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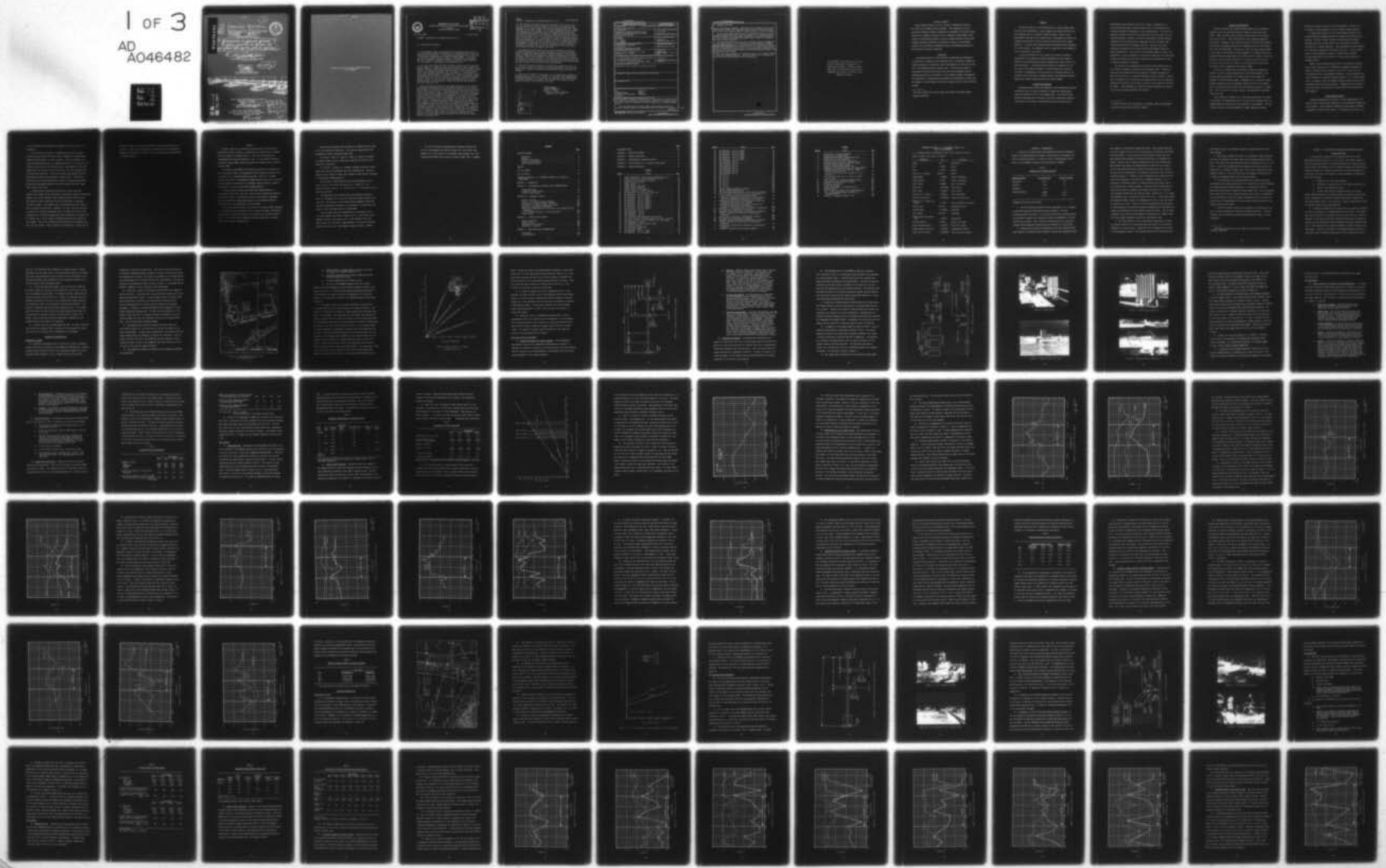

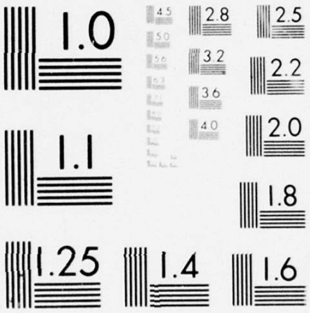

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DREDGED MATERIAL RESEARCH PROGRAM

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TECHNICAL REPORT D-77-15

(6)

OXYGENATION OF DREDGED MATERIAL BY DIRECT INJECTION OF OXYGEN AND AIR DURING OPEN-WATER PIPELINE DISPOSAL.

by

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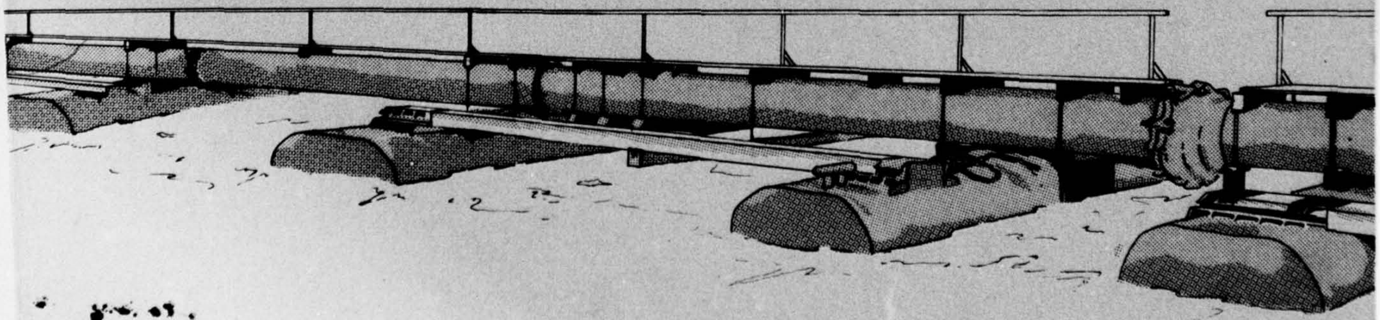

