point Island, cooperated by allowing use of his facilities and access to the experimental site.

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This work was conducted under the direction of EL personnel. The study was designed by John D. Lutz, Natural Resources Development Branch, in close cooperation with the principal investigators. The contract was managed by Mr. Lutz under the supervision of Dr. W. Gallaher, Branch Chief, and Dr. C. J. Kirby, Chief, Environmental Resources Division. The study was under the general supervision of Dr. H. K. Smith, Habitat Development Project Manager, and Dr. J. Harrison, Chief, EL. Directors of WES during the conduct of the study were COL G. H. Hilt, CE, and COL J. L. Cannon, CE. Technical Director was Mr. F. R. Brown.

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NOTE: Appendices A' through E' mentioned herein were reproduced on microfiche and are enclosed in an envelope attached inside the back cover of Volume II.

Habitat Development Field Investigations
Windmill Point Marsh Development Site
James River, Virginia

Appendix F: Environmental Impacts of
Marsh Development with Dredged Material:
Sediment and Water Quality

Volume I: Characteristics of Channel
Sediments Before Dredging and Effluent
Quality During and Shortly After Marsh
Habitat Development

PART I: INTRODUCTION

Background

1. In 1973 the Dredged Material Research Program (DMRP) of the U. S. Army Engineer Waterways Experiment Station (WES) was established to address environmental and technical alternatives for the disposal of dredged sediments from the Nation's waterways. One of the major programs under the DMRP was the Habitat Development Project (HDP) which was designed to evaluate and demonstrate potential fish and wildlife habitat development as a disposal alternative. Because of substantial loss of wetlands in the past decades, the major thrust of the HDP was toward the development of marshes from dredged material. Eight marsh development study locations were established throughout the United States. The Windmill Point site, located on the James River about 16 km downstream from Hopewell, Virginia, was one of these studies.

2. Shoaling on the James River has been a major problem to safe navigation and transport of cargo to the ports of Hopewell and Richmond (U. S. Army Engineer District, Norfolk 1974). As early as 1870, Congress approved the excavation of a channel between Richmond and Newport News (Pleasants 1973). Portions of the Jordan Point-Harrison Bar-Windmill

Point shoal, which is located approximately 93 km upstream of the river's mouth and the harbor of Hampton Roads, require annual maintenance. Biannual dredging of approximately 222,000 m³ from this 13-km channel and the subsequent open-water side channel disposal of the dredged material resulted in filling of the river bottom and the creation of a small 0.6-ha island south of the channel upstream from Windmill Point. The Windmill Point marsh development site, hereafter referred to as the "development site" or "artificial habitat," was established in early 1975 in shallow waters on the upstream side of this preexisting 0.6-ha island composed of dredged channel sediments.

3. The U. S. Army Engineer District, Norfolk, and the Environmental Laboratory (EL) at WES developed this artificial marsh-island complex as part of the normal maintenance dredging program of the navigational channel. Approximately 62,300 m³ of sand was pumped from a borrow area near Buckler's Point to construct retaining dikes for the artificial marsh (Figure 1). Between 21 January and 4 February 1975, approximately 166,540 m³ of channel sediments were pumped into the 6.1-ha rectangular (396 by 152 m) site (Table 1) to provide an average fill depth of 1.1 m. All dredged channel sediments entered the rectangular diked area at its northwest corner; the dredged material slurry traveled approximately 425 m within the dike before reaching the unrestricted effluent discharge point located at the dike's southeast corner and consisting of two 0.9 m diameter corrugated steel pipes. Following the completion of dredged material disposal activities, these effluent pipes along with a small breach that developed in the southern portion of the dike served as entry and exit locations for regular tidal influence on the experimental substrate. Before and after site development extensive studies were conducted by the HDP to document the chemical, biological, and geological alterations related to this marsh habitat development project.

4. The objectives of studies reported in the first volume of this appendix were (a) to document the chemical and sedimentological nature of the channel sediments before dredging, (b) to relate these findings to effluent water quality at the development site during dredging, and

(c) to document the mobilization of selected potential pollutants from the recently dredged substrate to the river water in the short term following site construction. Additional sediment and water quality investigations were conducted at the Windmill Point development site and at a reference marsh after site construction was completed. These additional studies were designed to contrast the physical and chemical characteristics of the substrate and tidal waters at the two marshes. The results of these studies comprise the second volume of this appendix entitled, "Substrate and Chemical Flux Characteristics of a Dredged Material Marsh."

5. Field studies were undertaken eight different times at the site over a period of 2 years to investigate conditions during and after marsh development. The first six field collections were conducted at the development site only and provided the data discussed in Volume I. The last two field collections included observations at both the development site and a reference marsh, situated 3.2 km upstream from the development site near the mouth of Herring Creek at Ducking Stool Point (Figure 2). These data are presented in Volume II. Data interpretation emphasized the relationships between the chemistry and geology of fine-grained sediments, the change in the chemistry and geology of the sediment and river water related to a specific dredged material disposal alternative, and the establishment of a fresh water marsh habitat. Results of these studies are applicable to Corps of Engineer (CE) requiring an understanding of (a) the chemistry and geology of fluvial-estuarine sediments in areas of rapid deposition, and (b) the chemical budgets in freshwater marsh ecosystems.

Approach and Chronology

6. Ten sediment cores were taken along a 1.5-km section of the navigational channel of the Jordan Point-Harrison Bar-Windmill Point shoal before dredging in January 1975. The effluent from the intertidal habitat containment area was sampled every 6 hours at one of the effluent pipes during four 48-hr periods: once during dredging (31 January to 1 February 1975); again during the dewatering period (6-8

February 1975) two days after dredging had ceased (Table 2), and two additional 48-hr periods on 18-20 April and 13-15 May 1975, approximately 2.5 and 3.5 months after dredging, respectively. Because of unusual weather conditions in April, when high winds prevented tidal water from entering the diked intertidal habitat, only the May sampling program will be reported.

7. The last 48-hr field water quality studies were conducted 18 (5-7 August 1976) and 24 months (8-10 January 1977) after dredging. These two programs were the most extensive of the field operations and were chosen to represent different seasons. Sediment studies were conducted by coring three different locations (subtidal, intertidal, and high marsh) at the development site on three different occasions (Table 2): July 1975 (6 months after dredging), August 1976 (18 months after dredging), and January 1977 (24 months after dredging). The reference marsh was sampled at corresponding locations during August 1976 and January 1977. At each of these locations, cores were collected within a 25-m² quadrant for a total of nine cores from each marsh for each period (Figures 2 and 3). Sediments from these cores were divided into specific depth intervals of 0 to 10 cm (surface), 11 to 24 cm (mid-depth), and 25 to 50 cm (deep). In addition, surface sediment grab samples and cores were collected within the development site in July 1976 (17 months after dredging) and July 1977 (29 months after dredging) for special studies (Table 2).

8. A listing of the various parameters examined throughout this study is presented in Table 2. Data plots for each of the parameters are presented in Appendix A', data tabulations are presented in Appendix B', and statistical tabulations are presented in Appendix C'.

Physical Setting

9. Windmill Point is located on the James River approximately 51 km below Richmond, Virginia, and 93 km above the harbor of Hampton Roads. Slightly upstream of Windmill Point is the Jordan Point-Harrison Bar-Windmill Point shoal located between Buckler's and Windmill Point

(Figure 1). Portions of the channel associated with this shoal require annual maintenance dredging and experience an overall sedimentation rate in the channel of about 90cm/yr. This specific portion of the channel was last dredged two years prior to being used for habitat development. A description of this section of the river is provided in Table 1. Only 16 km upstream of Windmill Point is the industrial city of Hopewell, which discharges effluent containing an average of 36,000 kg/day biochemical oxygen demand (BOD) (Diaz and Boesch 1977). Major manufacturing activities at Hopewell are chemicals, paper products, fertilizers, and synthetic fibers. Effluents from these industrial activities probably contribute to historical indications that bottom sediments near Windmill Point exceeded Environmental Protection Agency criteria for open-water disposal of dredged materials due to levels of chemical oxygen demand (COD), volatile solids, total Kjeldahl nitrogen (TKN), lead, and zinc.

10. Previous salinity data for the study area, which is part of the lower tidal freshwater James, indicated the absence of salt water during 1968 and 1969 (Brehmer 1972), yet it was suggested by Diaz and Boesch (1976), based on benthic faunal data, that during drought conditions in the mid-1960's intrusion probably occurred as far upstream as Hopewell. Salinity typically does not exceed 2 o/oo at Swann's Point located 30 km downstream of Windmill Point. Tidal currents of 0 to 80 cm/sec, with a normal range of 20 cm/sec, were reported for a section of the James River 20 km below the study area (Nichols 1972). The mean annual river discharge was approximately 212 m³/sec with recorded extremes of 0.3 to 9,200 m³/sec.

Water quality

11. One of the three major BOD peaks on the James River was reported near and below Hopewell (James River Comprehensive Water Quality Management Study 1972), where oxygen depression was a common occurrence in the summer. Dissolved nitrate-N was as high as 2 mg/l for the waters of the study area, while dissolved inorganic orthophosphate-P reached concentrations of 0.6 mg/l during October for this stretch of the river. Brehmer (1972) reported a mean pH of about 7.7, with a range of 6.8 to 8.6, for the freshwater section of the James River, while suspended

solids concentrations ranged between 29 to 44 mg/l with approximately 19 to 31 percent consisting of volatile matter (Brehmer and Haltiwanger 1966). Further data are provided in Table 3.

Sediment quality

12. The redox potential of the James River channel sediments ranged from -70 to +50 mV within the top 18 cm, while the interstitial pH was reported as 6.7 for two stations near the study area (Moncure and Nichols 1968). At stations below Windmill Point, these authors reported organic matter content varying between 0 and 4 percent. Analyses of channel sediments near Windmill Point indicated 10 percent volatile solids, 9 percent chemical oxygen demand (COD), 2,190 ppm total Kjeldahl nitrogen (TKN), 53 ppm lead, 0.3 ppm mercury, and 260 ppm zinc (U. S. Army Engineer District, Norfolk 1974). Other data (Lunz and Huggett 1974) gave values of 464 ppm total phosphorous, 28 ppm total copper, and 49 percent total solids. Further data are listed in Table 3.

13. Previous analyses of sediment particle size or cation exchange capacity have not been reported for the Windmill Point area. The lower 77-km section of the James River contains either silty clay, sand or a mixture of sand-silt-clay with an average of 39 percent clay (Moncure and Nichols 1968; Nichols 1972). These authors also reported a general decrease in sediment size sorting and water content from the estuary mouth upstream and from dredged channels to the shoals.

14. Quartz and feldspar dominated the sand-size sediment, with lesser amounts of fecal pellets, plant debris, heavy minerals, mica, coal fragments, fly ash, and cinder (Nichols 1972). Calcium carbonate contents of the sediments decreased from 41 percent at the mouth of the James River to 2 percent 77-km upstream. Nichols (1972) also reported that the clays consisted of 44 percent illite, 23 percent chlorite, 18 percent smectite, and 15 percent kaolinite in the vicinity of Hopewell, with decreasing amounts of smectite and illite downstream, while Feuillet (1976) listed 33 percent kaolinite, 30 percent mixed-layered clays, 20 percent illite, 12 percent vermiculite, less than 5 percent chlorite, and 3 percent smectite for the same area of the river. Because clay mineralogy values are imprecise and normally vary

by ± 15 to 20 percent, the only real difference between these two reports was the identification of vermiculite and mixed-layered clays by Feuillet (1976).

PART II: JAMES RIVER CHANNEL BOTTOM SEDIMENTS

Introduction

Purpose

15. Because previous data from this section of the James River suggested poor sediment quality, this portion of the study was designed to document the chemical and sedimentological nature of the material within the maintained channel. Such information was important for understanding potential detrimental effects to the successful development of a marsh, and for assessing any postdeposition mobilization of pollutants from the recently deposited substrate.

Physical setting

16. Although the James River erodes a wide variety of geologic units upstream (Calver 1973), local runoff from agricultural sources is suspected of contributing a substantial portion of the sediment load. Of the four counties (Prince George, Charles City, Chesterfield, and Henrico) bordering the James River both upstream and adjacent to the site, approximately 23 percent of the land was classified as farms in 1974 with about 36 percent of the farmland considered harvested cropland. Chesterfield, Henrico, and Prince George Counties have large sand and gravel operations (James River Comprehensive Water Quality Management Study 1972), while Lehigh Portland Cement and Carter Sand and Gravel are located 80 km upstream of Windmill Point..

17. The general circulation scheme observed for similar estuaries (Pritchard 1955) favors deposition in the dredged channels due to an oscillating net upstream transport of fine-grained sediment in the channels while surface water is transported downstream (Meade 1969). This prevents flushing of the channel sediment out of the estuary under nonflood conditions. The widening of the river from 0.5 km upstream to over 1.5 km above Windmill Point causes a reduction in current velocities and an increase in the sedimentation rate of finer particles to the bottom. Although the influence of salt water is negligible, organic matter derived from riverine wetland habitats (swamps and marshes) probably

contributes to the coagulation of fine-grained sediment and increased sedimentation. Because of these factors, the study area has the second highest deposition rate in the James River and averages about 90 cm/yr based on surveys by NAO between 1972 and 1974 (Table 4). Deposition in the channel was greater on the north side and, in places, the channel even eroded slightly on the south side (Figure 4).

Methods and Materials

Field

18. Ten stations were occupied on 9 January 1975 along a 1.5 km stretch of the James River channel (Figure 5). Coring was conducted by free-fall with a model 2171 Benthos (Benthos, Inc., North Falmouth, Mass) gravity corer with 2.45-m plastic core liners (outside diameter = 7.2 cm). After recovery of the cores, water overlying the sediments in a core tube was removed by suction and replaced with nitrogen gas. Probe analyses were conducted through predrilled holes for pH, redox potential (Eh), sulfide using the sulfide electrode potential (pS), and temperature. These measurements were done under an atmosphere of nitrogen gas at two or three locations along the length of the core liner. At each of these locations a sediment sample was collected and stored separately under nitrogen for measurement of total sulfides. The cores were kept under nitrogen and cooled with dry ice during transport and refrigerated (4°C) before interstitial water extraction or further processing, which occurred within one week.

Laboratory

19. Extrusion of the sediments from the core liners and interstitial water extraction was conducted in a nitrogen atmosphere. The core liners were placed in a plexiglass tube fitted to a glove box. Sediments were removed and transferred to polycarbonate or polyethylene bottles for centrifugation at 9000 rpm for 20 min at 4°C. The partial pressure of oxygen in the glove box was monitored with a YSI model 51A (Yellow Springs Instr. Co., Yellow Springs, Ohio) oxygen meter. The glove box was flushed with nitrogen gas when values above 0.5 ppm

oxygen were attained. All utensils were Teflon-coated and acid washed; all plastic ware was previously acid-soaked and liberally rinsed with deionized water.

20. The light yellow colored interstitial water, which was free of visible precipitates, was measured immediately for dissolved ammonium by the method developed by Solórzano (1969). Samples for other nutrients were passed through 47-mm diameter Nucleopore (Nucleopore Corp., Pleasanton, California; 0.4 μm pore size) filters by vacuum filtration; these were frozen unacidified in 75-ml polyethylene vials with snap-on caps. Interstitial water samples to be used for dissolved trace metals analysis were processed in a similar fashion. All water storage vials and the plastic filtration system were pre-cleaned by soaking in acid and -- rinsing with deionized water. Water samples for dissolved metals (50 to 60 ml) were acidified with 2 ml of distilled (all-Teflon still) reagent grade concentrated hydrochloric acid before freezing. After centrifugation and removal of interstitial water, sediments were stored for determination of mineralogy, cation exchange capacity, and measurements of total metals and total nutrients.

21. Within 48 hrs of coring, sediment subsamples were processed for total hydrogen sulfide. The method used was similar to that developed by Cline (1969) as described in Strickland and Parsons (1972), with minor modifications for sediments.

22. After frozen storage for 4-5 months and before the measurement of nitrogen compounds, interstitial water samples were acidified to eliminate a reddish ferric iron precipitate that contained crystalline low magnesium calcite as identified by X-ray diffraction. This precipitate had developed during storage and was evident in every sample. Thawed samples were basic (pH = 8.5 to 9.0) before addition of the acid. Dissolved total Kjeldahl nitrogen in the interstitial waters was determined by methods described in Strickland and Parsons (1972) using a manifold recommended for the Autoanalyzer II (EPA 1974). Dissolved nitrate and nitrite were analyzed with standard Autoanalyzer I manifolds. The automated procedure for the determination of nitrate was based on the cadmium-copper reduction column method developed by Wood et al.

(1967) and modified by Stainton (1974). The automated procedure for nitrite was an adaption of the diazotization method (Taras et al. 1971).

23. Dissolved inorganic orthophosphate in the interstitial water was analyzed by the automated ascorbic acid method outlined in Technicon Industrial Method 156-71W, which is adapted from the method described by Murphy and Riley (1962) as outlined in Strickland and Parsons (1972). The pH of each sample was adjusted to 1.5 to release phosphorus that was precipitated as a reddish material during 4-5 months frozen storage. Standards were also acidified to account for pH effects on the color development. Total dissolved phosphorus compounds in the interstitial water were determined by the same automated procedure for orthophosphate after digestion in micro-Kjeldahl flasks (Strickland and Parsons 1972) using a Kjeldahl digestant described by EPA (1974). Phosphate standards were digested with an equivalent amount of Kjeldahl digestant to account for any interference caused by the mercury catalyst in the digestion mixture. Acidified samples were adjusted to pH 2 with 30 percent sodium hydroxide. At pH values of approximately 2.5 or greater a red precipitate formed.

24. Measurements of total Kjeldahl nitrogen and total phosphorus in the sediments required minor modifications of existing procedures. One gram of freeze-dried sediment was mixed with 5 ml of Kjeldahl digestion reagent (EPA 1974) and deionized water. After the water had boiled off at 260°C, the digestion reagent was allowed to boil and fume over the sediments for an additional two hr, or until the mixture turned pale yellow. Then, 75 ml of hot deionized water was added, and the solution was allowed to boil down to 50 ml. The acidified samples were adjusted to pH 4 with 30 percent sodium hydroxide, and deionized water was added to a final volume of 100 ml. Half of this volume was used for the determination of total phosphorus using the method of Murphy and Riley (1962) and 0.6 ml of the remaining solution was diluted to 50 ml for total nitrogen measurement (Solórzano 1969).

25. Dissolved metals in the interstitial water were analyzed by flame atomic absorption using direct aspiration of acidified samples

into an air-acetylene flame. When concentration levels permitted, absorbances were measured with a Perkin-Elmer model DCR-1 (Perkin-Elmer Corp., Norwalk, Conn.) digital readout using 4X signal averaging. Scale expansion was generally necessary for detection of cadmium, chromium, copper, nickel, and lead. Dissolved mercury was measured by a cold vapor atomic absorption method adapted from Hatch and Ott (1968). Absorbances of freshly prepared standards were measured under similar conditions. The concentrations of unknowns were calculated from linear least squares regression equations developed with the standards. Equations for calculation of precision and accuracy are summarized in Table 5. Containers were acid-washed linear polyethylene.