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Monitored by Environmental Effects Laboratory
U. S. Army Engineer Waterways Experiment Station
P. O. Box 631, Vicksburg, Miss. 39180

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DEPARTMENT OF DEFENSE
UNITED STATES OF AMERICA

DEPARTMENT OF THE ARMY
WATERWAYS EXPERIMENT STATION, CORPS OF ENGINEERS
P. O. BOX 631
VICKSBURG, MISSISSIPPI 39180

IN REPLY REFER TO: WESYV

31 October 1977

SUBJECT: Transmittal of Technical Report D-77-15

TO: All Report Recipients

1. The technical report transmitted herein represents the results of one study concerned with the treatability of dredged material initiated within Task 6B (Treatment of Contaminated Dredged Material) of the Corps of Engineers' Dredged Material Research Program (DMRP). This task is part of the Disposal Operations Project of the DMRP and is concerned with the evaluation of physical, chemical, and/or biological methods for the removal of contaminants from dredged material.

2. In recent years there has been continued concern over the potential adverse impact of dredging and disposal operations on water quality and aquatic organisms. Rapid industrialization and population growth in areas adjacent to navigable waterways often contribute to the contamination of water bodies and many sediments that are dredged. It became apparent during the planning phases of the DMRP that it might be necessary, where unacceptable adverse effects are expected, to treat contaminated dredged material before it could be disposed at designated open-water disposal areas or before the effluent from upland containment areas could be discharged back to the waterways. Therefore, Task 6B was developed to meet this potential need.

3. When fine-grained sediments are dredged hydraulically, the chemical constituents associated with the fine-grained particles in the slurry will undergo an oxidization process which can reduce the dissolved oxygen levels in the slurry to zero. Field measurements (from this study) indicate that dissolved oxygen levels measured 120 feet from the discharge in the center of the turbidity plume generated by a typical (untreated) open-water disposal operation are depressed to approximate levels of 7 mg/ℓ at the surface, 5 mg/ℓ at mid-depth, and 2-3 mg/ℓ in near bottom water relative to background concentrations of 9-10 mg/ℓ throughout the water column. An earlier laboratory study (6B02) indicated that in-line oxygenation might provide a means of reducing the oxygen depletion in the water column in the vicinity of the disposal operation. The investigation described herein was designed to investigate the feasibility and effectiveness of injecting either air or oxygen into the discharge line of a pipeline dredge in order to reduce the depletion of dissolved oxygen in the water column during the open-water pipeline disposal operation. The investigation was undertaken by JBF Scientific Corporation of Wilmington, MA.

WESYV 31 October 1977
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4. Two full-scale demonstrations were conducted as part of the study. One test showed that direct injection of air into the discharge line resulted in only weak evidence that aeration mitigated dissolved oxygen depletion in the water column. In the second demonstration, pure oxygen was injected into the discharge line. Measurements made during this field demonstration showed that dissolved oxygen levels measured 120 feet from the discharge in the turbidity plume generated by the disposal operation averaged 7.5 mg/ℓ at the surface, 6 mg/ℓ at mid-depth, and 5.5 mg/ℓ in near bottom water. Considering the degree of oxygen enhancement gained by oxygenation, it does not appear that use of oxygen injection is warranted at every operation; however, since the use of oxygen may be advantageous in operations in some environmentally sensitive areas or situations, guidelines for its use and indications of the anticipated effectiveness of this technique are included.

5. The laboratory study section of the report describes the chemical processes responsible for the oxygen depletion in the receiving water during dredging and dredged material disposal operations. An analytical method for measuring and studying the immediate oxygen demand is also presented. Other items covered in the laboratory study were the effects of oxygenation on the elutriation of selected chemical constitutents and the reaction of several different types of dredged material with dissolved molecular oxygen in both bench-top and column systems.

6. The report includes a chapter that describes configuration and cost of injection systems for full-scale dredging operations. Alternate oxidants such as hydrogen peroxide and ozone-enriched oxygen are also considered.

7. Based on the results of this study, it is believed that oxygenation systems using pure oxygen are feasible and the design and implementation guidelines given herein are sufficient for immediate field applications. It should be pointed out, however, that whenever pure oxygen is used appropriate safety precautions must be taken.

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

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Dredged material disposal	Oxygenation
Injection	

20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

This report describes a study conducted to investigate the feasibility and effectiveness of injecting an oxidant into the discharge of a hydraulic dredge in order to reduce the depletion of dissolved oxygen in an open-water disposal area.

The rapid depletion of dissolved oxygen during disposal operations is caused by chemical oxidation of constituents which are present in a reduced

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20. ABSTRACT (Continued).

state in the anaerobic sediments. Oxygen may also be consumed by the action of microorganisms; however, this mechanism operates much more slowly and contributes little to the immediate demand for oxygen observed in open-water disposal.

Two full-scale field demonstrations were conducted as a part of the study. In the first demonstration pure oxygen was injected into the discharge line of a hydraulic dredge, and, in the second, compressed air was similarly injected. The report describes the equipment and methods used to conduct the demonstrations and the results obtained.

The laboratory study section describes the chemical processes responsible for the oxygen depletion in the receiving water during dredging and dredged material disposal operations. An analytical method for measuring and studying the IOD is also presented. Other items covered in the laboratory study are the effects of oxygenation on the elutriation of selected chemical constituents and the reaction of several dredged materials with dissolved molecular oxygen in both bench-top and column systems.

The final chapter examines the configuration and cost of injection systems for full-scale dredging operations. Alternate oxidants, such as hydrogen peroxide and ozone-enriched oxygen, are also considered.

EXECUTIVE SUMMARY

Rapid oxygen depletion is one of the most documented and noticeable effects of dredged material disposal. This phenomenon occurs to some extent whenever anaerobic sediments are dispersed in an aerobic water column and is commonly referred to as the immediate oxygen demand (IOD)*. A means of mitigating the impact of such an oxygen depletion under actual dredging operating conditions is desirable in light of the increased concern over the adverse environmental impacts of dredging operations on water quality and aquatic organisms.

Objectives

The primary purpose of this study was to determine the feasibility of injecting an oxidant into the discharge line of a hydraulic dredge and thereby eliminate or effectively control the depletion of dissolved oxygen (DO) in the dredged material disposal area. The study also sought to investigate the nature and causes of the IOD and any possible effects oxidation may have on the stability of the sediment chemical contaminants. The feasibility of using alternate oxidants was investigated to enable the development of system design criteria and typical costs for these alternate systems.

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* All IOD's referred to in this report are 15-min. IOD values unless otherwise specified.

Methods

The study focused on a field demonstration in which oxygen, generated from the vaporization of liquid oxygen, was injected directly into the discharge line of a hydraulic pipeline dredge. Direct in situ measurements were made in the disposal area to determine the effects the dredging operation had on the DO levels both with and without oxygen injection. A similar field demonstration was performed using compressed air as the oxidant. The equipment used to conduct each field demonstration is described in the report.

A critical evaluation of the relevant IOD literature enabled a description of the chemical processes responsible for the oxygen depletion in the receiving water during dredging and dredged material disposal operations. A refined *analytical* method for measuring the IOD was used to study these processes in actual sediment water slurries. The effect of oxygenation on the elutriation of selected chemical constituents and the reaction of dredged material with dissolved molecular oxygen were studied on both bench-top and column systems.

Oxidant Effectiveness

Measurements made during the oxygenation field demonstration showed conclusively that the direct injection of oxygen will significantly reduce the depletion of DO in the disposal area. The DO levels were seriously depressed near the bottom of the water column when oxygen injection was not occurring. During injection, the DO levels rose to approximately those observed at the 3-ft * depth. Oxygenation at a position providing longer oxidant residence time in the discharge pipe produced increased DO enhancement in the receiving water. IOD values for oxygenated sediment slurries were statistically lower than those for non-oxygenated samples. However, variability introduced by rapidly changing conditions in the pipeline and by conducting the IOD test under field conditions made this test somewhat uncertain. Finally, there were statistical variations in the solids fraction being pumped during the oxygen demonstration. Since the cost of providing oxygen is likely to be significant, it may be desirable to provide the capability for continuously sensing the pumping rate and solids fraction so as to modulate the rate at which the oxidant is injected.

The *aeration field demonstration* resulted in weak evidence that the air injection mitigated DO depletion in the disposal area. Inferences drawn from this demonstration were hindered by frequent discharges of material with little or no anaerobic sediment from the pipeline. Furthermore, the amount of air injected in this demonstration was not designed to satisfy the IOD fully, but was well in excess of that required to saturate the water. This combination of factors may have influenced the observation of little apparent benefit from aeration.

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* A table of factors for converting U.S. customary units of measurement to metric (SI) units can be found on page 15.

Laboratory Observations

The IOD is exerted when reduced chemical species in the anaerobic sediments react with dissolved molecular oxygen in the aerobic water column. There are three reduced chemical species which could theoretically cause the IOD. These include ferrous iron, manganous manganese and sulfide. Manganese is not rapidly oxidized at the pH levels commonly encountered in dredging operations and consequently does not practically affect the IOD measurement. Ferrous iron, which is nearly always present in the largest concentration of these parameters, is readily oxidized by dissolved molecular oxygen under most dredged material disposal conditions. Sulfide is also similarly oxidized but a competing oxidation reaction by ferric iron may lower its effect on the IOD because it takes place with little direct consumption of molecular oxygen.

The IOD of a sediment can be satisfied by extensive oxygenation. However, the IOD is slowly regenerated in the settled sediment by the microbiological decomposition of organic matter, which causes the sediment to become anaerobic again. Oxygenation in a closed-loop dredge pipeline simulation did not completely satisfy the IOD of the sediment after a 15-minute contact period with the theoretical quantity of oxygen gas. The DO content of the water, however, did approach air saturation within the loop.

Batch dumping of sediments in a column demonstrated that the degree of dispersion of sediment particles in the water had a greater effect on oxygen demand than indicated by bulk analysis of the sediments. The most probable chemical reaction mechanism for oxygen depletion involves oxidation of sulfide by ferric iron with oxidation of ferrous iron by molecular oxygen responsible for the observed oxygen depletion.

An oxygen mass balance for Fall River sediment dropped in the column showed good agreement between DO consumption and ferrous iron depletion. However, similar balances with Apalachicola sediment indicated that twice as much ferrous iron was reacted as could be accounted for by oxygen depletion. This discrepancy has been attributed to analytical problems in the ferrous iron test. A more detailed study of these phenomena is needed to clarify these important reaction mechanisms as they pertain to the open-water disposal of dredged material.

Several other observations were made in the laboratory studies. Particle-size distribution of exhaustively oxygenated sediments was skewed to smaller particle sizes that settle more slowly than the corresponding anoxic (nitrogenated) sediments. This was probably due to the formation of colloidal oxidation products. On a limited sample basis, an apparent causal relationship between sediment particle size and oxygen demand factors was observed. Oxygenation did not appear to alter the process of elutriation of heavy metals and nutrients from the sediments.

System Design Criteria

Although compressed air was used in a field demonstration, its effects were not sufficiently definite to allow conceptual designs and cost estimates. Other oxidants considered included ozone, potassium permanganate, chlorine, and nitrate. For these four substances, one or more undesirable characteristics eliminated them from further consideration.

For a variety of locations, it appears that the cost of oxygen injection would increase the total cost of dredging by a modest amount, ranging from less than 1 to about 3 percent. Both the laboratory and field work demonstrated that for residence times of 1 or 2 minutes in the pipeline, very little of the IOD was reacted. Nevertheless, sufficient oxygen went into solution so that the level of DO in the discharge area was appreciably increased. It may well be that less oxygen could have been injected, while still achieving a similar result. Future work, particularly in a field demonstration, should be directed toward determining the relationship between DO levels and oxygen flow over a much wider range of flow rates.