26. Unsieved sediment samples (1 to 2 g) from the channel cores were oven dried at 60°C to constant weight and digested for 5 hr at 95°C with approximately 20 ml of a one to one mixture of concentrated hydrochloric and nitric acids* (Anderson 1974). The remaining sediment was washed three times with one percent hydrochloric acid, centrifuged, added to the previous acid, and adjusted to 100 ml for total metal analysis. A nitrous oxide-acetylene flame was used in order to overcome aluminum and phosphate interferences in the measurement of calcium and to overcome iron influences in the analysis of chromium. In addition, lanthanum was added to a final concentration of 0.2 percent in order to minimize calcium ionization and overcome anion interferences. Other metals were analyzed in an air-acetylene flame, with the exception of total mercury, which was measured by the cold vapor method in the remaining digestant mixture after dilution with deionized water.

27. Sediment water content was determined by two methods: oven drying at 60°C and freeze drying to constant weight. Volatile solids were measured by combusting the dried samples for 15 min at 540°C. Weight losses at 110°C and at 1000°C were also obtained from selected samples to ascertain any further changes in weight of the dried sediments.

28. Standard size analyses were conducted on sediment samples

* See methods section in Volume II, Part II, for a special study of techniques for sediment drying and digestion.

after removal of organic materials and iron coatings (Jackson 1973; Folk 1974). Size parameters were calculated from the method of moments as outlined in Darby and Wobus (1976). Mineralogical analyses of the less than 2 μm , 2 to 62 μm , and greater than 62 μm size fractions were determined by X-ray diffraction after organic matter was removed and the sediments were dispersed. The coarser than 2- μm sediments were ground before analysis. Semiquantitative estimates of clay mineral percentages were obtained from equations adapted from several sources (Biscaye 1964; Darby 1975; Schultz 1964). The peak areas under diffraction maxima were determined from at least two planimeter traces for calculation of the following clays:

$$\begin{aligned} \text{Montmorillonite} &= (17 \overset{\circ}{\text{A}} \text{ PA gly})/4(10 \overset{\circ}{\text{A}} \text{ PA gly}) \\ \text{Vermiculite} &= \{(14 \overset{\circ}{\text{A}} \text{ PA gly}/10 \overset{\circ}{\text{A}} \text{ PA gly}) - (14 \overset{\circ}{\text{A}} \text{ PA unt}/10 \overset{\circ}{\text{A}} \text{ unt})\}/3 \\ \text{Kaolinite} &= 0.4 (7 \overset{\circ}{\text{A}} \text{ PA HCl})/(10 \overset{\circ}{\text{A}} \text{ PA HCl}) \\ \text{Chlorite} &= 0.4 (7 \overset{\circ}{\text{A}} 180^{\circ}\text{C})/(10 \overset{\circ}{\text{A}} \text{ PA } 180^{\circ}\text{C}) - \text{Kaolinite} \\ \text{Mixed-layered} &= 0.6 (10 \overset{\circ}{\text{A}} \text{ to } 14 \overset{\circ}{\text{A}} \text{ PA gly})/(10 \overset{\circ}{\text{A}} \text{ PA gly}) \\ \text{SUM} &= 1 + \text{Montmorillonite} + \text{Vermiculite} + \text{Kaolinite} + \text{Chlorite} + \\ &\quad \text{Mixed-layered} \end{aligned}$$

where gly = ethylene glycol wetted smear slide
unt = untreated smear slide
180^oC = heat-treated smear slide
HCl = hydrochloric acid digested smear slide
 $\overset{\circ}{\text{A}} = 1 \times 10^{-8} \text{ cm} = 1 \times 10^{-4} \mu\text{m}$
PA = diffraction maxima peak area

and

$$\begin{aligned} \% \text{ illite} &= 100/\text{SUM} \\ \% \text{ smectite} &= 100 \text{ Montmorillonite}/\text{SUM} \\ \% \text{ vermiculite} &= 100 \text{ Vermiculite}/\text{SUM} \\ \% \text{ kaolinite} &= 100 \text{ Kaolinite}/\text{SUM} \\ \% \text{ chlorite} &= 100 \text{ Chlorite}/\text{SUM} \\ \% \text{ mixed-layered expandable clay} &= 100 \text{ mixed-layered}/\text{SUM} \end{aligned}$$

Procedures for identifying the clay minerals based on X-ray maxima were from numerous sources (Biscaye 1964 and 1965; Carroll 1970; Carver 1971; Grim 1968; Jackson 1973). The percentages of quartz, feldspar, and muscovite were determined using similar minerals as standards (Schultz 1964) and checked by microscopic analysis.

29. The cation exchange capacity (CEC) was determined by saturation with calcium (CaEC) as well as with potassium (K/EC) involving a drying step for fixation (Jackson 1974). The CaEC method was chosen because calcium was suspected as being the primary ion in the exchange positions. The K/EC represents the CEC not blocked by potassium fixation with drying. The coarser than 2- μ m fractions were removed by centrifugation prior to CEC analysis because this fraction normally contributes less than 15 percent of the total sediment CEC. Thus, differences in CEC among samples could be assessed independently of size variations such as abundant sand which would lower the bulk or total sediment CEC. With the removal of the size variable, differences in CEC, if detected, could be related to compositional differences. Cleaned samples, with organic matter and iron coatings removed, were analyzed for CEC and K/EC in order to approximate the exchange capacity of the organic material plus iron colloids by comparison with untreated samples. Hydrogen peroxide (30 percent) and citrate-dithionite were used to clean the samples (Jackson 1973). Sonification was also employed to disperse untreated samples before size fractionation by centrifugation. Despite this, some size differences still existed for the less than 2- μ m size fractions between the untreated and cleaned sediment samples.

Results

Physical description of the James River Channel sediments

30. From visual observations through the core liners immediately after recovery, a brief description of the sediments is as follows: olive gray-brown color throughout with little evidence of an oxidized zone at the surface; homogeneous fine size with some sand in the bottom of a few cores, and occasional 1-to-2 cm diameter pebbles (possibly deposited from frequent gravel barge traffic); top sediment layers 10 to 30 cm were uncompacted and soupy; bottom halves were cohesive mud lacking obvious layering except in one core, number 10, where sandy mud was interstratified with mud; abundant plant debris was present along with black wood chips up to 3 cm long; and several gas vesicles (0.5 to

3 cm diameter) observed throughout each of the 10 cores.

31. The channel sediment temperature was relatively constant at $12.7^{\circ} \pm 2.8^{\circ}\text{C}$ in the upper portion and $14.5^{\circ} \pm 3.1^{\circ}\text{C}$ in the lower sections. Little water was observed above the core sediments during laboratory processing which would indicate insignificant compaction during handling. Water content (60°C drying) averaged 53 ± 4.4 percent with a range of 17 percent. There was an average weight loss of only 1.65 percent from samples dried at 60°C for 72 hr to those dried at 110°C (Table 6). Volatile solids averaged 13.8 ± 1.4 percent for the upper portion of the cores, while the lower sections had a mean of 15.3 ± 2.0 percent. There was an average 2.0-percent loss when the samples were further heated at 1000°C for 15 min which was probably due to dehydration of clay minerals.

Chemistry of the James River channel sediments

32. Nearly all the pH values were slightly acidic. The mean for the lower portion of the 10 cores was 6.63 ± 0.19 , while the upper sections were not greatly different with a mean pH of 6.77 ± 0.23 . Values from the sulfide ion electrode indicated negligible concentrations of sulfide ions in the sediment interstitial water, which would be expected at the low pH values. Most of the total hydrogen sulfide measured by the methylene blue method was probably present as HS^{-} and acid-soluble sulfides. Interference in the colorimetric measurement by dissolved humic compounds was also a possibility. The two highest values of 5.50 mg/l in core 12 and 7.98 mg/l in core 4 also corresponded with the most negative redox potentials (-121 and -159 mV, respectively). The average redox potential of -18 mV in the upper sediments to -34 mV for the lower portion (corrected for the saturated calomel electrode by adding +251 mV; Table 6) indicated what might be termed a slightly reducing environment. The reported redox potential was a computed average for two electrodes, the readings of which differed by as much as 224 mV. In the first six cores (numbers 2, 3, 4, 7, 8, and 12) redox measurements between the two electrodes were consistent and acceptable (Whitfield 1968) with a mean difference of 40 mV between the two electrodes. Because of a large average divergence of 92 mV between the two electrodes for the last four

cores, it was obvious that one of the electrodes was not functioning properly. Removal of these anomalous data resulted in an average redox potential of -51 mV for the channel sediments. The vertical distributions of pH and redox potential in the 10 cores are shown as Figures 1 and 2 in Appendix A'.

33. Total dissolved phosphorus (TDP) averaged 0.386 ± 0.135 mg/l in the interstitial water of the upper portion of the cores and 0.527 ± 0.142 mg/l in the lower portions (Table 7). Dissolved orthophosphate phosphorus accounted for 47 percent of TDP in the upper portions of the cores and 61 percent in the lower sections. Interstitial dissolved total nitrogen (TDN = 69.7 mg/l) was similar in concentration to interstitial ammonium ($\text{NH}_4 = 63.5$ mg/l) for both upper and lower segments of the 10 cores. There were slight concentrations of nitrate in the interstitial water, with negligible nitrite; however, because of problems associated with their measurements values for nitrate and nitrite should be viewed with caution.

34. Sediment dry weight concentrations of total phosphorus (TP) and total Kjeldahl nitrogen (TKN) averaged 662 ± 110 $\mu\text{g/g}$ for total phosphorus and 4577 ± 684 $\mu\text{g/g}$ for total nitrogen. Vertical distributions of the interstitial and total nutrients are illustrated in Figures 3 to 8 in Appendix A'.

35. Statistics for interstitial concentrations of nine metals are provided in Table 8, with the 10 cores divided into upper and lower segments. The average values of dissolved metals in the interstitial water of the sediments decreased in relative abundance as follows: calcium > iron > manganese at parts per million levels, with high to low parts per billion concentrations of zinc > lead > nickel > copper > cadmium > mercury. Major differences between the upper and lower sections of the 10 cores were only observed for interstitial dissolved manganese and zinc. Manganese was noticeably depleted in the deeper sediments, while dissolved zinc apparently increased with depth in the interstitial water of the cores. Total sediment dry weight concentrations of the same metals are also provided in Table 8. The overall total metal abundance in the sediments decreased as follows: iron > calcium >

manganese > zinc > lead > copper > nickel > cadmium > mercury. Iron, calcium, and manganese concentrations were at the parts per thousand to low percentage level. The vertical distributions of interstitial and total metals for the 10 cores are shown in Figures 9 to 26 in Appendix A'.

Geology of the James River channel sediments

36. Sediments from the channel were very poorly sorted fine silt with a mean size of $7.7 \phi^*$, or $4.8 \mu\text{m}$, and a sorting coefficient of 3.1ϕ (less than 1ϕ is well sorted). Such sorting characteristics are common for fine-grained, fluvial-type estuarine deposits. The silt/clay ratio averaged 1.25 in the upper sections of the cores and 1.07 in the lower portions, where the sand fraction was 15.8 percent or three times that found in the upper sediments. Besides an increase in sand for the lower sections of the cores, nearly all of the size parameters listed in Table 9 indicated little variation among the 10 cores or from top to bottom for each of the cores.

37. Despite the larger amount of organic material (average percent volatile solids = 14.5) the cation exchange capacity of the less than $2\text{-}\mu\text{m}$ size fraction was only about 31 meq/100 g, as determined by calcium saturation (CaEC; Table 10). Measurements decreased by an average of only one percent upon removal of organic matter, but exhibited a large standard deviation of 24 percent. The exchange capacity determined by potassium fixation (20 meq/100 g as the mean K/EC) confirmed the estimate of vermiculite abundance according to the procedure outlined by Jackson (1973). Like the size parameter, the mineral composition was also homogeneous among samples (Table 11). Most abundant was quartz (35 percent) followed by illite (16 percent), chlorite (9 percent), K-feldspar (9 percent), plagioclase (8 percent), muscovite mica (6 percent), mixed-layered illite-chlorite and illite-montmorillonite (5 percent), vermiculite (4 percent), smectite (3 percent), and kaolinite (2 percent). Heavy minerals, composed mostly of magnetite, tourmaline, hornblende, and epidote, were less than

* $\phi = -\log_2 (\text{diameter in mm})/1\text{mm}$.

one percent. Iron oxides other than magnetite were observed as coatings on sediment grains.

Discussion

38. Previous studies, which were substantiated by the present investigation, suggested that the James River channel sediments near Windmill Point were not suitable for open water disposal according to historical total sediment composition. Sediment parameters exceeding old EPA criteria were volatile solids, total Kjeldahl nitrogen, lead, and zinc. Mercury was about half of the one ppm concentration criteria, while chemical oxygen demand was not measured in this study. However, because total sediment composition provides little information concerning the effects of dredging on water quality or biological availability, it was difficult to interpret the possible environmental impact of such concentration levels. Study results presented in Volume II, Part II, of this Appendix* suggest 40 percent of the lead and zinc was associated with the residual mineralogical phases of these sediments and might therefore have markedly lower toxicities, chemical reactivity, or mobility than would dissolved or exchangeable-phase sediment constituents.

39. As previously described, this channel receives high rates of sedimentation; therefore, low levels of interstitial components might be expected because of the time required for mobilization from solid to liquid phases in the sediment pore waters. However, sediment deposition could be due to both sedimentation from above as well as slumping from the sides of the channel; the latter would confound equilibrium calculations for the sediment pore waters. Slumping would probably be related to the changes in channel slope subsequent to dredging. Steep channel slopes would be conducive to such phenomena especially in this highly fluidized sediment. This situation probably accounted for the apparent

* Masters thesis research by Mr. W. T. Nivens, Institute of Oceanography, ODU, which was completed during preparation of this report (Nivens, 1978), will be presented in Volume II of this report.

rapid deposition between December 1972 and August 1973 following dredging in November 1972 (see Table 4). The highest rates of sedimentation were observed on the north side of the channel because of the steeper slopes and the curve in the channel just upstream. Such topography would divert the tidal ebb flow against the south side of the channel. The greater concentration of sand in the lower portion of the cores (60- to 90- cm depth) and the fining upward sequence in sediment size was probably not due to increasing stream power (velocity times shear stress) during waning flood stage conditions as is characteristic for undredged rivers (Visher 1972). Instead, the upward decrease in sediment size was probably as a result of the more rapid settling of sand suspended in the channel during dredging or to the increased current velocities due to the change in the channel caused by dredging morphology. This could allow for the transport of sand into the channel from adjacent shoals like the sand borrow area used for dike construction (Figure 5). Because of the fine size and fluidized nature of the upper portion of the sediment cores, suspension settling also appears to be important in the channel. If the current velocities range from 0 to 80 cm/sec as reported by Nichols (1972), the effective settling diameter must be coarse silt to sand size for net deposition to occur. Thus, most of the finer size sediment would have to be flocculated or agglomerated (Schubel 1971).

40. Much of the volatile solid content was due to abundant plant debris which averaged less than 1 cm in size. Numerous gas vesicles observed in the sediment cores and thought to be methane were further evidence of the accumulation of organic matter and decomposition products.

41. High concentrations of total phosphorus (0.07 percent) and nitrogen (0.46 percent) in the channel sediments suggested a source of nutrients for plant growth once these sediments were placed within the dikes designed to contain the intertidal substrate. Dissolved orthophosphate in the interstitial water would originate from the release of bound inorganic phosphorus, as ferric phosphate or other compounds associated with the sediments, or from the decomposition of organically combined phosphorus (Baturin 1972). The short time of organic decomposi-

tion within the James River sediments between successive dredging activities (one to two years) reflected the relatively low concentrations of interstitial orthophosphate (approximately 0.25 mg/l) as compared to other depositional environments (Bricker and Troup 1975; Ho and Lane 1973, Matisoff et al. 1975, Sholkovitz 1973). In fact, literature values were usually 10 to 100 times greater than reported here. Interstitial orthophosphate-P represented approximately 50 percent of the total dissolved phosphorus in the pore waters of these 10 cores. This percentage increased with depth (see Table 7). High concentrations of interstitial ammonium, which was approximately equal to total dissolved nitrogen concentrations in the pore water, were similar to values for other fine-grained estuarine sediments (Bernier et al. 1970; Matisoff et al. 1975). This suggested that either the rates of organic decomposition and release of dissolved ammonium and orthophosphate to the interstitial waters were not similar or that processes for removal of dissolved orthophosphate were more active in these sediments. The $Fe^{2+} - Fe^{3+}$ system, which is one of the most electroactive redox couples and obviously important in the channel sediments (interstitial iron was about 1 mM), could have considerable influence in regulating the concentration of dissolved phosphate in the interstitial water (Adams et al. 1977). During disturbance of the sediments and mixing with overlying waters by dredging, ferrous iron would be oxidized and could precipitate dissolved orthophosphate. Dissolved orthophosphate was below detection (less than 0.001 mg/l) in interstitial water samples, which had been frozen five months with a sample pH of 8.5 to 9.0, where a reddish precipitate was present. Bound orthophosphate was released from this precipitate when water samples were acidified. Otuski and Wetzel (1972) reported a close relationship between orthophosphate and carbonates in lake water, while Nissenbaum et al. (1972) wrote that orthophosphate was preferentially removed from interstitial water of oxidizing sediment and was eventually precipitated out of solution as insoluble ferric phosphate or ammonium salts. It was possible that such processes were occurring in the James River channel sediments and would happen during dredging.

42. Interstitial calcium and iron were higher than reported for

pore waters from other freshwater environments (Müller 1969; Serruya et al. 1974; Weiler 1973). According to Nissenbaum et al. (1972), dissolved calcium in the sediment might be in equilibrium with some metastable phase of calcium carbonate and not with calcite. After standing, solids were reported to precipitate from interstitial water (Nissenbaum et al. 1972). This was also observed by Berner et al. (1970). These solids provided poorly defined X-ray diffractograms of calcium carbonate, which later converted to calcite upon standing (Nissenbaum et al. 1972). Similar events occurred for interstitial water from the James River where dissolved calcium averaged 215 mg/l; these precipitates contained crystalline low magnesium calcite as determined by X-ray diffraction. Nissenbaum et al. (1971) suggested that polymerized interstitial organic matter, with a concentration of calcium greater than 2 percent (dry weight), might play a role in the sedimentary calcium cycle. Therefore, it was expected that the solubilities of dissolved metals in the interstitial water of the James River cores might also be controlled by complexation with dissolved organic components of the pore water, as reported by numerous authors for other environments (de Groot 1973, Presley et al. 1972). Presley et al. (1972) reported that zinc, nickel, copper, and particularly iron, were highly enriched in the peroxide leach of coastal sediments, which suggested a close association with the organic fraction, while Lunz and Huggett (1974) calculated the percentage composition of organically bound metals in the channel near Windmill Point as 20 percent for copper, 30 percent for lead, and 46 percent for zinc. They considered the difference between a 0.1-M hydrochloric acid leach of the sediments and digestion for 24 hr with concentrated nitric acid as the organic fraction for these three metals. Therefore, the mobilization of metal-organic chelates or the polymerization and precipitation of organic ligands and their associated metals might be an important process during dredging even though the disturbed interstitial water probably is of greater short-term significance.

43. The concentrations of interstitial dissolved manganese, nickel, and copper in the 10 cores were similar to those of sediments from other

depositional environments (Brooks et al. 1969; Calvert and Price 1972, Duchart et al. 1973, Glass and Poldoski 1975, Presley et al. 1972). Dissolved zinc, lead, and mercury were slightly higher than was seen in other areas (Duchart et al. 1973; Lindberg et al. 1975). Concentrations of interstitial cadmium were relatively low.