A system based on hydrogen peroxide would be many times more expensive than oxygen if the same amount of available oxygen were delivered. However, for a given residence time, hydrogen peroxide, which is much more reactive, would satisfy more of the IOD than would a comparable fraction of oxygen. This suggests that less hydrogen peroxide could be used to achieve a given effect. However, it is not clear that reacting to satisfy the IOD would necessarily result in higher DO levels in the discharge area. Sufficient oxygen must still be available to replace any DO reacted, and it is not known how hydrogen peroxide might perform in this respect. The use of hydrogen peroxide should not be dismissed, however, for two reasons. First, because of its reactivity, it may still be effective enough at lower injection rates to reduce its unit cost considerably. Second, the high reaction rates may also be an advantage in dredging situations where sediment IOD's are high and the discharge line is relatively short.

PREFACE

The U.S. Army Corps of Engineers was authorized by the River and Harbor Act of 1970 to conduct a comprehensive nationwide study concerned with the disposal of dredged material. The task of developing and implementing the study was assigned to the U.S. Army Engineer Waterways Experiment Station (WES), which established the Dredged Material Research Program (DMRP).

The purpose of the DMRP is to provide more definitive information on the environmental impact of dredging and related disposal operations and to develop new or improved disposal practices. Task 6B of the DMRP, entitled "Treatment of Contaminated Dredged Material," has as its objective the development and evaluation of technically and economically feasible techniques for treating contaminated dredged material.

During hydraulic dredging operations when dredged material is discharged directly into open water, there can be a significant depletion of dissolved oxygen in the general vicinity of the point of discharge. This is caused by an oxygen demand exerted by the sediments within a relatively short time immediately after discharge.

In the work reported herein, the concept of utilizing direct injection of an oxidant into the discharge line of a hydraulic dredge to ameliorate the depletion of dissolved oxygen in the disposal area has been investigated. Two full-scale field demonstrations were performed: one using oxygen and the other compressed air.

The study was conducted under Contract No. DACW39-75-C-0105 (Neg.) to the JBF Scientific Corporation. The study was supervised by the Environmental Effects Laboratory (EEL), WES.

Mr. Robert W. Neal, Dr. Stuart P. Bowen, Dr. Robert B. Pojasek, Mr. Stephen Greene, and Mr. James Soden conducted the study for JBF Scientific Corporation.

Mr. Charles C. Calhoun, Jr., Manager, Disposal Operations Project (DOP), EEL, was the Contracting Officer's Representative. Contract Manager was Mr. Thomas K. Moore, DOP, manager of DMRP Task 6B "Treatment of Contaminated Dredged Material."

The Directors of WES during the study and preparation of the report were Col. G.H. Hilt, CE, and Col. J.L. Cannon, CE. The Technical Director was Mr. F. R. Brown and Mr. A. J. Breithaupt was the Contracting Officer.

The oxygenation field demonstration was performed during the week of 1 September 1975, and the air injection during the week of 19 July 1976. The success of both demonstrations depended a great deal upon the wholehearted cooperation of many people. In particular, the support of the following people is acknowledged:

For the oxygen injection demonstration at Apalachicola: the U.S. Army Engineer Area Office, Panama City, Mr. Alton Colvin, Area Engineer, and Mr. Larry White; the U.S. Army Engineer White City Repair Shops, Mr. Joe Sowell, Superintendent; and Captain John Hutto and the crew of the U.S. Army Engineer dredge, WILLIAM L. GUTHRIE.

For the air injection demonstration conducted in Mobile Bay: the U.S. Army Engineer Area Office, Mobile, Mr. Paul Warren, Area Engineer; Mr. Steve Benton, Vice President, OKC Dredging, Inc.; and Captain Harold Marks and the crew of the OKC dredge, PAUL F. JAHNCKE.

CONTENTS

FIGURES

TABLES

CONVERSION FACTORS, U. S. CUSTOMARY TO METRIC (SI) UNITS OF MEASUREMENT

U. S. customary units of measurement used in this report can be converted to metric (SI) units as follows:

Multiply	By	To Obtain
inches	25.4	millimetres
feet	0.3048	metres
yards	0.9144	metres
miles (U. S. statute)	1609.344	metres
square miles	2.589988	square kilometres
square inches	6.4516	square centimetres
cubic inches	16.38706	cubic centimetres
cubic feet	0.02831685	cubic metres
cubic yards	0.7645549	cubic metres
gallons (U. S. liquid)	3.785412	cubic decimetres
cubic feet per hour	0.02831685	cubic metres per hour
gallons (U. S. liquid) per minute	3.785412	cubic decimetres per minute
tons per day	907.1847	kilograms per day
pounds (mass)	0.4535924	kilograms
tons (short)	907.1847	kilograms
pounds (force per square inch	6.894757	kilopascals
feet per second	0.3048	metres per second
knots (international)	0.5144444	metres per second
pounds (mass) per minute	0.4535924	kilograms per minute
cubic feet per minute	0.02831685	cubic metres per minute

CHAPTER I: INTRODUCTION

1. Much of the concern about the potentially adverse environmental effects of dredging operations relates to the practice of open-water disposal of polluted materials. As shown in Table 1, approximately 60 percent of all maintenance dredging utilizes open-water disposal.

Table 1

Disposition of Dredged Material[1]

Disposal Method	Total Quantity*	Percent of Total
Open water	182.1	61
Confined	67.1	22
Unconfined	4.9	2
Undifferentiated	44.3	15
	298.4	100

* Numbers are million cubic yards.

2. The other disposal methods are diked containment (i.e., confined) or depositing material unconfined along the shoreline. The term "undifferentiated" was used to cover projects where both confined disposal and open-water disposal were practiced or where no breakdown of the total quantity was provided. Thus, as much as three-fourths of the materials dredged during maintenance operations may be disposed of in open water.

3. Potential water-quality problems which have been identified with these disposal techniques include increased turbidity and suspended solids,

and lowering of the dissolved oxygen (DO) level. Other effects which may occur are changes in pH and in the concentration of phosphorus, pesticides, and heavy metals. A recent review of the literature by May[2] has cited many studies which attempted to determine the effects of dredging operations. Based on that literature review and his own work in Mobile Bay, May concluded that almost all dredged material deposited in open waters settles very rapidly and forms a density flow along the bottom. Within the mud flow the concentration of DO generally was below 1 mg/ℓ and may be completely depleted. A number of other researchers also observed that DO levels were depressed in the vicinity of dredging operations. A U. S. Army Corps of Engineers study[3] of a highly polluted area showed that DO was depressed near a pipeline dredge. Brown and Clark[4] observed that DO levels were lowered by clamshell and dragline operations in a polluted tidal waterway between New York and New Jersey. Servizi et al.,[5] in studying sediments prior to dredging, concluded that due to a high oxygen demand and hydrogen sulfide release, the sediments were toxic to fish and should be disposed of on land. O'Neal and Sceva[6] concluded that the disturbance of bottom material by pipeline and grapple dredging and the subsequent discharge of the materials can significantly reduce DO levels. Many of these researchers have noted that the demand is concentrated in a density layer flow that quickly propagates outward from the disposal point.

4. The rapid depletion of DO during disposal operations is caused by chemical oxidation of constituents which are present in the anaerobic sediments in a reduced state. Oxygen may also be consumed by the action of microorganisms; however, this mechanism operates much more slowly and

contributes little to the immediate demand for oxygen observed in open-water disposal.

5. This report examines the nature of the sediment oxygen demand and the means of mitigating its impact under actual dredging operating conditions. Two full-scale field demonstrations were conducted as a part of the study. In the first demonstration pure oxygen was injected into the discharge line of a hydraulic dredge, and, in the second, compressed air was similarly injected. The report describes the equipment and methods used to conduct the demonstrations and the results obtained.

6. The laboratory study section describes the chemical processes responsible for the oxygen depletion in the receiving water during dredging and dredged material disposal operations. An analytical method for measuring and studying the immediate oxygen demand (IOD)* is also presented. Other items covered in the laboratory study are the effects of oxygenation on the elutriation of selected chemical constituents and the reaction of several types of dredged material with dissolved molecular oxygen in both bench-top and column systems.

7. The final chapter discusses the feasibility, configuration, and cost of injection systems for full-scale dredging operations. Alternate oxidants, such as hydrogen peroxide and ozone-enriched oxygen, are also considered.

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*All IOD's referred to in this report are 15-min IOD values unless otherwise specified.

CHAPTER II: OXYGENATION AND AERATION FIELD DEMONSTRATIONS

Purpose and Scope

8. An important component of this research study was a field demonstration series carried out at full scale. The primary purpose of the field demonstrations was to determine whether air or oxygen injected directly into the discharge line of a hydraulic dredge would significantly reduce the depletion of oxygen in the waters of an open discharge area. In addition, the tests were designed to obtain quantitative information about the following:

- a. Oxygen and air flow rates required.
- b. Influence of residence time in the dredge discharge line.
- c. Effects upon observed DO levels.
- d. Effects upon observed suspended solids in the plume.

Besides making observations and taking samples to obtain the above information, measurements were made and samples were taken to characterize the system without oxygen or air injection. Similar procedures were used for both the oxygen and air demonstrations.

9. It should be emphasized that these tests were conducted primarily to assess the mitigation of oxygen depletion at full scale. This assessment could be carried out reasonably well in a short-term test; some improvement in the data may have been produced by many hours of oxidant injection, but the anticipated slight improvement would have incurred great costs. These costs would be primarily caused by a massive system to provide oxygen. Therefore, the number of measurements made was limited to those that could be obtained during about 20 min of injection for each

test run. Air injections were conducted in a similar manner to enable comparison with the oxygen tests. The more detailed chemistry and longer term effects associated with in-pipe oxidation were investigated in the laboratory program; field verification of the laboratory studies was beyond the scope of these preliminary tests.

10. In the work using pure oxygen, five test runs were conducted. The first, called the "dry run," was intended as a practice run to check out all equipment and procedures. As initially planned, oxygen would not have been injected during the dry run. However, the operation was proceeding so smoothly at the point in the countdown when oxygen injection was scheduled to start, it was decided to proceed with injection. Consequently, additional data were obtained during this run. Of the subsequent four tests, two were run with the oxygen injection point near the discharge end of the pipeline and two were run with it closer to the dredge. The two positions provided a significant difference for the residence time of the oxygen in the pipeline.

11. The work using air included eight test runs. Of these, five were run with the air injection 1500 ft upstream of the discharge, and three were run with air injection 2300 ft upstream of the discharge.

Oxygenation Demonstration

Experimental design

12. Extensive investigations were carried out to select a dredging project that would be suitable for the oxygenation demonstration. Various projects within the Mobile District were considered, ranging from 12-in. contractor-owned dredges to a 27-in. dredge owned by the Corps and

scheduled for operations in Mobile Bay. The project finally selected was a maintenance dredging operation planned for the Gulf Intracoastal Waterway near Apalachicola, Florida. The project was scheduled to be running during the period December 1975 through February 1976, approximately. The general location of the oxygenation tests is shown in Figure 1. The dredge was the WILLIAM L. GUTHRIE, a 16-in. hydraulic cutter head dredge.

13. There were a number of advantages associated with the particular project selected. It was located in an area where good support and accommodations were available nearby. The Army Engineer White City Repair Shop, which has excellent facilities, was available for building the test section of pipeline and for assisting in the installation of oxygen equipment. In addition, the dredge GUTHRIE was well equipped to provide support during the demonstration. The fact that the GUTHRIE is a 16-in. dredge (rather than 27-in. or larger) was also an advantage in that the required oxygen flow rate and, therefore, the size of the oxygen equipment, could be kept within reasonable bounds.