44. Total lead, mercury, manganese, and possibly zinc and copper, might be above average in the channel sediments at Windmill Point due to anthropogenic sources. Concentrations of total iron, calcium, nickel, and cadmium were approximately the same as reported for other estuarine environments. Because depositional environments are never exactly alike and analytical techniques may vary slightly, comparisons of total metal data with other studies are somewhat tenuous. Six of the sediment metals (iron > zinc > lead > copper > nickel > cadmium) were much greater than reported for a Florida estuarine embayment (Segar and Pellenburg 1973), while three of these (iron, copper, and nickel) were similar to sediment concentrations in Saanich Inlet, British Columbia (Presley et al. 1972). However, copper and nickel, as well as zinc and lead, were much lower in silty sediments from the Hudson Submarine Canyon (Carmody and Yasso 1973) as compared to the James River.

45. From the high concentrations of dissolved calcium and iron in the interstitial waters it was expected that oxidation of ferrous iron during dredging, and the precipitation of both ferric and calcium salts due to supersaturation conditions, would coprecipitate a considerable fraction of the dissolved metals, such as cadmium, copper, lead, and zinc as proposed by Windom (1972). Dissolved ammonium, on the other hand, would probably remain at elevated levels during dredging. Observations of effluent quality during and following dredging are reported in Part III of this Appendix volume.

46. Despite the high organic content of the James River sediments, as indicated by volatile solids, the cation exchange capacity (CEC) was about the same as reported for sediments in the lower Chesapeake Bay with half the volatile solids content (Toth and Ott 1970). Although about 50 percent of the CEC for other fine-grained sediments were due to organic matter, such as humic and fulvic acids (Rashid 1969), the effect

of the 30 percent H_2O_2 treatment on James River channel sediments was erratic. After removal of the organic material, the CEC of some samples increased as much as 39 percent while others decreased by 61 percent. Because the less than 2- μm size fraction used for H_2O_2 treated and untreated samples was obtained by centrifugation, the untreated samples represented somewhat finer sediments because of incomplete dispersion. This would not explain the observed changes in CEC, however, because the untreated samples would be composed of both finer sediments and the associated organic matter. Subsequent analysis of total channel sediment by the sodium saturation method (Chapman 1965) confirmed this erratic behavior of CEC with respect to the H_2O_2 treatment. A possible explanation would be the interference caused by aluminum in the atomic absorption analysis of calcium for the H_2O_2 treated samples. Organically complexed aluminum and iron would also be released to solution during H_2O_2 treatment. Iron and possibly aluminum could also precipitate as oxide coatings, thus preventing further oxidation of organic matter and the blockage of exchange sites (Sequi and Aringhieri 1977). These same authors found that the addition of phosphate (as $Na_4P_2O_7$) would complex the released Fe and Al and could even cause higher CEC values after H_2O_2 treatment than before. But this increase in CEC may be due to adsorption of phosphate. Besides adding to the CEC, organic matter may also occlude to some of the sorption sites on mineral surfaces. Subsequent removal of this organic material may then increase the CEC of the minerals (Sequi and Aringhieri 1977). Thus, the contribution of organic matter to the sediment CEC cannot always be accurately determined by H_2O_2 treatment. Even though it was unclear what the role of organic matter was with respect to the cation exchange capacity, the clay minerals measured in the James River could account for the entire CEC of these sediments (Table 12). Thus, the organic matter in the channel sediments contributed less to the cation exchange capacity than normally found in similar environments.

PART III: EFFLUENT QUALITY AT THE MARSH DEVELOPMENT SITE
DURING AND SHORTLY AFTER DREDGING

Introduction

Purpose

47. This chapter describes the effluent water quality at the diked containment area during dredging, two to four days after dredging during the dewatering period, and 3.5 months later before extensive vegetation had developed on the new substrate. The purpose of this phase of the investigation was to document water quality during these three sampling intervals and to discuss any changes that occurred at the effluent pipe during this period.

Physical setting

48. During the period from 1968 to 1971, approximately 184,000 m³ of dredged channel sediments had formed an extensive shoal area parallel to the southern shore of the James River about 700 to 800 m west of Windmill Point. Tidal depths over this shoal averaged about one meter. The intertidal containment area was developed on this shoal (see Figure 1) by constructing dikes with approximately 62,300 m³ of sand from a borrow area south of Buckler's Point. During normal channel maintenance, which started on 21 January and finished 4 February 1975, approximately 166,500 m³ of channel shoal material was pumped into the dike containment area at its northwest corner; effluent left the containment area 425 m away at the southeast corner (Figure 3). The average depth of fill was 1.1 m in the 6.1-ha site (152 by 396 m). The total area of bottom covered by dikes and interior sediments was approximately 8.9 ha.

Methods and Materials

49. Suspended sediment samples were collected using two different methods. Most samples were collected with a model 1391 ISCO (Instrumentation Specialities Co., Lincoln, Neb.) automatic water sampler at a 18.3-m long effluent pipe (see location in Figure 3). Four additional

samples were obtained by hand near the ISCO inlet probe. The ISCO sampler failed on numerous occasions, and there was difficulty in obtaining a representative sample from the 0.9-m diameter outfall pipe due to a large vertical gradient in the concentration of suspended solids and the sampler's inability to accurately sample when concentrations were above 2000 mg/ℓ. A study conducted in May 1975, comparing samples collected by hand near the ISCO inlet probe with the ISCO samples, evidenced the value of ISCO collected samples at low (less than 2000 mg/ℓ) concentrations of suspended solids only (Figure 6).

50. The 48-hr studies were conducted during the dredging (31 January to 1 February 1975) and dewatering (6-8 February 1975) periods. Water samples were collected every 2 hr at the effluent pipe with the ISCO sampler. These were iced, returned to the laboratory, and filtered immediately. Because of poor recovery from the ISCO sampler, suspended solids were insufficient for metal analyses during the dewatering period. Both filtered and unfiltered samples were frozen for nutrient analyses.

51. Two 48-hr tidal studies were conducted at the intertidal containment area during 18-20 April and 13-15 May 1975, approximately 2.5 and 3.5 months after dredging. Individual samples were collected at one effluent pipe at six-hr intervals. A delta of fine-grained sediments, which formed during filling of the containment area, was still evident east of the effluent pipe. High winds during April kept the food tide out of the intertidal containment area during the latter half of the sampling period, therefore, this period was not included in the report. Water samples were filtered, stored on ice, and frozen upon return from the field. Laboratory techniques were similar to those described in Chapter II. Computer-generated plots for each of the measured variables, with the exception of suspended solids, are provided in Appendix A' for the dredging, dewatering, and 3.5-months after dredging periods.

Results

52. Based on analysis of samples collected by hand, effluent concentrations of suspended sediments leaving the dike during active

dredging were approximately 161 ± 8 g/l (16 percent). During the settling and dewatering stage this decreased to about 645 ± 109 mg/l (0.6 g/l). At the same time suspended solids averaged 53 mg/l in the channel between the site and the south shore of the James River. Suspended solids at the effluent pipe averaged about 10.9 g/l (or 1.4 g/l without one large value of 39,350 mg/l) at low tide 3.5 months after dredging. By this time, 14 May 1975, the high tide values had decreased to 100 mg/l (Table 13) and were only double the concentrations measured in the nearby channel. Temperature data indicated a normal diurnal variation in May, but during ebb tide pH (6.32 ± 0.31) and dissolved oxygen (2.50 ± 0.93 mg/l) were lower than during the flood (7.47 pH, 10.76 mg/l dissolved oxygen; Table 13).

Chemistry

53. Nutrients. The concentrations of dissolved orthophosphate at the effluent pipe averaged 0.03 ± 0.01 mg/l during active dredging, while ammonium was 18 ± 6 mg/l (Table 14). Although there was an abrupt decrease in dissolved ammonium between dredging and ebb tide collections during dewatering of the site (0.25 ± 0.29 mg/l), there was little further change in dissolved orthophosphate-P. It should be remembered that during the period of settling and dewatering of the site, the time of collection was not clearly defined as maximum low slack water as was the case for May. There was an obvious increase in dissolved nitrates and nitrites from the dredging period to both the dewatering and 3.5 months after dredging periods (Tables 14 and 15). Dissolved orthophosphate-P was approximately 50 percent of total dissolved phosphorus (TDP) at the effluent pipe, which was similar to the interstitial water composition of the James River channel. Even though this was the case for the May low tide samples, dissolved orthophosphate composed 30 percent of the total dissolved phosphorus concentration during high tide. Dissolved ammonium was similar in concentration to total dissolved nitrogen (TDN) in the interstitial water of the channel sediments, yet during May it varied from 20 percent of the TDN during high tide to 60 percent for the low tide samples.

54. Dissolved metals. During the period of active dredging, the concentrations of dissolved metals in the dike effluent decreased compared to their interstitial water concentrations in the channel sediments

(Table 16) as follows: calcium > iron > zinc > manganese at the parts per million level, with high to low parts per billion concentrations of lead > copper > nickel > cadmium > mercury. With the exception of zinc and copper, the relative order in the concentrations of metals in the effluent was the same as in the interstitial water of the channel. During settling and dewatering, the relative concentrations (low slack water samples only) for dissolved metals changed to the following order: calcium occurred in parts per million levels; manganese > iron > zinc nickel > cadmium > copper > mercury ranged from high to low parts per billion concentrations; lead was below detection. Compared with the dewatering period, the low tide sampling period in May was characterized by decreased concentrations of dissolved calcium, cadmium, and zinc; copper, mercury, and nickel concentrations did not change; iron and manganese concentrations increased (Table 17).

55. Suspended sediment metals. Concentrations of metals in the suspended sediments (and other suspended materials) collected from the effluent during active dredging were as follows: iron > manganese > zinc > lead > copper > nickel > cadmium; mercury was below detection (Table 18). Calcium concentration information was not developed. The concentration of zinc (dry weight) in the suspended materials decreased by eleven percent relative to total sediment dry weight concentrations in channel sediments. Concentrations of other suspended particulate metals increased when compared with channel sediment concentrations:

| | | |
|-----------|-----------|------------|
| cadmium | increased | 85 percent |
| nickel | increased | 27 percent |
| lead | increased | 26 percent |
| copper | increased | 25 percent |
| manganese | increased | 17 percent |
| iron | increased | 5 percent |

The results for manganese and iron should be considered the most reliable. Despite the changes in concentration, the relative concentration order among metals remained similar to that which occurred in the channel cores. Relative metals concentrations in May 1975, 3.5 months after site development, followed the order iron > manganese > zinc > lead >

copper > nickel > mercury (Table 19). Mercury was detectable in only one May sample and cadmium was below detection. Based on the relationship between sample size and detection limits, mercury and cadmium observations could be attributed to an insufficient sample weight of suspended materials rather than to any compositional differences. With respect to total sediment metal concentrations in the channel, the largest increases in metals associated with the suspended sediments leaving the diked development site during ebb tide, 3.5 months after dredging, occurred with mercury (200 percent), zinc (110 percent), lead (73 percent), iron (66 percent), nickel (64 percent), copper (33 percent), and manganese (24 percent). As stated above, because of suspended material weights, the accuracy of these calculations is questionable; mercury calculations were based on a single detectable concentration associated with a low tidal May 1976 sample; iron and manganese values were the most reliable.

Geology

56. Sediment size, sorting, and mineral composition. The sediment size, sorting, and mineral composition did not change frequently during dredging and sedimentation in the diked containment area (Tables 20 and 21). The silt/clay ratio of the suspended sediment at the effluent pipe during dredging was 1.32 ± 0.6 , which closely resembled the dispersed silt/clay ratio for the channel sediments (1.25 ± 0.5). Because of a 20-percent loss in the sand fraction of the channel sediments between the inlet and effluent pipes, there was a change in mean sediment particle size from 7.2ϕ ($5 \mu\text{m}$) to 8.1ϕ ($3.7 \mu\text{m}$) leaving the diked containment area. Despite this loss in sand, some of the coarsest sediments ($>2 \text{ mm}$) remained in suspension for a distance of approximately 425 m. By May 1975, the mean particle size of the suspended sediments at the effluent pipe had decreased from the after dredging value of 8.1ϕ ($3.7 \mu\text{m}$) to 8.7ϕ ($2.4 \mu\text{m}$). During this time, the silt/clay ratio did not change significantly decreasing from 1.32 ± 0.6 to 0.99 ± 0.8 .

57. Cation exchange capacity. The cation exchange capacity of the H_2O_2 tested suspended sediments leaving the diked containment area during dredging was $57 \pm 44 \text{ meq/100g CaEC}$ (N=2); suspended sediments collected 3.5 months after dredging had values of $27 \pm 7 \text{ meq/100g CaEC}$ (N=4).

The overall average for the CaEC (H_2O_2 treated) of the suspended sediments at the effluent pipe during the dredging and 3.5 months after dredging period was 37.2 ± 25.6 meq/100g (Table 22).

Discussion

58. Changes in dissolved nutrients, dissolved metals and suspended metals were observed during dredging. The source of these dissolved nutrients and metals was apparently the channel sediment interstitial water and the easily exchanged or otherwise surficially bound components of the sediment. The observed concentration was then the result of these contributions modified by mixing with the James River water during the dredging and disposal operation. A budget for dissolved chemical species during dredging was calculated based on the following assumptions:

- a. Contributions from suspended particulate material in the James River (approx. 30 mg/l) were negligible.
- b. Suspended solids concentrations at the effluent pipe during active dredging averaged 161 g/l or 16% and did not vary significantly.
- c. Concentrations of dissolved nutrients and metals in the James River water, which mixed with the dredged sediment during marsh site development in January 1975, could be approximated by using the results of the analyses of James River flood tidal waters collected in January 1977.
- d. Where channel concentration information was not available from January 1977 data, then values equal to one-half of the detection limit (Table 5) were used for budget calculations.

The reason for the 16 percent suspended solids value at the effluent pipe compared with normal dredging operations of 10-15 percent was probably due to the loss of approximately 4-6 percent of the incoming waters through the sand dike (a conservative estimate). Six of the dissolved metals (zinc > copper > cadmium > lead > nickel > mercury) increased during dredging when compared with calculated concentration values of channel sediment interstitial water mixed with James River water (Table 23). The same calculations suggested that concentrations of dissolved iron decreased while calcium and manganese concentrations remained relatively constant. Dissolved ammonium increased (+41 percent); dissolved orthophosphate decreased (-64 percent). Because of analytical difficulties no changes for nitrate and nitrite were estimated.

59. An explanation for the observed mobilization of dissolved metals as a result of dredging was attempted by examining the association between various metals and various analytically defined sediment fractions or phases. It was hypothesized that the ability for transformation of a free metal ion, or a more complex molecule containing the metal ion, from a solid (sediment) phase to a dissolved phase would be largely controlled by the physical and chemical forces binding the metal to the sediment. These binding forces were documented using a selective serial chemical extraction procedure developed by Engler et al. (1977) and applied to core samples collected at the development site and reference marsh in August 1976. A presentation of the selective extraction procedure with detailed results is contained in Volume II of this report. However, it was assumed that the relationships between metals and sediment phases in the development site in August 1976 were similar to those that existed in the James River channel in the winter of 1975. The findings of the selective extraction were then used to explain some observed mobilization trends. Though 50 percent of the total calcium was associated with the exchangeable phase, calcium either did not mobilize or it was rapidly precipitated. The 63 mg/l calcium concentration measured at the effluent pipe during active dredging represented four times the saturation value for CaCO_3 . If all of the exchangeable calcium had been released from the suspended sediments exiting through the pipe, the calcium concentration would have been approximately 480 mg/l. Therefore, either precipitation must have occurred or exchangeable calcium was not desorbed from the sediments, or only a fraction of the exchangeable calcium was desorbed from the sediments and rapidly precipitated. Dissolved iron concentrations in the interstitial waters of the James River channel sediments were approximately ten thousand times the saturation values for FeS (other solid phases of iron are even less soluble). Dissolved iron, therefore, was probably precipitated during dredging. Loss of ferric iron (0.1 mM) would have accounted for complete removal of dissolved orthophosphate (0.002 mM); the major precipitates, therefore, along with ferric phosphate were probably ferric hydroxides and oxides. The oxidation of ferrous iron during dredging did not appear to

scavange cadmium, copper, lead or zinc as reported by Windom (1972) because three of these metals increased from 631 to 7700 percent during dredging relative to calculated concentrations (Table 23). Release of exchangeable sediment zinc (approx. 8 percent of the total zinc was exchangeable) could have accounted for 3 mg/ℓ at the effluent pipe or half the measured Zn concentration increase. Organically bound zinc (approx. 13 percent of the total zinc was organically bound) could have contributed to the entire zinc concentration of 5 mg/ℓ at the effluent pipe. It is assumed that portions of both the exchangeable and organically bound zinc phases were released during dredging. Fourteen percent of the sediment copper was associated with the organically bound fraction. The 0.05-mg/ℓ copper concentration in the dredging effluent probably originated from this fraction.

60. During development site dewatering two to four days after dredged material disposal (after active dredging had ceased) cadmium was the only metal that remained at a level that was increased relative to calculated concentrations. Even though temporal changes in dissolved cadmium were obviously related to ebb tide drainage at the development site, the source could not be clearly explained because the ebb tide samples collected at slack before flood at the effluent pipe were almost twice the concentration measured in the interstitial water of the James River channel sediments (Tables 8 and 16 and data plots in Appendix A'). Because of its toxicity, it is obvious that further studies need to address problems associated with the solubility of cadmium during dredging. If comparisons were made between the dewatering and the 3.5 months after dredging ebb tide periods, all metals but dissolved iron and manganese decreased substantially (Table 24). As the sediments became more consolidated and reducing conditions were reestablished within the development site sediments, oxidized species of iron (III) and manganese (IV) were again reduced and became soluble within the sediment pore waters. This resulted in increased concentrations of soluble iron (II) and manganese (II) during ebb tide 3.5 months after dredging.

61. Dissolved ammonium at the effluent pipe during dredging was only slightly greater than calculated values, which suggested that it

was relatively conservative. The calculated increase of 41 percent was probably due to the mobilization of NH_4^+ from the exchangeable fraction of the sediments. The intertidal diked containment area still continued to drain relatively high levels of both dissolved ammonium (2 mg/l) and other dissolved nitrogen compounds (4 mg/l) during low slack water 3.5 months after dredging (Table 24). Dissolved orthophosphate almost doubled during ebb tide 3.5 months later as compared to the dredging period (presented as data plots in Appendix A'). This increase of dissolved orthophosphate as well as dissolved iron suggested reducing conditions were reestablished within the marsh substrate and that drainage of interstitial water higher in these species was occurring. The absolute concentrations of total dissolved phosphorus (TDP) did not vary over the tidal cycle at the effluent pipe 3.5 months later, even though its composition did. Dissolved orthophosphate was 50 percent of TDP as water left the diked containment area. This ratio changed to 33 percent during flood tide. The ebb tide relationship of PO_4 to TDP was close to pore water values (55 percent) for the channel sediments before dredging. These changes were also evident for dissolved ammonium and total dissolved nitrogen (TDN), where ammonium comprised 60 percent of the TDN during ebb tide and only 19 percent for the flood tide samples. The relationship for James River sediments before dredging was 1:1, or dissolved ammonium comprised about 100 percent of the total dissolved nitrogen measured in the interstitial waters. This suggested that the interstitial waters of the diked containment area actively mixed with the incoming James River water, and that the pore waters of the site provided a greater percentage of low molecular weight dissolved components (PO_4 and NH_4) as compared to TDP and TDN.