14. The demonstration required an oxygen injection system that would deliver oxygen at a rate sufficient to satisfy the demand of the slurry being pumped. In order to be conservative, it was decided that the oxygen demand should be considered to comprise two components: that required to satisfy the IOD of the sediments; and that required to fully saturate the water (based on the assumption that there would be no DO in the water at the point of oxygen injection).

15. The demand was therefore determined for the following conditions and assumptions:

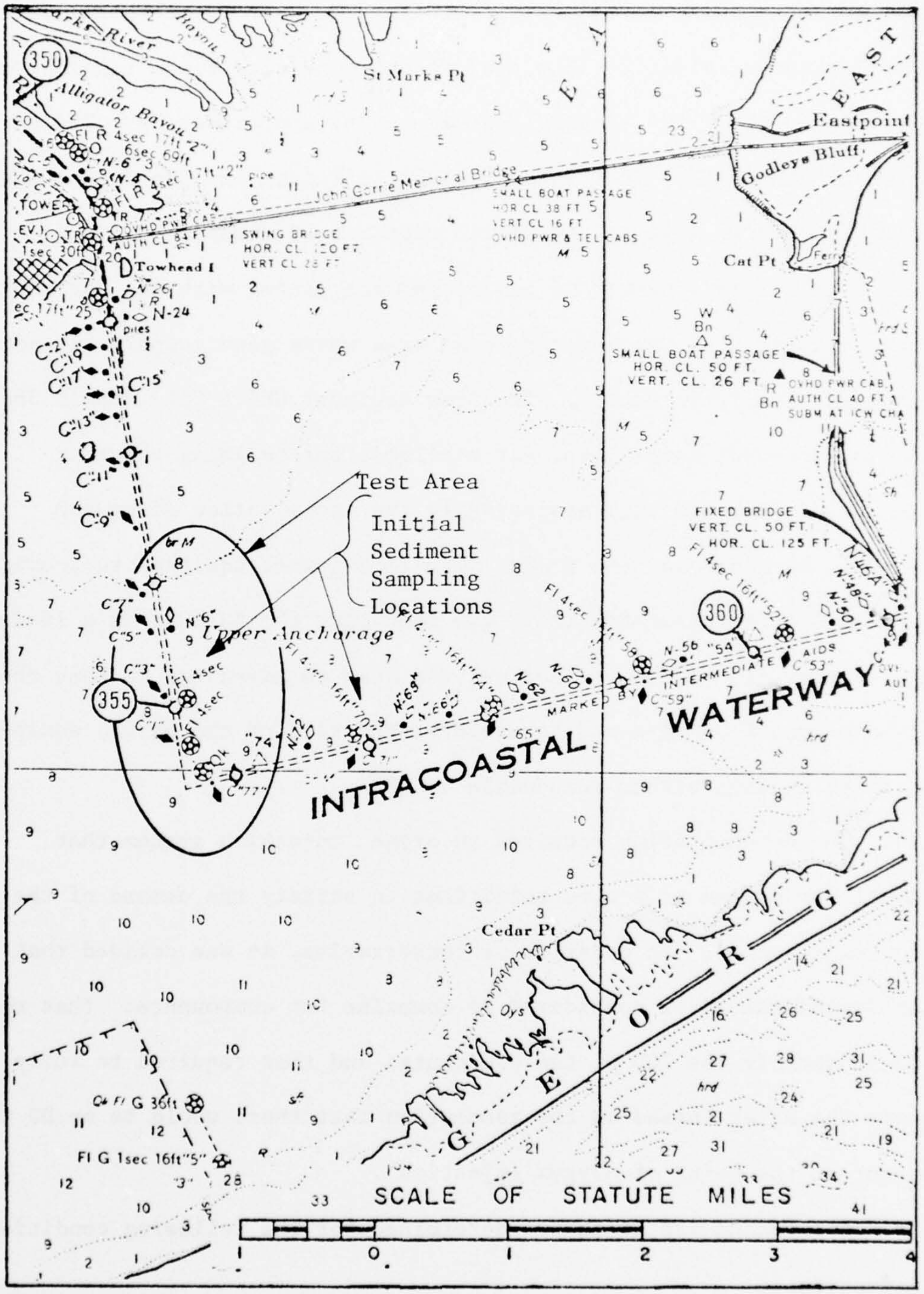


Figure 1. Field demonstration test area for oxygenation tests

a. Solids content of dredged material would be 20 percent (by weight) at a specific gravity of 2.5.

b. Saturation concentration of oxygen in equilibrium with the water would be 45.5 mg/ℓ.

c. Initial concentration of DO would be zero.

d. The IOD of the dredged sediments would be 1.0 mg/g.

Samples of bottom sediments at the two locations shown in Figure 1 were taken in July 1975. The IOD of these samples was measured and found to be approximately 0.8 mg/g; therefore, the assumption of 1.0 mg/g was thought to be conservative insofar as the required oxygen flow rate was concerned.

16. The oxygen required for various conditions as a function of the dredge discharge rate was determined and is shown in Figure 2. The lowest curve indicates the amount of oxygen required only to saturate the water. The uppermost curve indicates the total amount that would be required to satisfy both the IOD and the amount to fully saturate the water. The intermediate curves show the oxygen required to satisfy 25 percent and 50 percent of the IOD and to saturate the water. For the demonstration, the oxygen equipment was designed to supply as near the maximum rate as possible. Based upon design calculations for the oxygen system and upon estimates of the dredge pump performance, it was predicted that test conditions would fall within the "planned operating region" shown in the figure. During the test runs, however, the conditions that prevailed were as indicated by the "actual operating region." The discrepancy, which is in fact minor, was due primarily to the fact that the dredge pump would not operate satisfactorily at a flow rate of 7000 gpm as had been