62. Approximately half of the material in suspension at the diked containment area effluent pipe was less than 2 μm . The mean size was 2.4 μm , which was close to the colloidal size range and indicated a high probability that metals were transported as colloidal material. As suggested by Campbell et al. (1977), this could be the mechanism for the transport of dissolved copper, i.e. as colloidal copper (II) hydroxides, or other species that are stabilized by dissolved humic acids.

Disruption during dredging could have released such colloidal species resulting in the high percentage increase in concentrations at the effluent pipe (Table 23). Suspended inorganic sediment leaving the diked containment area during ebb tide contained more sand-size mica flakes and clay-size material, while sediment entering during flood tide contained a greater amount of silt-size material. This resulted in a net loss of the less than 2- μ m size fraction, which usually accounts for about 85 to 90 percent of the cation exchange capacity. This size fraction also contained nearly all of the smectite and vermiculite. The removal of these minerals during dredging was substantiated by changes between their concentrations in the channel sediments and suspended samples collected at the effluent pipe. With the loss of fine-sized sediments and high exchange capacity minerals from the diked area there is a possibility of nutrient and cation depletion, both of which are necessary for future plant growth. This process, however, did not appear to have been a critical short-term factor based on the luxuriant growth in the containment area for two successive summers.

63. Besides colloidal transport, metals and nutrients can be adsorbed onto clay particles to the extent of the sediment exchange capacity. Although the average calcium exchange capacity (CaEC) for the suspended sediment at the effluent pipe was nearly the same as the channel sediments (31 meq/100 g), the range was 20 to 90 meq/100 g. This larger range of CaEC for suspended sediments might be due to the greater variability in mineral percentages and organic content at the effluent pipe as compared to the channel sediments. Yet, variations in the percentage of vermiculite and smectite, which commonly have high exchange capacities, were not obviously related to tidal phases. Based on ammonium acetate leaching of selected total sediment samples from the diked containment area, calcium occupied most of the exchange sites with fewer sites occupied by magnesium, manganese, ammonium, potassium and sodium, in this order Nivens (1978). Because only 30 percent of the CEC could be accounted for by these ions, and cadmium, nickel, copper, mercury, and lead were below detection in the NH_4OAc leachate, the cation capacity of these sediments was probably not a major factor in the transport of

trace transition metals with exception of manganese, iron, and zinc.

64. The concentrations of six metals (cadmium, nickel, lead, copper, manganese, and iron) associated with the suspended material increased at the effluent pipe during dredging as compared to their average values in the channel sediments (see Table 25 and Appendix A'). These ranged from an 85 percent increase for cadmium (which should be questioned because of poor analytical precision) to 5 percent for iron. Part of this increase was due to the removal of about 20 percent sand and coarse silt during transit from the dredge inlet pipe to the effluent pipe with the apparent consequence of increasing the metal concentrations because these species are associated primarily with the finer sediments. Some of the measured gains in suspended sediment metals over total channel sediment concentrations were probably due to the oxidation of dissolved iron and manganese during dredging, which formed metal oxides and hydroxides. These would certainly be measured at the effluent pipe in the particulate phase and could be responsible for the 17 percent increase in manganese and five percent for iron. Particulate zinc concentrations decreased during this same time period, while particulate mercury was below detection. The change in zinc was probably due to solubilization of either the exchangeable or organic phases, as mentioned previously. Also, both zinc and mercury could have been depleted by association with the organic scums observed floating from the diked area during dredging (also evident as a large loss of volatile solids between the channel sediments and sediments within the development site six months after dredging).

65. During the tidal period 3.5 months later, suspended sediment cadmium was not detected due to insufficient quantity of sample. Overall, there was an increase during ebb tide 3.5 months later in the concentrations of seven suspended sediment metals (mercury, zinc, lead, iron, nickel, copper, and manganese) in the effluent from the diked area as compared to their average values in the total channel sediments. Values for iron and manganese were considered the most reliable due to their abundance. Because of the greater concentrations of suspended solids leaving the diked area during ebb tide, there was a net loss of five metals (iron,

copper, manganese, zinc, and lead). The export of iron from the diked area during one tidal cycle was as great as 115 times its import value, while the lowest calculated difference was 31 times for lead. The suspended sediment metals were probably transported from the diked area as finer grained sediments which were suspended by tidal currents. During the 3.5 months interval after dredging, dissolved iron (II) could have increased in the sediment pore water resulting in a higher loss to the overlying tidal waters and a greater net export as particulate iron after rapid oxidation to ferric (III) oxides and hydroxides (Stumm and Morgan 1970).

PART IV: SUMMARY

66. River bottom sediments from the Windmill Point and Jordan Point shoals of the James River Navigation Channel were composed of fine textured and poorly sorted mineral and organic particles. High sediment volatile solids values can be attributed to partially decomposed plant materials probably produced in local swamp and freshwater marsh habitats. Sediments were flocculated or agglomerated and contained high concentrations of total phosphorus and nitrogen suggesting input from local agricultural, domestic and/or industrial sources. Approximately 50 percent of the total dissolved phosphorus in the sediment interstitial water was inorganic phosphate while 90 percent of the total dissolved nitrogen in the interstitial water was ammonium. The cation exchange characteristics of the sediments could be accounted for by identified clay minerals suggesting that inorganic cation exchange reactions could be controlling exchangeable cation concentrations. Sediment concentrations of iron, calcium and manganese were at the low percent to parts per thousand levels while, zinc, lead, copper and nickel ranged from 30 to 250 parts per million concentrations. Cadmium was slightly above one part per million; mercury was less than one part per million.

67. Approximately 40 percent of the dredged sediments placed into the dike for marsh substrate development remained within the dike at the completion of dredging, the rest was lost as suspended material through the effluent discharge points. About two-thirds of the volatile solids originally contained in the channel sediments were lost during the dredging operation along with some high cation exchange capacity inorganic particles consisting of smectite and vermiculite.

68. A predictive dilution - mixing model was developed that assumed sediment interstitial waters were mixed with James River waters in a 1:5 ratio during the active dredging operation. Concentrations of dissolved chemical substances at the effluent discharge point that exceeded predicted concentrations were related to mobilization from the solid sediment phase under conditions effected by dredging and disposal. Observations suggested the mobilization of dissolved zinc, copper,

cadmium, lead, nickel, mercury, and ammonium. Calcium and manganese concentrations were as predicted; iron and inorganic phosphate concentrations fell below predicted values.

69. The application of selective sediment chemical extraction procedures suggested that observed mobilization was probably the result of the release of metallic or nutrient substances from exchangeable and/or organically bound sediment fractions. Precipitation and co-precipitation reactions appear to be important in effecting the release of iron, calcium, manganese and inorganic phosphorus.

70. The establishment of chemically reduced microhabitats within the intertidal dredged material substrate was apparent during tidal influent-effluent monitoring 3.5 months after dredging for site construction. When compared with effluent concentrations observed during the dewatering period, ebb tide concentrations of dissolved iron, manganese, orthophosphate and ammonium were increased; the concentration of nitrate plus nitrite decreased slightly during this period.

71. The effluent water leaving the marsh development site 3.5 months after its construction was substantially different than the river water flooding it. Compared with flood tidal water quality entering the dike through the effluent pipes 3.5 months after site construction, ebb tide drainage was characterized by higher concentrations of suspended material, dissolved total nitrogen and ammonium, and dissolved iron, manganese, mercury, calcium, and zinc. Dissolved oxygen concentrations and pH values were lower during ebb tide.

72. Compared with the dredging observation period, suspended sediment concentrations of iron and zinc and possibly manganese and lead were higher in the ebb drainage leaving the dike 3.5 months after site construction. Based on only a few samples and the ebb and flood tide concentrations of suspended material at the effluent pipe, a net export of particulate iron, copper, manganese, zinc, and lead was calculated.

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Table 1

Tidal and Areal Statistics for the 93-97 km Section of the James River,
which includes Portions of the Jordan Point-Harrison Bar-Windmill
Point Shoal (Taken From Cronin, 1971) and Dredging Operations
at this Channel During January 21 to February 4, 1975

Mean low water volume of James River to kilometer 97

$$2272 \times 10^6 \text{ m}^3$$

Mean low water area of James River to kilometer 97

$$606 \times 10^6 \text{ m}^2$$

Below kilometer 97 to Newport News, VA

90 percent of mean low water volume of tidal James

92 percent of mean low water area of tidal James

Statistics for the 93-97 km stretch

Average depth: 3.62 m

Average cross section area: $0.6 \times 10^4 \text{ m}^2$

Average tidal range: 0.71 m

Tidal cycle: 12.42 hrs

Duration of rise: 5.70 hrs

Duration of fall: 6.72 hrs

Dredging operations

Total pipe-line dredging operations for filling the diked
containment area: 10.5 days

Filling dates: January 21 and 22, 1975

(Stopped to repair dikes for five days)

Filling again from January 27 to 0700 hrs February 4, 1975

Approximate amount of sand for dikes: $62,300 \text{ m}^3$

Approximate amount of channel sediments pumped into the diked
containment area: $166,540 \text{ m}^3$

Table 2

Sampling Program at the James River Artificial Habitat Development Site and a Reference Marsh
Before and After Dredging

| PERIODS | TIME/LOCATION | FIELD OPERATIONS | ANALYSES |
|-----------------------------|---------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Predredging | Jan 9, 1975 James River | 10 channel cores (Figure 5) | Field sediment pH, Eh, temperature, pS, subsample for total H ₂ S for lab analyses, description Laboratory: 1. IW and bulk Ca, Cd, Cu, Fe, Hg, Mn, Ni, Pb, Zn 2. IW PO ₄ , TDP, NH ₄ , NO ₃ , NO ₂ , TDN and bulk P, N 3. Water content, volatile solids, sediment size, mineralogy of clay, silt and sand, CEC |
| Dredging | Jan 31-Feb 1 Artificial Habitat | Six-hr. effluent water sampling at site AP (Figure 3) | Laboratory: 1. Suspended solids, dissolved and particulate Ca, Cd, Cu, Fe, Hg, Mn, Ni, Pb, Zn 2. Dissolved PO ₄ , NO ₃ , NO ₂ , NH ₄ , and unfiltered TP, TKN 3. Suspended sediment size, CEC |
| <u>POSTDREDGING PERIODS</u> | | | |
| Dewatering (2-4 days) | Feb 6 - 8 Artificial Habitat | Six-hr. water sampling at site AP (Figure 3) | Laboratory: 1. Suspended solids, dissolved and particulate Ca, Cd, Cu, Fe, Hg, Mn, Ni, Pb, Zn 2. Dissolved PO ₄ , NO ₃ , NO ₂ , NH ₄ , and unfiltered TP, TKN 3. No particulate metals |
| 2.5 Months | April 18-20 Artificial Habitat | Data not useful due to high winds and negligible flood tide | |
| 3.5 Months | May 13 - 15 Artificial Habitat | Six-hr. water sampling at site AP (Figure 3) | Field: Water pH, Eh, temperature, alkalinity, dissolved oxygen Laboratory: 1. Suspended solids, dissolved and particulate metals same as dredging period 2. Dissolved PO ₄ , TDP, NO ₃ , NO ₂ , NH ₄ , TDN, and unfiltered TP, TKN 3. Suspended sediment size, CEC |
| 6 Months | July 1975 Artificial Habitat | 6 cores for chemistry, 11 cores for geology, 14 additional cores for probe analyses, % H ₂ O, IW - NH ₄ , and total H ₂ S. Vane shear at 22 locations (Figure 7 in Volume II) | Field: Sediment program same as predredging channel cores (except temperature during coring at top and bottom) Laboratory: 1. Same as predredging channel cores (except deleted dissolved Hg and obtained water content and volatile solids from separate samples collected during coring), added IW Cr and DOC, bulk Cr and total organic carbon for sediments 2. Added Atterberg limits and photography of sediments after splitting cores |

(continued)

Table 2 (Concluded)

| POSTDREDGING PERIODS (Continued) | | | | |
|----------------------------------|-----------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|
| 17 Months | July 1976 Artificial Habitat | 19 surface grab samples (Figure 8 in Volume II) | Laboratory: sediment CEC | |
| 18 Months | August 5-7 (Summer Season) Artificial Habitat Reference Marsh | 18 cores for chemistry and geology (9 at Artificial Habitat, 9 at reference marsh) vane shear at coring sites Hourly water samples at 4 sites in duplicate (A and B) (2 sites at Artificial Habitat - AP + AB, and 2 sites at reference marsh-- RL + RS) Most hourly water samples composited according to tidal stages (see Figures 2 and 3) | Field: sediment program same as July 1975 cores; water pH, temperature, dissolved oxygen, turbidity, alkalinity data was too poor to report Laboratory: 1. Same as 6 months' sediment program (except measured dissolved Hg and deleted Atterberg limits and photography) 2. Added description of one core from reference marsh site RS 3. Same as 3.5 months' water program (except dissolved Ca, Fe, Mn, Zn analyzed hourly in duplicate, DOC and VOC analyzed hourly), added current velocity at 3 channels, conductivity, chlorophyll, phaeophytin, Fo/Fa ratio on hourly basis 4. Dissolved parameters composited according to tidal stages: PO ₄ , TDP, NO ₃ + NO ₂ , NH ₄ , TIN 5. Particulate parameters composited according to tidal stages: Unfiltered P and TKN, metals except Hg, silt/clay ratio, CEC | |
| 24 Months | January 8-10 (Winter Season) Artificial Habitat Reference Marsh | Same as during August 5-7 period Hourly water samples at 4 locations* (see Figures 2 and 3) | Field: Sediment program same as July 1975 cores (except total sulfides deleted) water program same as August 1976 Laboratory: 1. Same as August 1976 sediment program 2. Same as August 1976 water program, added filtered TOC for composited tidal stages | |
| 28 Months | June 1977 Artificial Habitat | 4 cores | Laboratory: Special study of IW for dissolved metals at different centrifugation speeds for core from site A1 and AS | |

Abbreviations: IW = Interstitial water, Eh = redox potential, PS = sulfide activity electrode, TDP = total dissolved phosphorus
TDN = total dissolved nitrogen, CFC = cation exchange capacity, DOC and VOC = dissolved total organic carbon and volatile organic carbon
Fo/Fa ratio = chlorophyll measurement before and after acidification

*A discussion of the hourly water sampling program is presented in Volume II of this appendix.

Table 3

Water and Sediment Quality for the Study Area near Windmill Point, James River, Virginia. When Available, Data from This Report Are Provided as Comparison

| WATER QUALITY | | | |
|----------------------------------------------------|---------------------|------------|----------------|
| Parameter | Concentration | Date | Comments |
| pH | 7.7 range 6.8 - 8.6 | 1969 | Seasonal study |
| Alkalinity (meq/l) | 0.7 range 0.4 - 1.2 | 1969 | Seasonal study |
| Alkalinity (meq/l) | range 0.5 - 0.9 | 1965 | May |
| Suspended Solids (mg/l) | 29, 44 | 1965, 1966 | May, Jan |
| Dissolved PO ₄ (mg/l) | 0.01 | 1965, 1966 | May, Jan |
| Dissolved TP (mg/l) | 0.02 | 1965, 1966 | May, Jan |
| Total Phosphorus (mg/l) | 0.09, 0.16 | 1965, 1966 | May, Jan |
| Total Phosphorus (mg/l) | 0.06 - 0.2 | 1969 | Jan - Sept |
| Dissolved NO ₃ + NO ₂ (mg/l) | 2.2 | 1966 | Jan |
| Particulate Organic Nitrogen (mg/l) | 0.1, 0.24 | 1965, 1966 | May, Jan |
| Total Nitrogen (mg/l) | 0.7 - 2.8 | 1969 | Sept - Jan |

| SEDIMENT QUALITY | | | |
|----------------------|---------------|----------------------|-------------------------|
| Parameter | Concentration | Comments | This Study ⁺ |
| Volatile Solids (%) | 10, 8.2 | Channel sediments | 14.5 ± 1.9 |
| COD (%) | 9, 7.2 | Channel sediments | not measured |
| Water (%) | 51.2 | Channel sediments | 50.8 ± 6.4 |
| TKN (μg/g) | 2190, 2018 | Channel sediments | 457 ± 683 |
| TP (μg/g) | 464, 250 | Channel sediments | 661 ± 110 |
| Total Copper (μg/g) | 28 | Channel sediments | 49 ± 14 |
| Total Lead (μg/g) | 53, 49 | Channel sediments | 62 ± 14 |
| Total Mercury (μg/g) | 0.3, 0.14 | Channel sediments | 0.52 ± 0.17 |
| Total Mercury (μg/g) | 1.3 - 1.9 | <62 μm fraction | |
| Total Zinc (μg/g) | 260, 178 | Channel sediments | 240 ± 55 |
| Sediment Eh mV | -70 to +50 | first 18 cm of depth | -020 ± 54 |
| Sediment pH | 6.7 | | 6.70 ± 0.22 |

* Mean and range for flood tide at Artificial Habitat breach and reference marsh tidal channels during August 1976 and January 1977

** Same as previous footnote except only for January 1977 data (Presented and discussed in Volume II of this appendix)

+ From 10 cores collected in the James River channel near Windmill Point in January 1975 (see Part II of text)

+⁺ Norfolk District Corps of Engineers, Norfolk, Virginia

Table 4

Deposition Rates (cm/year) in the Channel at the Jordan Point-
Harrison Bar-Windmill Point Shoals, James River, Virginia,
for the Two-Year Period Before Coring in January 1975
and for a 2.2-Year Period After Coring

| <u>BEFORE CORING</u> | | | | |
|-------------------------------------------|--------------------------------------------------|----------------------------------------------------|---------------------------------------------------|----------------------------------|
| <u>In Vicinity of Core Number</u> | <u>Dec 1972 to Aug 1973 (cm/yr)</u> | <u>Aug 1973 to April 1974 (cm/yr)</u> | <u>April 1974 to Nov 1974 (cm/yr)</u> | <u>Avg. Rate (cm/yr)</u> |
| 2 | 209 | 0 | 174 | 128 |
| 3 | 166 | 50 | 123 | 113 |
| 4 | 56 | 0 | 137 | 64 |
| 5 | 95 | 46 | 46 | 62 |
| 6 | 211 | 48 | 46 | 102 |
| 7 | 31 | 69 | 101 | 67 |
| 8 | 0 | 64 | 169 | 78 |
| 9 | 128 | 57 | 114 | 100 |
| 10 | 202 | 27 | 9 | 79 |
| 12 | 36 | 0 | 197 | 78 |
| | Overall mean | | 87 ± 22 cm/yr | |
| <u>POSTCORING</u> | | | | |
| <u>In Vicinity of Core Number</u> | <u>Feb 1975 to July 1976 (cm/yr)</u> | <u>July 1976 to April 1977 (cm/yr)</u> | | <u>Avg. Rate (cm/yr)</u> |
| 2 | 19 | 193 | | 79 |
| 3 | 27 | 213 | | 91 |

(Continued)