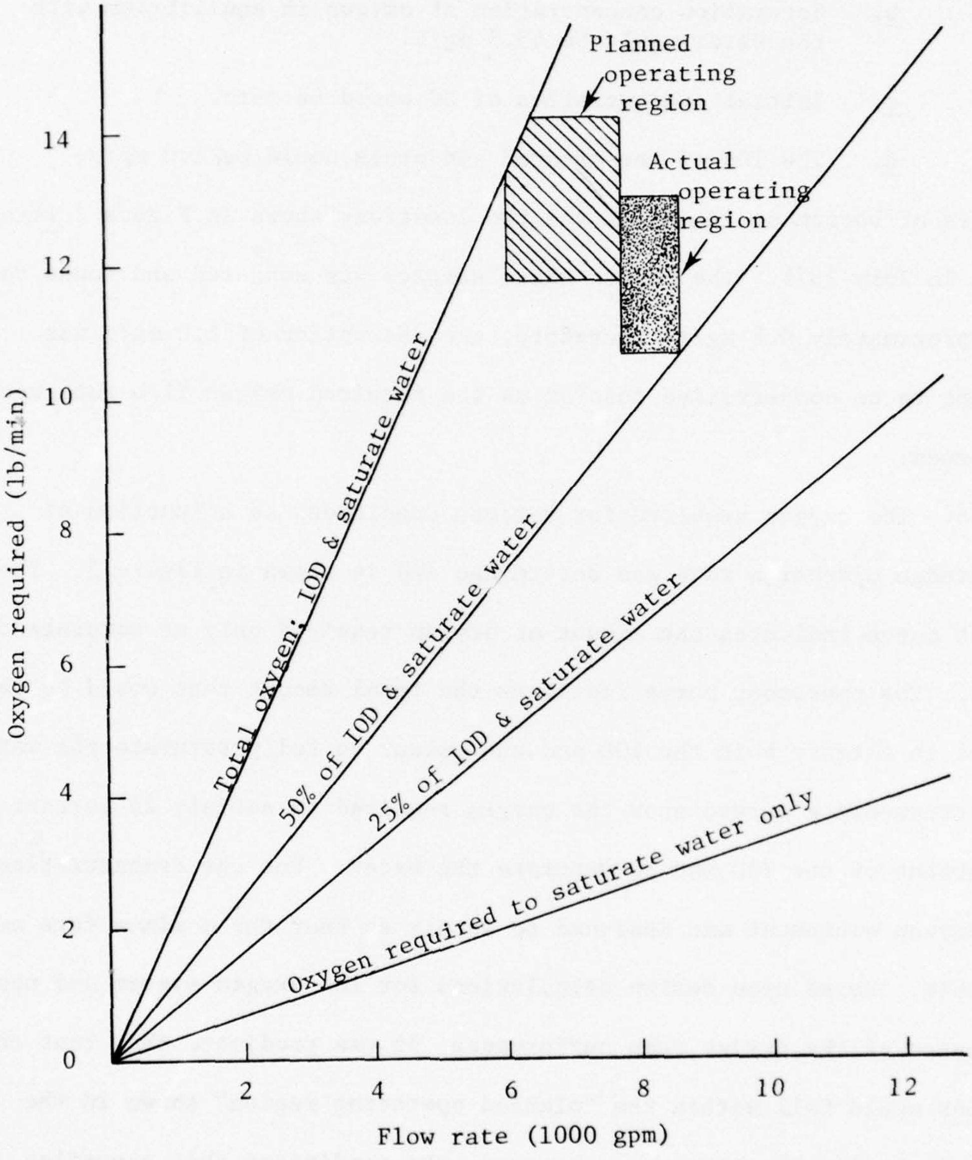


Figure 2. Oxygen required vs. dredge discharge flow rate

hoped. During this period, the dredge normally operated at a pump speed of 390 rpm. For the oxygen tests the pump speed was reduced, but it was found that any speed less than about 350 rpm resulted in unsteady flow and fluctuations in the vacuum and discharge pressure at the pump. Hence, test operations were conducted at 350 rpm, which resulted in a line velocity of 13 fps and a flow rate of 8147 gpm.

17. To limit the oxygen flow rate to reasonable values, it was desirable to reduce the flow rate in the pipeline as much as practicable. However, in order to assure turbulence and effective mixing of injected oxygen gas, it was desirable that the flow rate be sufficient to maintain a high Reynolds number. For the test conditions the actual Reynolds number was approximately 1.6×10^6, which was more than adequate to assure good mixing.

18. During the tests, the GUTHRIE was operated with a total of approximately 1500 ft of pipeline from the dredge pump to the discharge. This provided sufficient line to select two injection points well separated without having to operate the oxygen system close to the dredge itself. The lengths of pipeline and the positions of the injection points are shown schematically in Figure 3.

Test facilities and equipment

19. Sampling equipment and sample analysis. The environmental measurements portion of the oxygenation demonstration consisted of sampling the sediments, the water in the discharge area, and the discharge from the pipeline; in situ measurements in the disposal area; and laboratory measurements of the samples obtained.