Table 4 (Concluded)

| <u>In Vicinity of Core Number</u> | <u>Feb 1975 to July 1976 (cm/yr)</u> | <u>July 1976 to April 1977 (cm/yr)</u> | <u>Avg. Rate (cm/yr)</u> |
|-------------------------------------------|--------------------------------------------------|----------------------------------------------------|----------------------------------|
| 4 | 19 | 106 | 49 |
| 5 | 26 | 30 | 27 |
| 6 | 10 | 290 | 106 |
| 7 | -13 | 145 | 42 |
| 8 | -36 | 79 | 4 |
| 9 | 55 | 180 | 98 |
| 10 | -21 | 221 | 62 |
| 12 | 15 | 118 | 51 |

Overall mean 61 ± 33 cm/yr

Table 5

Sensitivity, Detection Limit, Accuracy, and Precision for Metal Analysis
by Atomic Absorption Spectrometry

| Element | Sensitivity* (mg/l) | Detection Limit** (mg/l) | Flame | Lamp [†] | Accuracy ^{††} (±%) | Precision [‡] (±%) |
|------------------|------------------------|--------------------------------|------------------------------------------------|-------------------|--------------------------------|--------------------------------|
| Al | 0.9 | 0.9 | N ₂ O•C ₂ H ₂ | HC | -- | -- |
| As | 2.0 | 2.0 | Air•C ₂ H ₂ | EDL | -- | -- |
| Ca | 0.07 | No S.E. used | Air•C ₂ H ₂ | HC | 6.1 | 1.0 |
| Cd | 0.025 | 0.002 | Air•C ₂ H ₂ | EDL | 10.4 | 2.9 |
| Cr ^{‡‡} | 0.1 | 0.015 | N ₂ O•C ₂ H ₂ | HC | 12.5 | 4.8 |
| Cu | 0.10 | 0.006 | Air•C ₂ H ₂ | HC | 10.3 | 1.7 |
| Fe | 0.1 | 0.025 | Air•C ₂ H ₂ | HC | 5.7 | 0.8 |
| Hg | 0.0001 [§] | 0.0001 [§] | (Cold Vapor) Flameless | Hg vapor | 10 | 5.5 |
| Mn | 0.05 | 0.021 | Air•C ₂ H ₂ | HC | 5.2 | 1.2 |
| Ni | 0.1 | 0.015 | Air•C ₂ H ₂ | HC | 6.3 | 1.3 |
| Pb | 0.5 | 0.050 | Air•C ₂ H ₂ | EDL | 12.3 | 2.8 |
| Zn | 0.015 | 0.004 | Air•C ₂ H ₂ | EDL | 6.5 | 1.0 |

* Defined as one percent absorbance

** Defined as approximately equal to the sensitivity divided by the maximum scale expansion (SE)

† EC = Perkin-Elmer single element Intensitron[®] Hollow Cathode source lamp
 EDL = Perkin-Elmer electrodeless discharge source lamp (single element)

†† Defined as $[\sum(E)^2]^{1/2}$, where E is expressed as percent error

‡ Defined as $\frac{\sum|E(\%)|}{n_i}$, the average relative standard deviation of replicate determinations about the mean of these measurements

‡‡ Chromium was added during July 1975 and subsequent field operations

§ Calculated for a 100 ml sample

Table 6

Statistics for Percent Water, Temperature, pH, pS, Total H₂S, Eh, and
Volatile Solids for 10 Cores from the James River near Windmill
Point (See Figure 5)

| <u>Parameter</u> | <u>Units</u> | <u>Core Section</u> | <u>Mean</u> | <u>Standard Deviation</u> | <u>Range</u> | <u>n</u> |
|---------------------|--------------|-------------------------|-------------|-------------------------------|---------------|----------|
| Temp.* | °C | upper | 12.7 | 2.76 | 8 - 17 | 11 |
| | | lower | 14.5 | 3.05 | 9 - 18 | 11 |
| pH* | — | upper | 6.77 | 0.23 | 6.48 - 7.09 | 10 |
| | | lower | 6.63 | 0.19 | 6.36 - 6.93 | 11 |
| pS*** | mV | upper | -023 | 10.5 | -038 - -003 | 11 |
| | | lower | -022 | 11.7 | -043 - -008 | 11 |
| H ₂ S | mg/l | upper | 2.90 | 0.91 | 1.94 - 5.08 | 9 |
| | | lower | 4.11 | 1.70 | 2.34 - 7.98 | 10 |
| Eh*.† | mV | upper | -018 | 41.1 | -103 - +044 | 11 |
| | | lower | -034 | 66.9 | -159 - +044 | 11 |
| Water ^{††} | % | upper | 56.0 | 4.35 | 46.0 - 59.9 | 10 |
| | | lower | 49.1 | 4.17 | 42.8 - 58.1 | 10 |
| Water* | % | upper | 54.8 | 5.42 | 44.6 - 62.2 | 11 |
| | | lower | 46.5 | 4.47 | 36.7 - 51.4 | 11 |
| Loss at 110°C‡ | % | upper | 1.52 | 0.47 | 0.82 - 2.52 | 10 |
| | | lower | 1.79 | 0.37 | 0.89 - 2.19 | 10 |
| Loss at 540°C‡ | % | upper | 13.80 | 1.40 | 11.25 - 16.65 | 10 |
| | | lower | 15.27 | 2.04 | 12.40 - 18.98 | 10 |
| Loss at 1000°C‡ | % | upper | 1.83 | 0.56 | 1.18 - 2.53 | 4 |
| | | lower | 2.19 | 0.50 | 1.69 - 2.88 | 4 |

* Sedimentary parameters listed in these columns were measured at the same place or processed from subsamples collected with special 50-cc syringes (% water and total H₂S). Water content was determined by drying at 60°C to constant weight; this measurement was used for calculating interstitial H₂S concentration. Temperature, pH, pS, and Eh were measured (under nitrogen) through predrilled holes immediately after recovery of the core

** Potential of an Orion silver/silver-sulfide specific ion electrode. Values were corrected for the potential of the saturated calomel electrode (SEC)

† Calculated from the average of two platinum electrodes inserted through the same predrilled hole in the core liner. Both were connected to a common reference electrode, and values were corrected for the potential of the SCE

†† Analyzed by breeze drying to constant weight

‡ Percent weight loss at specified temperatures from constant weight at 60°C (dried for 72 hrs) for the 110°C and 540°C and for further weight loss from 540°C for the 1000°C temperature.

Table 7

Statistics for Interstitial (mg/l) and Total (µg/g Sediment, Dry Weight) Sediment Nutrients for 10 Channel Cores Collected from the James River Near Windmill Point (See Figure 5)

| <u>Parameter</u> | <u>Section*</u> | <u>Mean (mg/l)</u> | <u>Standard Deviation (mg/l)</u> | <u>Range (mg/l)</u> | | <u>n</u> |
|---------------------------------------------------|-----------------|------------------------|------------------------------------------|-------------------------|-------|----------|
| <u>INTERSTITIAL WATER CONCENTRATIONS</u> | | | | | | |
| TDP** | upper | 0.386 | 0.135 | 0.183- | 0.584 | 10 |
| | lower | 0.527 | 0.142 | 0.328- | 0.784 | 10 |
| ortho-PO ₄ | upper | 0.183 | 0.103 | 0.072- | 0.417 | 10 |
| | lower | 0.321 | 0.167 | 0.056- | 0.533 | 10 |
| TDN** | upper | 65.08 | 18.31 | 38.7 - | 106 | 10 |
| | lower | 74.35 | 9.73 | 59.5 - | 86.4 | 10 |
| NH ₄ [†] | upper | 58.33 | 12.71 | 36.0 - | 78.3 | 18 |
| | lower | 67.20 | 11.16 | 44.9 - | 91.0 | 25 |
| NO ₃ | upper | 0.055 | 0.012 | 0.038- | 0.072 | 10 |
| | lower | 0.061 | 0.022 | 0.040- | 0.109 | 10 |
| NO ₂ | upper | 0.006 | 0.003 | 0.002- | 0.010 | 10 |
| | lower | 0.007 | 0.003 | 0.003- | 0.013 | 10 |
| <u>TOTAL SEDIMENT (DRY WEIGHT) CONCENTRATIONS</u> | | | | | | |
| | | <u>(µg/g)</u> | <u>(µg/g)</u> | <u>(µg/g)</u> | | |
| TP ^{††} | upper | 637 | 136 | 179 - | 720 | 19 |
| | lower | 685 | 74 | 456 - | 761 | 20 |
| TKN ^{††} | upper | 4,451 | 696 | 2,660 - | 5,660 | 19 |
| | lower | 4,698 | 667 | 3,630 - | 6,360 | 20 |

* Upper portion of the core was usually assigned as the 0-43 cm vertical section (0 = surface of the sediments), while the lower was the remainder. The division between the upper and lower sections varied from a 35-cm level in core number 3 to a 58-cm level in core 7

** TDP and TDN from filtered and frozen interstitial water which was thawed, acid digested, and analyzed for phosphorus and nitrogen

† NH₄ was analyzed immediately after centrifugation (at 4°C) for removal of interstitial water

†† After removal of interstitial water, sediments were freeze-dried, acid digested, and analyzed for phosphorus and nitrogen

Table 8
 Statistics for Interstitial (mg/l) and Total (µg/g Sediment, Dry Weight) Metals, Listed in Order of Abundance, for 10 Cores from the James River near Windmill Point (See Figure 5)

| INTERSTITIAL WATER CONCENTRATIONS* | | | | | | |
|------------------------------------|----------------|-------------|---------------------------|--------------|----------|----|
| Parameter | Core Section** | Mean (mg/l) | Standard Deviation (mg/l) | Range (mg/l) | | n |
| Ca | upper | 218.1 | 35.4 | 127.9 | - 272.4 | 23 |
| | lower | 213.5 | 78.5 | 90.0 | - 477.8 | 21 |
| Fe | upper | 55.87 | 25.84 | 2.70 | - 142.4 | 23 |
| | lower | 58.80 | 28.16 | 22.99 | - 146.1 | 21 |
| Mn | upper | 8.825 | 4.005 | 0.527 | - 16.95 | 23 |
| | lower | 4.879 | 2.487 | 1.350 | - 12.61 | 21 |
| Zn | upper | 0.183 | 0.304 | 0.005 | - 1.220 | 17 |
| | lower | 0.448 | 0.980 | 0.005 | - 3.561 | 17 |
| Pb | upper | 0.078 | 0.021 | 0.046 | - 0.153 | 21 |
| | lower | 0.075 | 0.025 | 0.048 | - 0.133 | 18 |
| Ni | upper | 0.056 | 0.016 | 0.021 | - 0.098 | 23 |
| | lower | 0.051 | 0.019 | 0.021 | - 0.083 | 21 |
| Cu | upper | 0.010 | 0.005 | 0.006 | - 0.027 | 17 |
| | lower | 0.011 | 0.009 | 0.006 | - 0.046 | 19 |
| Cd | upper | 0.009 | 0.004 | 0.002 | - 0.020 | 23 |
| | lower | 0.010 | 0.003 | 0.002 | - 0.014 | 21 |
| Hg | upper | 0.0033 | 0.0021 | 0.0005 | - 0.0074 | 12 |
| | lower | 0.0031 | 0.0019 | 0.0005 | - 0.0086 | 12 |

| TOTAL SEDIMENT (DRY WEIGHT) CONCENTRATIONS† | | | | | | |
|---------------------------------------------|----------------|-------------|---------------------------|--------------|----------|----|
| Parameter | Core Section** | Mean (µg/g) | Standard Deviation (µg/g) | Range (µg/g) | | n |
| Fe | upper | 40,990 | 6,290 | 28,030 | - 51,120 | 15 |
| | lower | 40,470 | 10,640 | 19,190 | - 55,080 | 10 |
| Ca ^{††} | upper | 1,266 | 811 | 3,710 | - 6,500 | 10 |
| | lower | 3,961 | 500 | 3,340 | - 4,640 | 10 |
| Mn | upper | 1,063 | 148 | 870.8 | - 1,385 | 15 |
| | lower | 1,153 | 267 | 794.4 | - 1,724 | 10 |
| Zn | upper | 230.0 | 51.92 | 115.2 | - 314.2 | 15 |
| | lower | 250.6 | 57.21 | 161.2 | - 353.6 | 10 |
| Pb | upper | 60.94 | 11.38 | 39.80 | - 79.26 | 15 |
| | lower | 64.09 | 18.46 | 26.16 | - 94.13 | 10 |
| Cu | upper | 45.43 | 7.89 | 32.16 | - 58.25 | 15 |
| | lower | 54.47 | 18.94 | 24.87 | - 91.70 | 10 |
| Ni | upper | 31.61 | 7.11 | 19.30 | - 48.58 | 15 |
| | lower | 36.39 | 7.40 | 24.10 | - 48.58 | 10 |
| Cd | upper | 1.26 | 0.55 | 0.68 | - 2.95 | 15 |
| | lower | 1.41 | 0.58 | 0.36 | - 2.45 | 10 |
| Hg | upper | 0.513 | 0.130 | 0.250 | - 0.720 | 13 |
| | lower | 0.522 | 0.243 | 0.110 | - 0.821 | 6 |

* Filtered, acidified, and frozen in acid-cleaned polyethylene. Thawed and analyzed by flame atomic absorption (with exception of mercury)

** Upper portion of the core was usually assigned as the 0-43 cm vertical section (0 = surface of the sediments), while the lower was the remainder. The division between the upper and lower sections varied from a 35-cm level in core number 3 to a 58-cm level in core number 7

† After removal of interstitial water, sediments were oven dried at 60°C, acid digested, and analyzed for metals by flame atomic absorption (with exception of mercury)

†† Calcium analyzed on different samples than the other bulk metals

Table 9

Sediment Size Statistics for 10 Cores from the James River
near Windmill Point (See Figure 5)

| <u>Parameter</u> | <u>Core Section</u> | <u>Mean</u> | <u>Standard Deviation</u> | <u>Range</u> |
|------------------------|---------------------|-------------|---------------------------|-----------------|
| Mean (ϕ) | Upper | 7.8 | 0.7 | 6.5 - 9.5 |
| | Lower | 7.5 | 1.3 | 5.5 - 10.2 |
| Sorting (ϕ) | Upper | 2.90 | 0.44 | 1.77 - 3.52 |
| | Lower | 3.20 | 0.26 | 2.88 - 3.77 |
| Skewness | Upper | 0.125 | 0.204 | -0.362 - 0.295 |
| | Lower | 0.187 | 0.234 | -0.390 - 0.453 |
| Kurtosis | Upper | -0.468 | 0.137 | -0.652 - -0.231 |
| | Lower | -0.416 | 0.159 | -0.593 - -0.068 |
| Sand % | Upper | 5.17 | 3.70 | 2.28 - 14.79 |
| | Lower | 15.83 | 15.52 | 2.09 - 42.88 |
| Silt % | Upper | 50.78 | 13.93 | 12.42 - 60.53 |
| | Lower | 43.44 | 12.18 | 22.77 - 60.30 |
| Clay % | Upper | 44.05 | 11.03 | 34.54 - 72.79 |
| | Lower | 40.73 | 14.65 | 23.79 - 74.95 |
| Coarse Mode (ϕ) | Upper | 4.74 | 0.45 | 3.69 - 5.40 |
| | Lower | 4.29 | 1.10 | 1.62 - 5.63 |
| Silt Mode (ϕ) | Upper | 7.40 | 1.70 | 6.25 - 11.0 |
| | Lower | 5.93 | 1.77 | 3.37 - 7.84 |
| Fine Mode (ϕ) | Upper | 8.95 | 0.58 | 8.29 - 9.39 |
| | Lower | 9.37 | 2.37 | 5.86 - 12.50 |

Table 10

Statistics for Cation Exchange Capacity of the Clay Fraction and Mineralogy
of the Total Sediment Fraction for 10 Cores from the James River near Windmill Point

(See Figure 5)

| <u>CATION EXCHANGE CAPACITY</u> | | | | |
|---------------------------------|---------------------|---------------------------|--------------------------------------------|---------------|
| <u>Parameter</u> | <u>Core Section</u> | <u>Mean meq/100 g</u> | <u>Standard Deviation meq/100g</u> | <u>Range</u> |
| Untreated* | upper | 30.94 | 6.59 | 23.70 - 42.07 |
| CaEC | lower | 30.79 | 5.76 | 24.96 - 41.56 |
| Cleaned** | upper | 31.28 | 3.44 | 25.43 - 35.36 |
| CaEC | lower | 31.37 | 3.39 | 25.98 - 36.29 |
| Untreated* | upper | 19.34 | 7.57 | 11.87 - 36.28 |
| K/EC | lower | 16.12 | 6.90 | 8.08 - 29.60 |
| Cleaned** | upper | 21.78 | 4.08 | 15.99 - 29.11 |
| K/EC | lower | 17.52 | 2.87 | 12.61 - 22.02 |

| <u>MINERALOGY</u> | | | | |
|-------------------|---------------------|---------------------|---------------------------------------|----------------------|
| <u>Parameter</u> | <u>Core Section</u> | <u>Mean (%)</u> | <u>Standard Deviation (%)</u> | <u>Range (%)</u> |
| Quartz | upper | 32 | 7 | 20 - 45 |
| | lower | 37 | 8 | 32 - 47 |
| Plag. feldspars | upper | 7 | 2 | 3 - 11 |
| | lower | 9 | 3 | 3 - 13 |
| K-feldspars | upper | 9 | 3 | 2 - 13 |
| | lower | 10 | 3 | 2 - 13 |
| Muscovite | upper | 8 | 2 | 5 - 14 |
| | lower | 5 | 2 | 1 - 8 |
| Illite | upper | 18 | 5 | 13 - 31 |
| | lower | 16 | 6 | 10 - 30 |
| Kaolinite | upper | 2 | 1 | 1 - 4 |
| | lower | 2 | 1 | Tr - 4 |
| Smectite | upper | 3 | 1 | 2 - 4 |
| | lower | 3 | 2 | 2 - 7 |
| Vermiculite | upper | 5 | 2 | 2 - 7 |
| | lower | 4 | 3 | 1 - 8 |
| Mixed-layered | upper | 5 | 2 | 3 - 8 |
| | lower | 5 | 3 | 2 - 11 |
| Chlorite | upper | 11 | 7 | 2 - 26 |
| | lower | 9 | 5 | 5 - 22 |

* Samples were washed in distilled water to remove salts and to separate the <2µm size fraction, which was used here

** Samples were chemically treated to remove colloidal carbonate coatings, organics and colloidal Fe coatings. Only the <2 µm fraction was used here

Table 11

Statistics for Mineralogy of the Clay, Silt, and Sand Fractions for 10 Cores
from the James River near Windmill Point (See Figure 5)

CLAY FRACTION (<2 μm)

| | Illite (%) | Chlorite (%) | Mixed- Layered Illite- Chlorite (%) | Vermiculite (%) | Smectite (%) | Kaolinite (%) |
|-----------|---------------|-----------------|-------------------------------------------------|--------------------|-----------------|------------------|
| Mean | 41 | 23 | 12 | 10 | 8 | 5 |
| Std. Dev. | 4.1 | 7.8 | 4.3 | 5.2 | 2.7 | 3.0 |
| Range | 33-47 | 5-36 | 6-24 | 2-20 | 5-16 | 0-12 |

SILT FRACTION (2-62 μm)

| | Quartz (%) | K-feldspar (%) | Plagioclase Feldspar (%) | Muscovite Mica (%) | Amphibole (%) |
|-----------|---------------|-------------------|--------------------------------|--------------------------|------------------|
| Mean | 58 | 16 | 13 | 11 | Tr |
| Std. Dev. | 8 | 4 | 3 | 4 | -- |
| Range | 41-80 | 7-22 | 10-20 | 3-25 | Tr-3 |

SAND FRACTION (>62 μm)

| | Quartz (%) | K-feldspar (%) | Plagioclase Feldspar (%) | Muscovite Mica (%) |
|-----------|---------------|-------------------|--------------------------------|--------------------------|
| Mean | 62 | 17 | 15 | 7 |
| Std. Dev. | 9 | 6 | 5 | 7 |
| Range | 46-84 | 5-24 | Tr-21 | 0-15 |

Table 12

Comparison of Predicted Cation Exchange Capacity (CEC) Based on Pure
Clays and Average Clay Percentages in the Windmill Point Channel
Sediments, James River, Virginia

| | CEC of Pure Clay (meq/100 g) | Average Clay Minerals (<2 μ m) in James River Channel (%) | Expected CEC Contribution to James River Sediments (meq/100 g) |
|-----------------|------------------------------------|---------------------------------------------------------------------------|----------------------------------------------------------------------------|
| Kaolinite (GA)* | 3 | 5 | 0.15 |
| Smectite (MS)* | 80 | 8 | 6.4 |
| Illite (IL)* | 23 | 41 | 9.4 |
| Chlorite** | 20 | 23 | 4.6 |
| Vermiculite** | 100 | 10 | 10.0 |
| Mixed-Layered** | 30 | 12 | 3.6 |
| | | Total expected inorganic CEC: | 34.2 |
| | | Average measured inorganic CEC (CaEC) for channel sediments: | 31 \pm 3 |

* CEC value from this locality reported in Busenberg and Clemency, 1973

** Taken from Grim, 1968

Table 13

Statistics for Temperature, Suspended Solids, pH, Alkalinity, Eh, and
Dissolved Oxygen at the Effluent Pipe of the Intertidal Diked
Containment Area on the James River near Windmill Point
During a Tidal Period in May (3.5 Months
After Dredging)

| <u>Parameter</u> | <u>Units</u> | <u>Tidal Period</u> | <u>Mean</u> | <u>Standard Deviation</u> | <u>Range</u> | <u>n</u> |
|----------------------|--------------|-------------------------|---------------------|-------------------------------|--------------|----------|
| Temperature | °C | low | 23.2 | 7.67 | 15.4 - 30.3 | 4 |
| | | high | 21.3 | 4.17 | 17.1 - 25.2 | 4 |
| Suspended* Solids | mg/liter | low | 10,853 [†] | 19,004 | 708 - 39,350 | 4 |
| | | high | 105 | 14.9 | 86 - 121 | 4 |
| pH | | low | 6.32 | 0.31 | 5.90 - 6.63 | 4 |
| | | high | 7.47 | 0.70 | 6.67 - 8.20 | 4 |
| Eh** | mV | low | +456 | 47.2 | +424 - +526 | 4 |
| | | high | +432 | 20.5 | +408 - +456 | 4 |
| Dissolved Oxygen | mg/liter | low | 2.50 | 0.93 | 1.50 - 3.30 | 4 |
| | | high | 10.76 | 2.33 | 8.29 - 13.9 | 4 |

* Collected by hand near the ISCO inlet port

** Corrected for the potential of the saturated calomel electrode

[†] Mean would be 1,400 mg/l with removal of the one high (39,350 mg/l) datum

Table 14

Statistics for Dissolved and Total Nutrients (mg/l) at the Effluent Pipe of the Intertidal Diked Containment Area on the James River near Windmill Point During the Periods of Active Dredging and Dewatering. Data Are Listed with Respect to the Nearest Tidal Period

| Parameter | Tidal Period | Active Dredging Period (Jan 31 - Feb 1, 1975) | | | | Settling and Dewatering Period* (Feb 6 - Feb 8, 1975) | | | |
|-------------------------------------|--------------|--------------------------------------------------|---------------------------------|-----------------|---|----------------------------------------------------------|---------------------------------|-----------------|----|
| | | Mean (mg/l) | Standard Deviation (mg/l) | Range (mg/l) | n | Mean (mg/l) | Standard Deviation (mg/l) | Range (mg/l) | n |
| <u>DISSOLVED NUTRIENTS**</u> | | | | | | | | | |
| ortho-P0 ₄ | low | 0.030 | 0.010 | 0.020 - 0.040 | 4 | 0.026 | 0.004 | 0.021 - 0.030 | 4 |
| | high | 0.041 | 0.011 | 0.033 - 0.048 | 2 | 0.027 | 0.007 | 0.017 - 0.040 | 9 |
| NH ₄ | low | 18.43 | -- [†] | -- | 1 | 0.250 | 0.287 | 0.052 - 0.579 | 3 |
| | high | 18.00 | 5.65 | 14.88 - 26.46 | 4 | -- [†] | -- | -- | -- |
| NO ₃ [†] | low | 0.029 | 0.016 | 0.013 - 0.043 | 4 | 0.356 | 0.106 | 0.217 - 0.475 | 4 |
| | high | 0.031 | 0.012 | 0.022 - 0.039 | 2 | 0.320 | 0.132 | 0.120 - 0.515 | 9 |
| NO ₂ [†] | low | 0.015 | 0.008 | 0.007 - 0.024 | 4 | 0.027 | 0.008 | 0.016 - 0.035 | 4 |
| | high | 0.012 | 0.002 | 0.010 - 0.013 | 2 | 0.024 | 0.013 | 0.009 - 0.050 | 9 |
| <u>TOTAL NUTRIENTS^{††}</u> | | | | | | | | | |
| TP | low | 0.120 | 0.055 | 0.075 - 0.200 | 4 | 0.031 | 0.005 | 0.025 - 0.035 | 4 |
| | high | 0.073 | 0.004 | 0.070 - 0.075 | 2 | 0.058 | 0.046 | 0.035 - 0.180 | 9 |
| TKN | low | 24.03 | 1.16 | 23.0 - 25.5 | 4 | 14.50 | 10.99 | 4.60 - 30.2 | 4 |
| | high | 18.45 | 2.76 | 16.5 - 20.4 | 2 | 10.44 | 4.31 | 4.20 - 16.7 | 9 |

* Incoming flood tides crossed a delta consisting of fine suspended material before entering the effluent pipe of the diked containment area

** Water samples were collected with an ISCO Automatic sampler and stored individually (500 ml polyethylene bottles) in an insulated box. Bottles were recovered every 24 hours, stored on ice during transit, and processed immediately upon return to the laboratory (dissolved and filtered samples)

† Periodic interference in the measurement

†† Total nutrients measured on unfiltered acid-digested water samples

Table 15

Statistics for Dissolved and Total Nutrients (mg/ℓ) at the Effluent
Pipe of the Artificial Habitat on the James River near Windmill
Point During a Tidal Period in May 1975 (3.5 Months After
Dredging) with Respect to the Nearest Tidal Period

| <u>Parameter</u> | <u>Tidal Period</u> | <u>Mean (mg/ℓ)</u> | <u>Standard Deviation (mg/ℓ)</u> | <u>Range (mg ℓ)</u> | <u>n</u> |
|----------------------------|-------------------------|------------------------|------------------------------------------|-------------------------|----------|
| <u>DISSOLVED NUTRIENTS</u> | | | | | |
| TDP | low | 0.102 | 0.046 | 0.046-0.147 | 4 |
| | high | 0.097 | 0.050 | 0.028-0.142 | 4 |
| ortho-PO ₄ | low | 0.048 | 0.020 | 0.038-0.078 | 4 |
| | high | 0.032 | 0.005 | 0.029-0.040 | 4 |
| TDN | low | 3.87 | 0.87 | 2.768-4.784 | 4 |
| | high | 0.95 | 0.27 | 0.587-1.168 | 4 |
| NH ₄ | low | 1.98 | 0.51 | 1.350-2.492 | 4 |
| | high | 0.26 | 0.05 | 0.201-0.296 | 4 |
| NO ₃ | low | 0.238 | 0.201 | 0.091-0.532 | 4 |
| | high | 0.231 | 0.019 | 0.207-0.249 | 4 |
| NO ₂ | low | 0.023 | 0.004 | 0.018-0.027 | 4 |
| | high | 0.021 | 0.001 | 0.019-0.022 | 4 |
| <u>TOTAL NUTRIENTS*</u> | | | | | |
| TP | low | 0.899 | 0.330 | 0.538-1.334 | 4 |
| | high | 0.160 | 0.056 | 0.090-0.216 | 4 |
| TKN | low | 5.23 | 1.00 | 4.18 -6.55 | 4 |
| | high | 1.28 | 0.41 | 0.93 -1.83 | 4 |

* Total nutrients measured on unfiltered acid-digested water samples

Table 16

Statistics for Dissolved Metals (mg/£) at the Effluent Pipe of the Intertidal Diked Containment Area on the James River near Windmill Point During the Periods of Active Dredging and Dewatering. Data Are Listed with Respect to the Nearest Tidal Period and in Order of Greatest Abundance During the Dredging Period

| Parameter | Tidal Period | Active Dredging Period* (Jan 5. - Feb 1, 1975) | | | Settling and Dewatering Period** (Feb 6 - Feb 8, 1975) | | | | |
|-----------|--------------------|---------------------------------------------------|---------------------------------|-----------------|-----------------------------------------------------------|----------------|---------------------------------|-----------------|----------------|
| | | Mean (mg/£) | Standard Deviation (mg/£) | Range (mg/£) | n [†] | Mean (mg/£) | Standard Deviation (mg/£) | Range (mg/£) | n [†] |
| Ca | low | 62.55 | 24.11 | 38.30 - 95.86 | 4 | 37.73 | 24.33 | 16.45 - 64.26 | 3 |
| | high | 48.58 | 6.40 | 44.05 - 55.10 | 2 | 27.53 | 12.37 | 8.62 - 42.89 | 6 |
| Fe | low | 6.010 | 6.637 | 0.250 - 15.01 | 4 | 0.119 | 0.058 | 0.054 - 0.166 | 3 |
| | high | 0.532 | 0.357 | 0.279 - 0.784 | 2 | 1.056 | 2.327 | 0.025 - 5.803 | 6 |
| Zn | low | 5.504 | 4.608 | 1.144 - 9.487 | 4 | 0.103 | 0.070 | 0.037 - 0.176 | 3 |
| | high | 2.495 | 0.824 | 1.912 - 3.077 | 2 | 0.039 | 0.019 | 0.023 - 0.069 | 3 |
| Mn | low | 1.187 | 0.658 | 0.428 - 1.924 | 4 | 0.198 | 0.157 | 0.066 - 0.572 | 3 |
| | high | 0.202 | 0.016 | 0.190 - 0.213 | 2 | 0.286 | 0.433 | 0.032 - 1.161 | 6 |
| Pb | low ⁺⁺ | 0.142 | 0.012 | 0.133 - 0.150 | 2 | --- | --- | --- | --- |
| | high ⁺⁺ | 0.323 | --- | --- | 1 | --- | --- | --- | --- |
| Cu | low | 0.051 | 0.045 | 0.008 - 0.100 | 4 | 0.006 | 0.000 | 0.006 - 0.006 | 2 |
| | high | 0.035 | 0.021 | 0.020 - 0.050 | 2 | 0.020 | 0.022 | 0.006 - 0.045 | 3 |
| Ni | low ⁺⁺ | 0.035 | 0.022 | 0.017 - 0.059 | 3 | 0.027 | 0.010 | 0.016 - 0.034 | 3 |
| | high ⁺⁺ | 0.020 | --- | --- | 1 | --- | --- | --- | --- |
| Cd | low | 0.019 | 0.016 | 0.005 - 0.037 | 4 | 0.018 | 0.010 | 0.011 - 0.029 | 3 |
| | high | 0.005 | --- | --- | 1 | 0.013 | 0.007 | 0.006 - 0.026 | 6 |
| Hg | low | 0.0021 | 0.0008 | 0.0012 - 0.0032 | 4 | 0.0007 | 0.0001 | 0.0006 - 0.0007 | 2 |
| | high | 0.0034 | --- | --- | 1 | 0.0009 | 0.0002 | 0.0006 - 0.0012 | 6 |

* Water samples were collected with an ISCO automatic sampler and stored individually (500-ml polyethylene bottles) in an insulated box. Bottles were recovered every 24 hours, stored on ice during transit, and processed immediately upon return to the laboratory (for dissolved and particulate samples)

** Incoming flood tide crossed a delta, which consisted of fine suspended materials, before entering the diked containment area. Therefore, the tidal variations might not be apparent

[†] Numbers below the analytical detection limit for each particular parameter are not included

⁺⁺ Below detection limit for dissolved metals during the Feb 6-8, 1975 sampling period

Table 17

Statistics for Dissolved Metals (mg/ℓ) at the Effluent Pipe of the Intertidal Diked Containment Area on the James River near Windmill Point During a Tidal Period in May 1975 (3.5 Months After Dredging). Data Are Listed with Respect to the Nearest Tidal Period and in Order of Greatest Low Tide Abundance

| <u>Parameter</u> | <u>Tidal Period</u> | <u>Mean (mg/ℓ)</u> | <u>Standard Deviation (mg/ℓ)</u> | <u>Range (mg/ℓ)</u> | <u>n*</u> |
|------------------|---------------------|------------------------|------------------------------------------|-------------------------|-----------|
| Ca | low | 16.23 | 5.97 | 8.45 - 21.40 | 4 |
| | high | 13.70 | 0.45 | 13.08 - 14.11 | 4 |
| Fe | low | 0.518 | 0.226 | 0.351 - 0.837 | 4 |
| | high | 0.225 | 0.113 | 0.114 - 0.329 | 4 |
| Mn | low | 0.384 | 0.133 | 0.269 - 0.504 | 4 |
| | high | 0.026 | 0.011 | 0.018 - 0.042 | 4 |
| Zn | low | 0.034 | 0.015 | 0.015 - 0.048 | 4 |
| | high | 0.011 | 0.003 | 0.008 - 0.014 | 4 |
| Ni | low | 0.024 | 0.003 | 0.022 - 0.026 | 2 |
| | high** | --- | --- | --- | -- |
| Cd | low [†] | 0.003 | --- | --- | 1 |
| | high** | --- | --- | --- | -- |
| Hg | low | 0.0012 | 0.0012 | 0.0003- 0.0024 | 3 |
| | high | 0.0002 | 0.0000 | 0.0002- 0.0002 | 3 |
| Cu | low [†] | 0.006 | --- | --- | 1 |
| | high** | --- | --- | --- | -- |
| Pb | low** | --- | --- | --- | -- |
| | high** | --- | --- | --- | -- |

* Numbers below the analytical detection limit for each particular parameter are not included

** Below detection limit for each water sample during the sampling period

† Only one value, therefore listed along with level in order of abundance

Table 18

Statistics for Suspended Particulate Metals ($\mu\text{g/g}$) at the Effluent Pipe of the Intertidal Diked Containment Area on the James River near Windmill Point During the Period of Active Dredging. Data Are Listed with Respect to the Nearest Tidal Period and in Order of Greatest Abundance

| Parameter* | Tidal Period | Mean ($\mu\text{g/g}$) | Standard Deviation ($\mu\text{g/g}$) | Range ($\mu\text{g/g}$) | n** |
|-----------------|--------------------|-------------------------------------------|----------------------------------------------|------------------------------|-----|
| Fe | low | 47,800 (42,672) [†] | 14,410 | 31,720 - 59,540 | 3 |
| | high | 34,980 | 1,541 | 33,890 - 36,070 | 2 |
| Ca | low ^{††} | --- | --- | --- | -- |
| | high ^{††} | --- | --- | --- | -- |
| Mn | low | 1,323 (1,276) [†] | 71.08 | 1,250 - 1,392 | 3 |
| | high | 1,206 | 108.2 | 1,129 - 1,282 | 2 |
| Zn | low | 212.8 (213) [†] | 20.26 | 198.6 - 236.0 | 3 |
| | high | 213.6 | --- | --- | 1 |
| Pb | low | 81.86 ₊ (77.8) [†] | 5.77 | 77.92 - 88.48 | 3 |
| | high | 71.66 | 9.03 | 65.27 - 78.04 | 2 |
| Cu | low | 62.71 (60.3) [†] | 7.08 | 55.86 - 70.00 | 3 |
| | high | 56.80 | 13.09 | 47.54 - 66.05 | 2 |
| Ni | low | 46.91 (41.6) [†] | 8.67 | 37.27 - 54.07 | 3 |
| | high | 33.66 | 1.29 | 32.75 - 34.57 | 2 |
| Cd | low | 2.58 (2.43) [†] | 0.30 | 2.38 - 2.92 | 3 |
| | high | 1.98 | --- | --- | 1 |
| Hg [‡] | low | --- | --- | --- | -- |
| | high | --- | --- | --- | -- |

* Water samples were collected with an ISCO automatic sampler and stored individually (500-ml polyethylene bottles) in an insulated box. Bottles were recovered every 24 hours, stored on ice during transit, and processed immediately upon return to the laboratory (concentrations expressed on dry weight basis)

** Numbers below the analytical detection limit for each parameter are not included (detection limit is a function of the particulates available for digestion and the analytical sensitivity for each metal)

[†] Mean for both tidal periods

^{††} Data inaccurate due to aluminum interference during analysis by atomic absorption. From other suspended sediment data, calcium in the particulate phase would probably rank in second place in order of abundance

[‡] Below detection limit because of inadequate sample weight

Table 19

Statistics for Suspended Particulate Metals ($\mu\text{g/g}$) at the Effluent Pipe of the Intertidal Diked Containment Area on the James River near Windmill Point During a Tidal Period in May 1975 (3.5 Months After Dredging). Data Are Listed with Respect to the Nearest Tidal Period and in Order of Greatest Abundance at Low Tide

| <u>Parameter*</u> | <u>Tidal Period</u> | <u>Mean ($\mu\text{g/g}$)</u> | <u>Standard Deviation ($\mu\text{g/g}$)</u> | <u>Range ($\mu\text{g/g}$)</u> | <u>n**</u> |
|-------------------|----------------------|------------------------------------------|--------------------------------------------------------|-------------------------------------------|------------|
| Fe | low | 67,770 | 7,652 | 57,690 - 75,120 | 4 |
| | high | 66,510 | 4,242 | 63,050 - 71,240 | 3 |
| Mn | low | 1,354 | 315 | 1,005 - 1,637 | 4 |
| | high | 3,253 | 1,823 | 1,710 - 5,265 | 3 |
| Zn | low | 496 | 151 | 301 - 636 | 4 |
| | high | 1,868 | 1,520 | 364 - 3,403 | 3 |
| Pb | low | 107.2 | 16.83 | 84.7 - 124.3 | 4 |
| | high | 416.3 | 317.1 | 146.2 - 765.5 | 3 |
| Cu | low | 64.31 | 13.05 | 53.98- 79.0 | 3 |
| | high | 160.1 | 192.6 | 23.96- 269.3 | 2 |
| Ni | low | 54.43 | 21.94 | 31.5 - 79.4 | 4 |
| | high [†] | --- | --- | --- | -- |
| Hg | low | 1.58 | --- | --- | 1 |
| | high [†] | --- | --- | --- | -- |
| Ca | low ^{†,++} | --- | --- | --- | -- |
| | high ^{†,++} | --- | --- | --- | -- |
| Cd | low [†] | --- | --- | --- | -- |
| | high [†] | --- | --- | --- | -- |

* Concentrations determined as $\mu\text{g/g}$ dry weight of suspended material collected on 0.4 μm filters

** Numbers below the analytical detection limit for each parameter are not included (detection limit depends upon the suspended solid available for digestion)

[†] Below detection limit

⁺⁺ Data inaccurate due to aluminum interference during analysis by atomic absorption. From other suspended sediment data, calcium in the particulate phase would probably rank in second place in order of abundance

Table 21

Statistics for the Estimated Abundance of Minerals in the Suspended Sediments at the James River
Artificial Habitat Development Site During Dredging and 3.5 Months Later as Compared to
Mineral Abundance Estimates for the James River Channel near Windmill Point

| Sampling Period | Location | Statistic | Illite (%) | Quartz (%) | Chlorite (%) | Mixed-Layered (%) | K-feldspar (%) | Plagioclase Feldspar (%) | Mica (%) | Vermiculite (%) | Smectite (%) | Kaolinite (%) |
|-----------------------------------------|---------------------------------------|-----------|------------|------------|--------------|-------------------|----------------|--------------------------|----------|-----------------|--------------|---------------|
| Jan 1975 (Before Dredging) | James River Channel (See Figure 5) | Mean | 17 | 35 | 10 | 5 | 9 | 8 | 7 | 5 | 3 | 2 |
| | | Std. Dev. | 6 | 7 | 6 | 3 | 3 | 3 | 2 | 3 | 1 | 1 |
| | | Number | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| Active Dredging (1/30-2/2/75) | Habitat Effluent Pipe (AP) | Mean | 28 | 23 | 18 | 8 | 6 | 5 | 6 | 2 | 2 | 1 |
| | | Std. Dev. | 2 | 4 | 0.6 | 0.6 | 1 | 0 | 3 | 2 | 0 | 0 |
| | | Number | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| May 1975 (3.5 Months After Dredging) | Habitat Effluent Pipe (AP) | Mean | 28 | 21 | 13 | 10 | 7 | 5 | 7 | 5 | 4 | 3 |
| | | Std. Dev. | 2 | 4 | 1 | 3 | 0.4 | 1 | 2 | 2 | 2 | 1 |
| | | Number | 4 | 3 | 4 | 4 | 3 | 3 | 3 | 3 | 4 | 4 |

Table 22

Statistics for Cation Exchange Capacity of Untreated and H₂O₂ Treated Suspended Sediments at the
James River Artificial Habitat Development Site Effluent Pipe (AP) During Dredging and
3.5 Months Later

| <u>Sampling Period</u> | <u>Statistic</u> | <u>CaEC Untreated meq/100 g</u> | <u>CaEC H₂O₂ Treated meq/100 g</u> | <u>K/EC Untreated meq/100 g</u> | <u>K/EC H₂O₂ Treated meq/100 g</u> |
|--------------------------------------------|------------------|-----------------------------------------|------------------------------------------------------------------|-----------------------------------------|------------------------------------------------------------------|
| Active Dredging (1/30-2/2/75) | Mean | — | 57.4 | — | 12.4 |
| | Std. Dev. | | 43.8 | | 0.2 |
| | Number | | 2 | | 2 |
| May 1975 (3.5 Months After Dredging) | Mean | 31.0 | 27.0 | 11.7 | 20.0 |
| | Std. Dev. | 8.7 | 6.8 | 2.3 | 9.0 |
| | Number | 4 | 4 | 4 | 4 |

Table 23

Budget for Dissolved Metals and Nutrients During Dredging at the Diked
Containment Area on the James River Near Windmill Point

| Parameter | Concentration (mg/l) | | Calculated (mg/l) | Measured (mg/l) | Change* (%) |
|-----------------------------------|-----------------------|--------------------|----------------------|--------------------|----------------|
| | Interstitial Water | James River Water | | | |
| Ca | 216 | 12 (13.7)** | 52.8 (54.2) | 63 | +18 |
| Cd | 0.009 | 0.001 [†] | 0.0026 | 0.019 | +631 |
| Cu | 0.011 | 0.003 [†] | 0.0046 | 0.051 | +1,009 |
| Fe | 57.3 | 0.31 (0.255)** | 11.71 (11.66) | 6.01 | -49 |
| Hg ^{††} | 3.0 | 0.24 (0.3)** | 0.79 (0.84) | 2.0 | +146 |
| Mn | 6.85 | 0.028 (0.036)** | 1.39 (1.40) | 1.19 | -15 |
| Ni | 0.05 | 0.008 [†] | 0.016 | 0.04 | +150 |
| Pb | 0.08 | 0.03 [†] | 0.04 | 0.14 | +250 |
| Zn | 0.12 [‡] | 0.050 (0.063)** | 0.064 (0.074) | 5.31 | +7,700 |
| TDN | 69.66 | 2.20 (2.40)** | 15.69 (15.85) | --- | --- |
| NH ₄ | 63.49 | 0.44 (0.455)** | 13.05 (13.06) | 18.43 | +41 |
| NO ₃ + NO ₂ | 0.065 | 1.55 (1.76)** | 1.25 (1.42) | 0.044 [§] | --- |
| TDP | 0.456 | 0.097 (0.125)** | 0.169 (0.191) | --- | --- |
| PO ₄ | 0.252 | 0.033 (0.042)** | 0.076 (0.084) | 0.030 | -64 |

* Relative change between the calculated and measured concentration at the effluent pipe during dredging

** Concentration in the James River water (January 1977) during flood tide at the reference marsh (at Habitat breach)

† Half the detection limit in Table 5

†† Concentrations of mercury (Hg) are expressed in µg/l

‡ Three measurements over 1 mg/l (n = 31) were rejected as nonrepresentative (with these included the mean would equal 0.32 mg/l)

‡‡ Not measured during the dredging period

§ This number is doubtful because of analytical problems in measuring NO₃ + NO₂ in the interstitial water during dredging

SAMPLE CALCULATION

Effluent consisted of 16% solids, 16% channel sediment interstitial water, and 68% James River overlying water. Therefore, if sediments are ignored, the water consisted of 20% interstitial water and 80% James River water.

$$\begin{aligned} \text{Ca} &= (0.2) (216) + (0.8) (12) = 52.8 \text{ mg/l} \\ &= (0.2) (216) + (0.8) (13.7) = 54.2 \text{ mg/l} \end{aligned}$$

Table 24

Temporal Changes of Dissolved Metals and Nutrients at the Effluent Pipe of the Intertidal Diked Containment Area on the James River Near Windmill Point During Periods of Active Dredging, Immediate Dewatering of the Sediments Within the Site, and 3.5 Months Later (Low Water Sampling Periods). Interstitial Concentrations for the Channel Sediments Before Dredging Are Provided as well as Computed Concentrations from Table 23

| | DISSOLVED METALS (mg/l)* | | | | | | | | |
|------------------------|-----------------------------|-----------------------|-----------------|-----------------|-----------------|-----------------|--------|--------|--------|
| | Ca | Cd | Cu | Fe | Hg | Mn | Ni | Pb** | Zn |
| Interstitial Porewater | 216 | 0.009 | 0.011 | 57.3 | 0.003 | 6.85 | 0.05 | 0.08 | 0.32 |
| Computed Value | (54) | (0.005) | (0.005) | (11.7) | (0.0008) | (1.4) | (0.02) | (0.04) | (0.07) |
| Active Dredging | 63 | 0.019 | 0.051 | 6.01 | 0.002 | 1.19 | 0.04 | 0.14 | 5.31 |
| Dewatering | 38 | 0.018 | 0.006 | 0.12 | 0.001 | 0.20 | 0.03 | -- | 0.10 |
| 3.5 Months Later | 16 | 0.003 | 0.006 | 0.52 | 0.001 | 0.38 | 0.02 | -- | 0.03 |
| | DISSOLVED NUTRIENTS (mg/l)* | | | | | | | | |
| | TDP | ortho-PO ₄ | TDN | NH ₄ | NO ₃ | NO ₂ | | | |
| Interstitial Porewater | 0.457 | 0.252 | 69.72 | 63.49 | 0.058 | 0.007 | | | |
| Computed Value | (0.18) | (0.08) | (15.8) | (13.1) | (1.3) | | | | |
| Active Dredging | -- [†] | 0.030 | -- [†] | 18.43 | 0.029 | 0.015 | | | |
| Dewatering | -- [†] | 0.026 | -- [†] | 0.25 | 0.356 | 0.027 | | | |
| 3.5 Months Later | 0.102 | 0.048 | 3.87 | 1.98 | 0.238 | 0.023 | | | |

* Values are statistical averages for the 10 cores and for each sampling period

** After the second period dissolved lead was below the detection limits

[†] Parameter was not measured during active dredging and dewatering periods

Table 25

Temporal Changes and Low Tide/High Tide Concentration Ratios of Suspended Particulate Metals, and Total Phosphorus and Kjeldahl Nitrogen at the Effluent Pipe of the Intertidal Diked Containment Area During Periods of Active Dredging, Immediate Dewatering (for Total P and N Only), and 3.5 Months Later (Low Water Sampling Periods). Channel Sediment Dry Weight Concentrations Are Provided as Initial Conditions

| | SUSPENDED PARTICULATE METALS ($\mu\text{g/g}$)* | | | | | | | | |
|-------------------|---------------------------------------------------|------------------|----|--------|--------------------|------|----|-----|-----|
| | Ca | Cd | Cu | Fe (%) | Hg | Mn | Ni | Pb | Zn |
| Channel Sediments | 4100 | 1.3 | 49 | 4.1 | 0.5 | 1100 | 34 | 62 | 240 |
| Active Dredging** | -- [†] | 2.4 | 60 | 4.3 | -- ^{††} | 1276 | 42 | 78 | 213 |
| 3.5 Months Later | -- [†] | -- ^{††} | 64 | 6.8 | (1.6) [‡] | 1350 | 54 | 107 | 496 |

| | LOW/HIGH TIDE CONCENTRATION RATIOS | | | | | | | | |
|------------------|------------------------------------|------|------|------|----|------|------|------|------|
| Active Dredging | 0.27 | 1.30 | 1.10 | 1.37 | -- | 1.10 | 1.39 | 1.14 | 0.99 |
| 3.5 Months Later | -- | -- | 0.40 | 1.02 | -- | 0.42 | -- | 0.26 | 0.27 |

| | TOTAL PHOSPHORUS (TP) AND TOTAL KJELDAHL NITROGEN (TKN) | | | | LOW/HIGH TIDE CONCENTRATION RATIOS | |
|-------------------|---------------------------------------------------------|-------------------------------|------|-------------------------------|------------------------------------|-----|
| | TP | | TKN | | TP | TKN |
| Channel Sediments | 662 | $\mu\text{g/g}$ ^{‡‡} | 4577 | $\mu\text{g/g}$ ^{‡‡} | -- | -- |
| Active Dredging | 0.08 | mg/l [§] | 10 | mg/l [§] | 2.3 | 1.2 |
| Dewatering | 0.01 | mg/l | 14 | mg/l | 0.2 | 1.4 |
| 3.5 Months Later | 0.85 | mg/l | 1.4 | mg/l | 6.5 | 3.6 |

* Concentrations are expressed as $\mu\text{g/g}$ dry weight sediment with exception of iron (%)

** Both high and low tide samples were combined during active dredging because of the obvious export of dredge spoil during all phases of the tidal cycle

[†] Data inaccurate due to aluminum interference during analysis by atomic adsorption

^{††} Below detection limit for the particulate metal

[‡] One datum point

^{‡‡} Concentrations are expressed as sediment dry weight

[§] Calculated as particulate phosphorus and nitrogen (unfiltered sample) less the dissolved component (less $0.84 \times$ dissolved component for active dredging period)

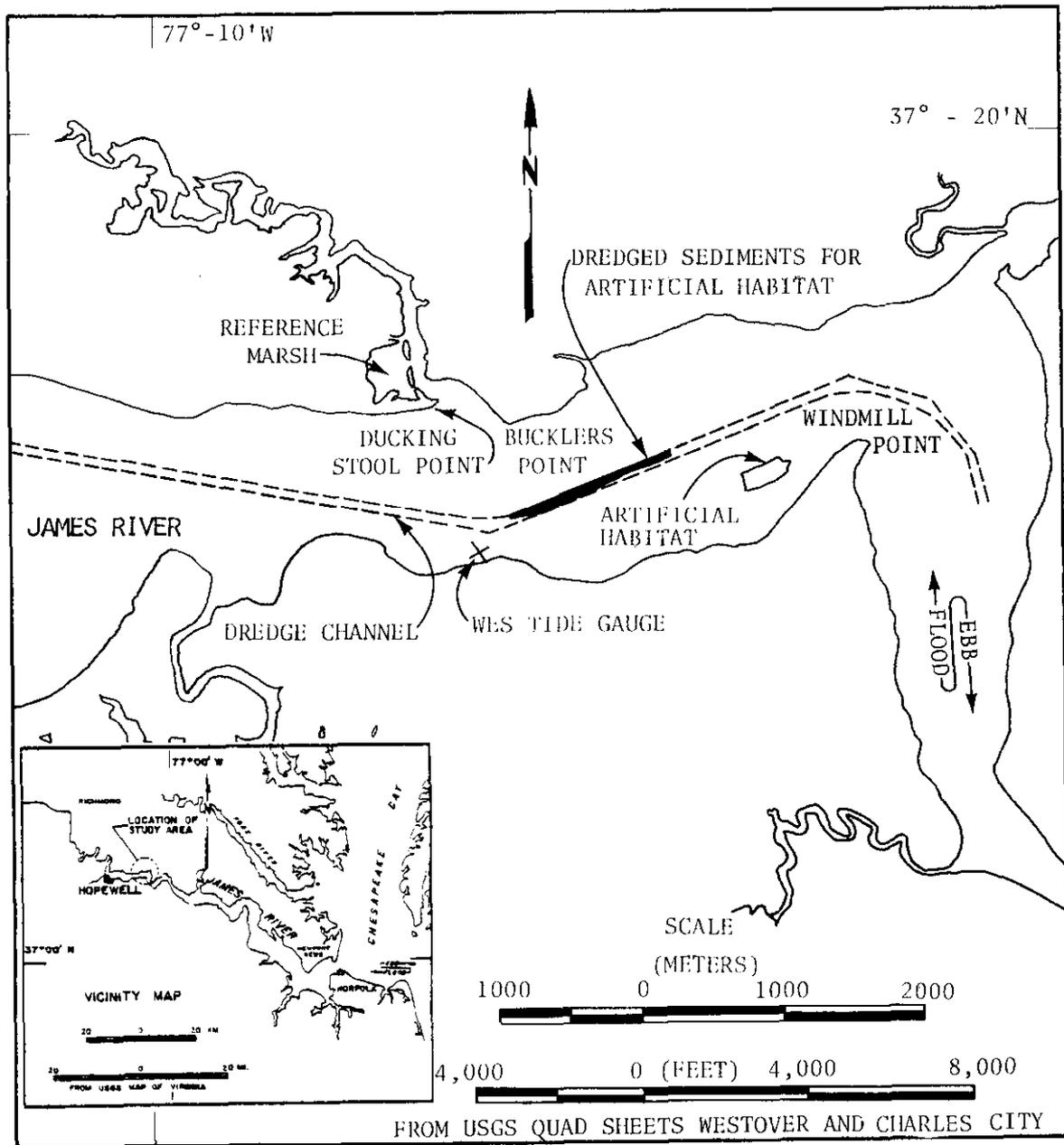


Figure 1. Locations of the James River Artificial Habitat Development Site, reference marsh, and Waterways Experiment Station tide gauge approximately 13 - 16 km downstream of Hopewell, Virginia.

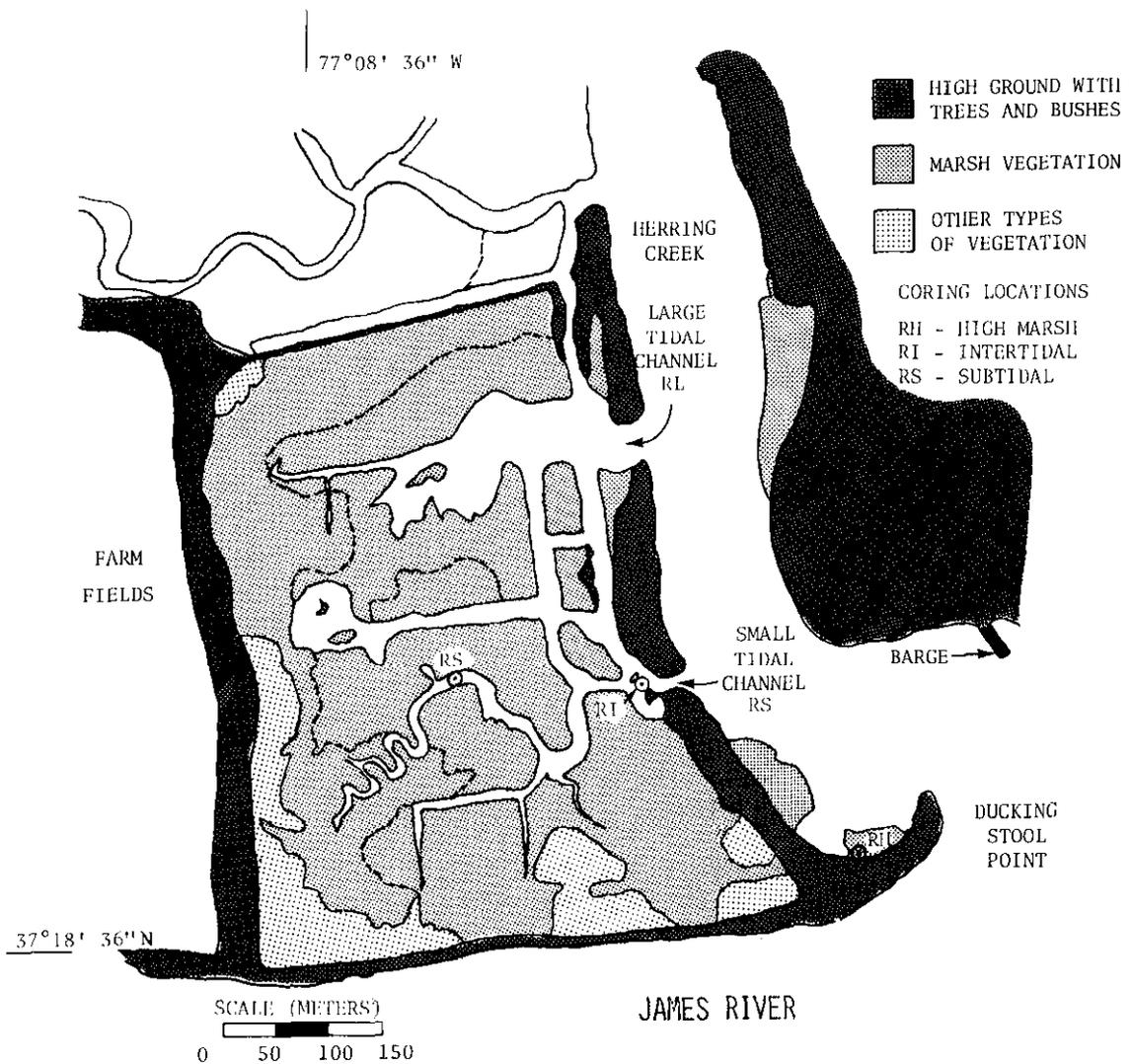


Figure 2. Reference marsh near Ducking Stool Point, James River, approximately 13 km downstream of Hopewell, Virginia. Locations of tidal channels (RL = large, RS = small) and coring sites (RH = high marsh, RI = intertidal, RS = subtidal) are designated.

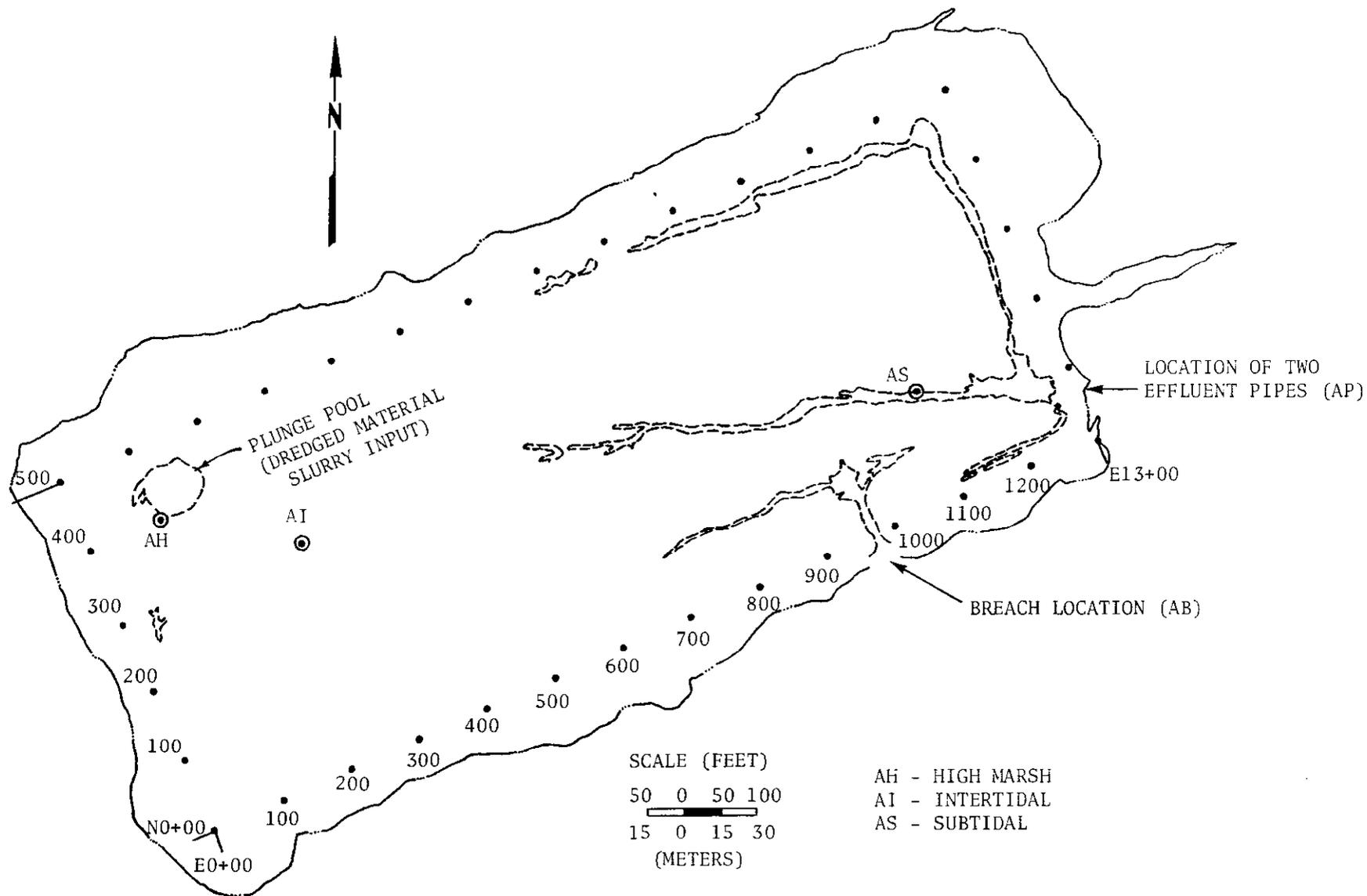


Figure 3. Locations of tidal channels (pipe = AP, breach = AB) and coring sites at the James River Artificial Habitat Development Site near Windmill Point, 16 km below Hopewell, Virginia. Scale around dikes is in feet.

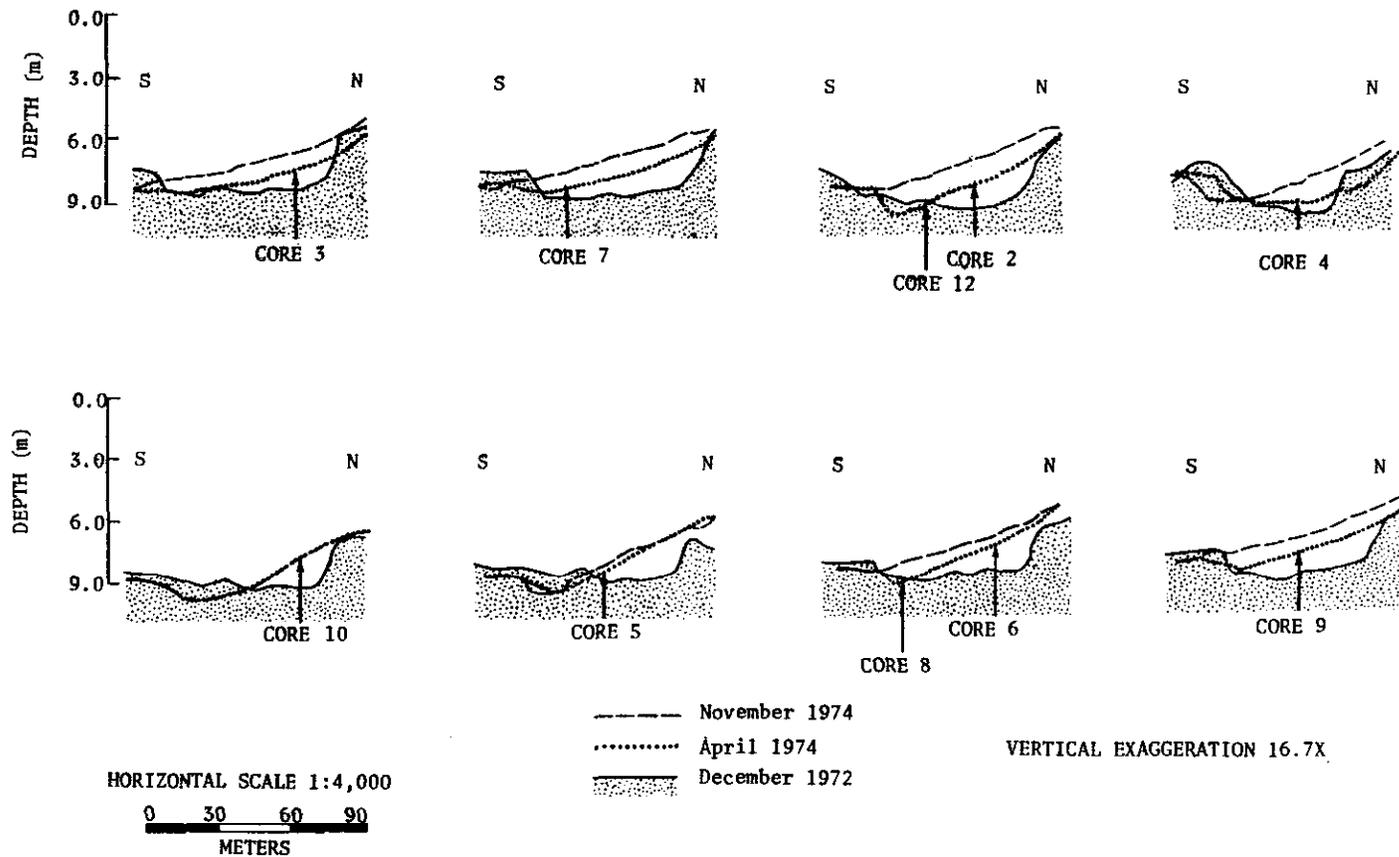


Figure 4. Cross sections of the channel at the Jordan Point-Harrison Bar-Windmill Point shoals, James River, prior to coring in January 1975. These were taken from surveys of the channel conducted on December 11-12, 1972 (stippled area), April 3-4, 1974 (dotted line), and again on November 22-23, 1974 (dashed line) by the Norfolk District Corps of Engineers. Core locations are illustrated in each cross section.

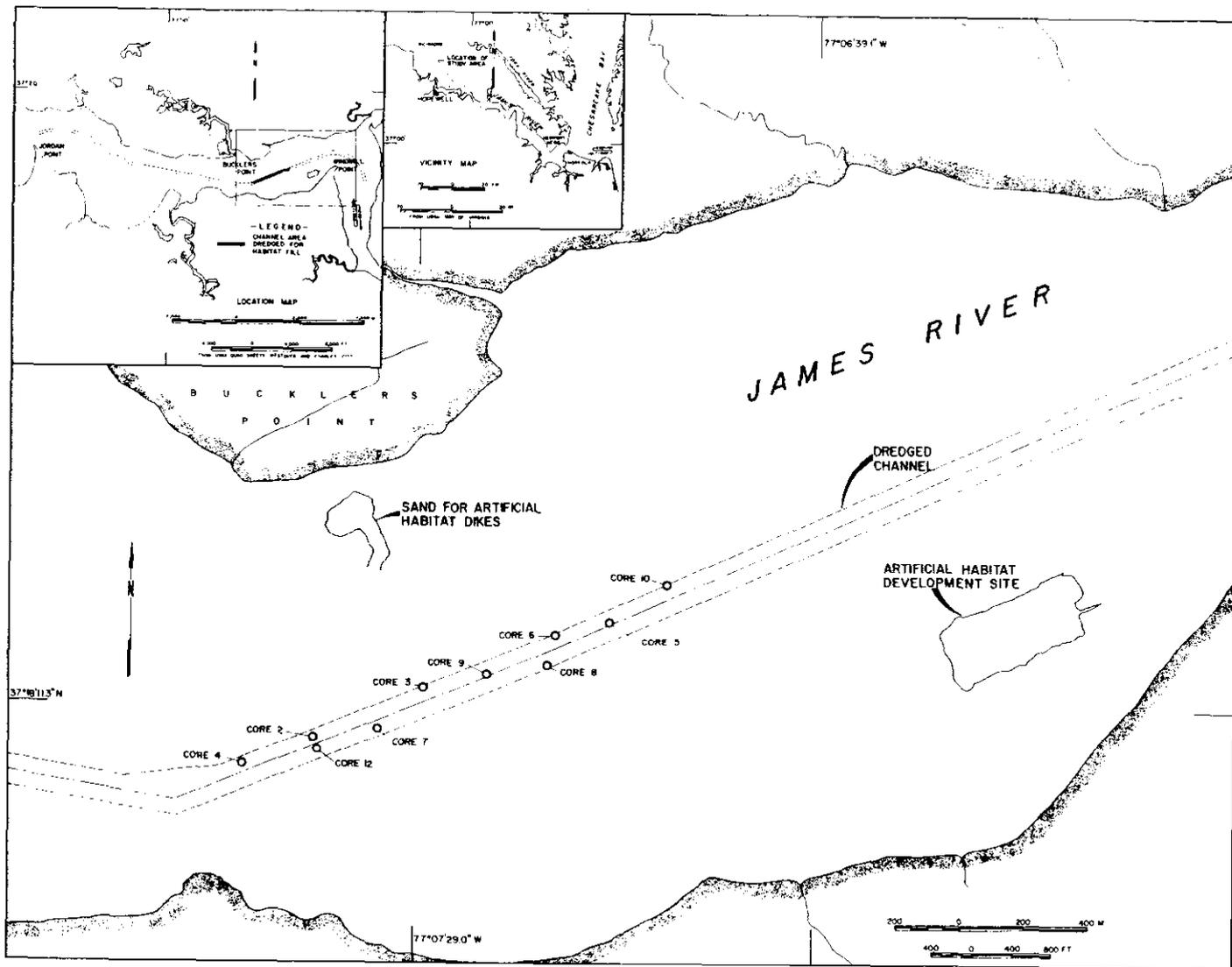


Figure 5. Locations of 10 channel cores from the Jordan Point-Harrison Bar-Windmill Point Shoal of the James River.

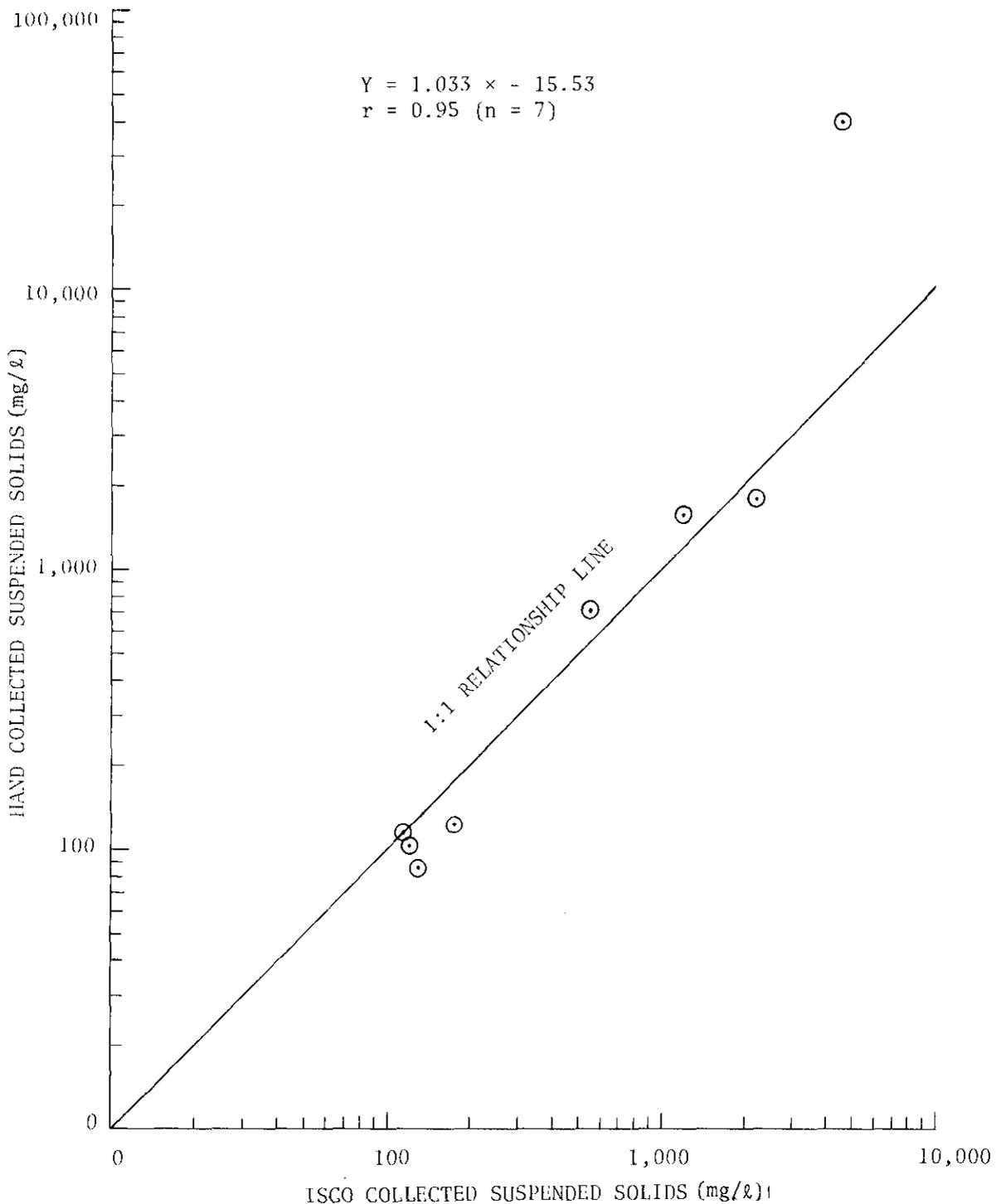


Figure 6. Relationship of suspended solids at the effluent pipe of the intertidal containment area for hand collected water samples and those procured with an ISCO automatic sampler, May 1975 (see text for discussion). The solid line represents an ideal 1:1 fit for the data. A linear least squares equation for suspended solids concentrations less than 2300 mg/l is provided.

In accordance with letter from DAFN-RDC, DAEN-ASI dated 22 July 1977, Subject: Facsimile Catalog Cards for Laboratory Technical Publications, a facsimile catalog card in Library of Congress MARC format is reproduced below.

Adams, Donald D

Habitat development field investigations, Windmill Point marsh development site, James River, Virginia; Appendix F: Environmental impacts of marsh development with dredged material: sediment and water quality; Volume I: Characteristics of channel sediments before dredging and effluent quality during and shortly after marsh habitat development / by Donald D. Adams, Department of Chemistry, Wright State University, Dayton, Ohio, Dennis A. Darby and Randolph J. Young, Department of Physics and Geophysical Sciences and Institute of Oceanography, Old Dominion University, Norfolk, Virginia. Vicksburg, Miss. : U. S. Waterways Experiment Station ; Springfield, Va. : available from National Technical Information Service, 1978.

i, 45, [33] p. : ill. ; 27 cm. (Technical report - U. S. Army Engineer Waterways Experiment Station ; D-77-23, Appendix F, v.1) Prepared for Office, Chief of Engineers, U. S. Army, Washington, D. C., under Contract Nos. DACW65-75-C-0051 and DACW65-76-C-0039 (DMRP Work Unit Nos. 4A11D, 4A11G, 4A11H)

Appendices A'-E' on microfiche in pocket of vol. 2.

Literature cited: p. 41-45.

(Continued on next card)

Adams, Donald D

Habitat development field investigations, Windmill Point marsh development site, James River, Virginia; Appendix F: Environmental impacts of marsh development with dredged material: sediment and water quality; Volume I: Characteristics of channel sediments before dredging and effluent quality during and shortly after marsh habitat development ... 1978. (Card 2)

1. Chemistry. 2. Dredged material. 3. Dredged material disposal. 4. Environmental effects. 5. Field investigations. 6. Habitat development. 7. Habitats. 8. Interstitial water. 9. James River. 10. Marsh development. 11. Metals. 12. Nutrient chemistry. 13. Sediment. 14. Waste disposal sites. 15. Water quality. 16. Windmill Point. I. Darby, Dennis A., joint author. II. Young, Randolph J., joint author. III. Old Dominion University. Dept. of Physical and Geophysical Sciences. IV. Old Dominion University. Institute of Oceanography. V. United States. Army. Corps of Engineers. VI. Wright State University. Dept. of Chemistry. VII. Series: United States. Waterways Experiment Station, Vicksburg, Miss. Technical report; D-77-23, Appendix F, v.1. TA7.W34 no.D-77-23 Appendix F v.1