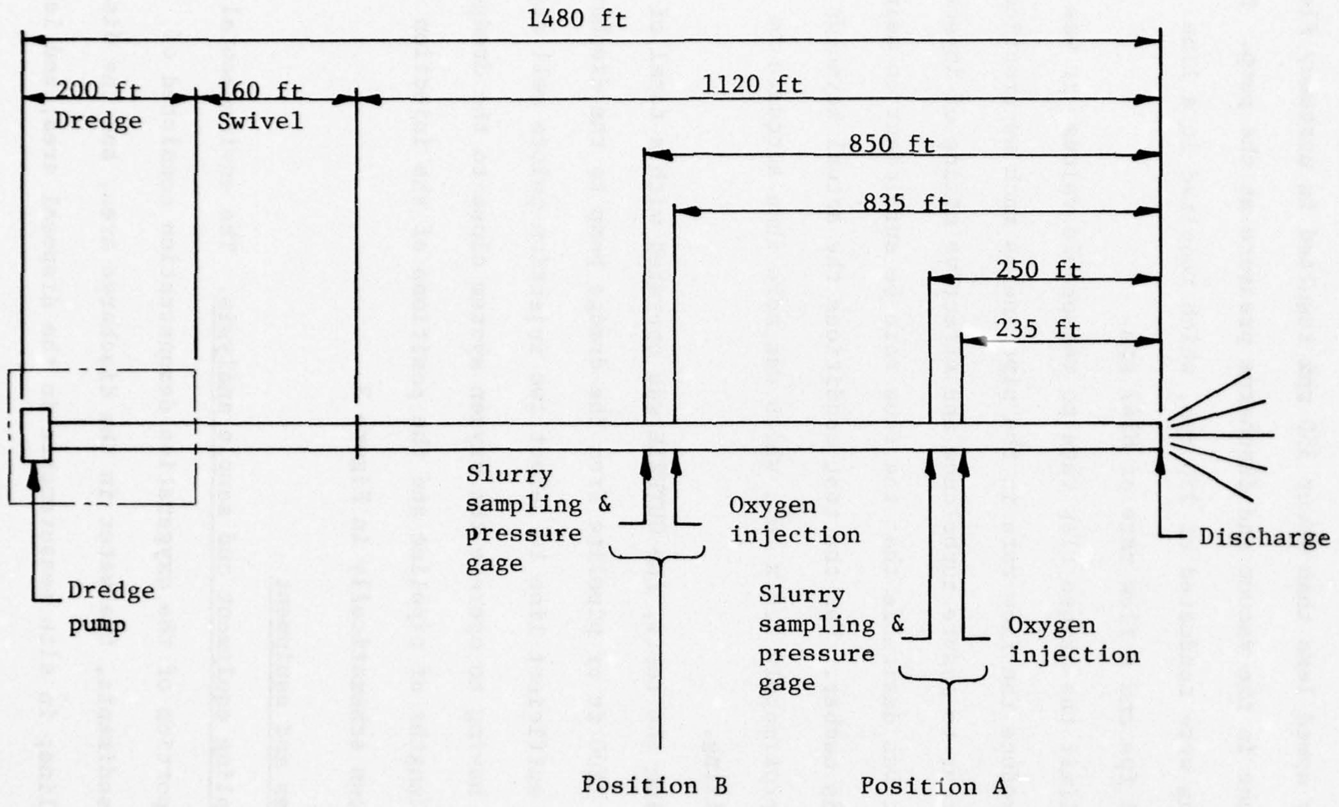


Figure 3. Positions of test points in pipeline

a. Sampling. Sediment samples were obtained with a Petersen type grab dredge and transferred to glass sample jars for shipment to the laboratory. Water samples were pumped from various depths with submersible pumps powered by 12-v batteries. Pipeline samples of slurry just prior to oxygen injection were taken from a sample port located on the side of the dredge discharge pipe. Samples from the end of the pipe were obtained with a Pitot tube-type device mounted on a cradle and chained to the pipe. Although plugging was a problem, sufficient sampling was accomplished to characterize the suspended solids concentration and obtain samples for IOD determination at the point of discharge.

b. In situ measurements. DO concentration was determined with polarographic DO meters manufactured by Yellow Springs Instrument Company. Water temperature was determined with the thermistor built into the DO probe. Salinity values were established with a YSI Model 33 conductivity/salinity meter. Water current measurements were made with a Hydro Products Model 460 current meter. Transmissivity was measured with a Hydro Products Model 612S transmissometer.

c. Laboratory measurements. Laboratory measurements were made both at the field laboratory and at the JBF laboratory in Burlington, Massachusetts. Suspended solids in the water column and percent solids in the pipeline slurry samples were determined by filtering and weighing. Turbidity values were determined with a Hach Model 2100A turbidimeter. Values of pH were found with a portable Fisher Accumet Model 150 pH meter. IOD values were determined for both pipeline samples and sediment samples by a procedure which is discussed in greater detail in Chapter III. Briefly, a known amount of sediment was added to a sealed bottle containing water with a known concentration of DO. The bottle was continuously stirred with a magnetic stirrer and monitored with a polarographic DO meter.

20. Oxygenation equipment. The oxygenation demonstration was planned to include four test runs in which oxygen would be injected for a period of 20 min during each run at a nominal flow rate of approximately 10,000 scfh (standard cubic feet per hour). Thus, the total quantity of oxygen required was a minimum of 13,300 scf. In order to provide a conservative margin, it was decided that the system should have a storage capability for about twice that quantity.

21. The discharge line of the GUTHRIE is made up of standard 40-ft sections of 16-in. I.D. steel pipe, each attached to and supported by a double pontoon float. A special test section for injecting the oxygen was made by modifying one of these floats. The entire system was installed on the test section, allowing it to be moved as a unit and placed in the discharge line at any desired location. This approach also precluded the need for any special precautions against relative motions that would have occurred had the oxygen system been installed on a separate barge moored alongside the test section.

22. Because the standard pontoon floats provide only limited space and reserve buoyancy, the size and weight of the oxygen system had also to be limited. Storage of the oxygen in high pressure gas cylinders was considered, but proved to be totally impractical. Approximately 135 standard cylinders weighing a total of 27,000 lb would have been required, far exceeding the allowable limits. Consequently it was decided that the oxygen would be stored as a liquid and vaporized prior to injection.

23. A schematic of the oxygen system is shown in Figure 4, and the complete installation is illustrated in Figures 5 and 6. The liquid oxygen was stored in six commercially available cylinders, each having a capacity sufficient to deliver 4500 scf of oxygen gas. In operation, the containers were manifolded in pairs to deliver liquid to an air-warmed, natural convection vaporizer. The vaporizer was sized to deliver up to 10,000 scfh of gas at a temperature within a few degrees of ambient. The vaporizer is shown in Figure 7.

24. The oxygen gas was injected into the pipeline through eight

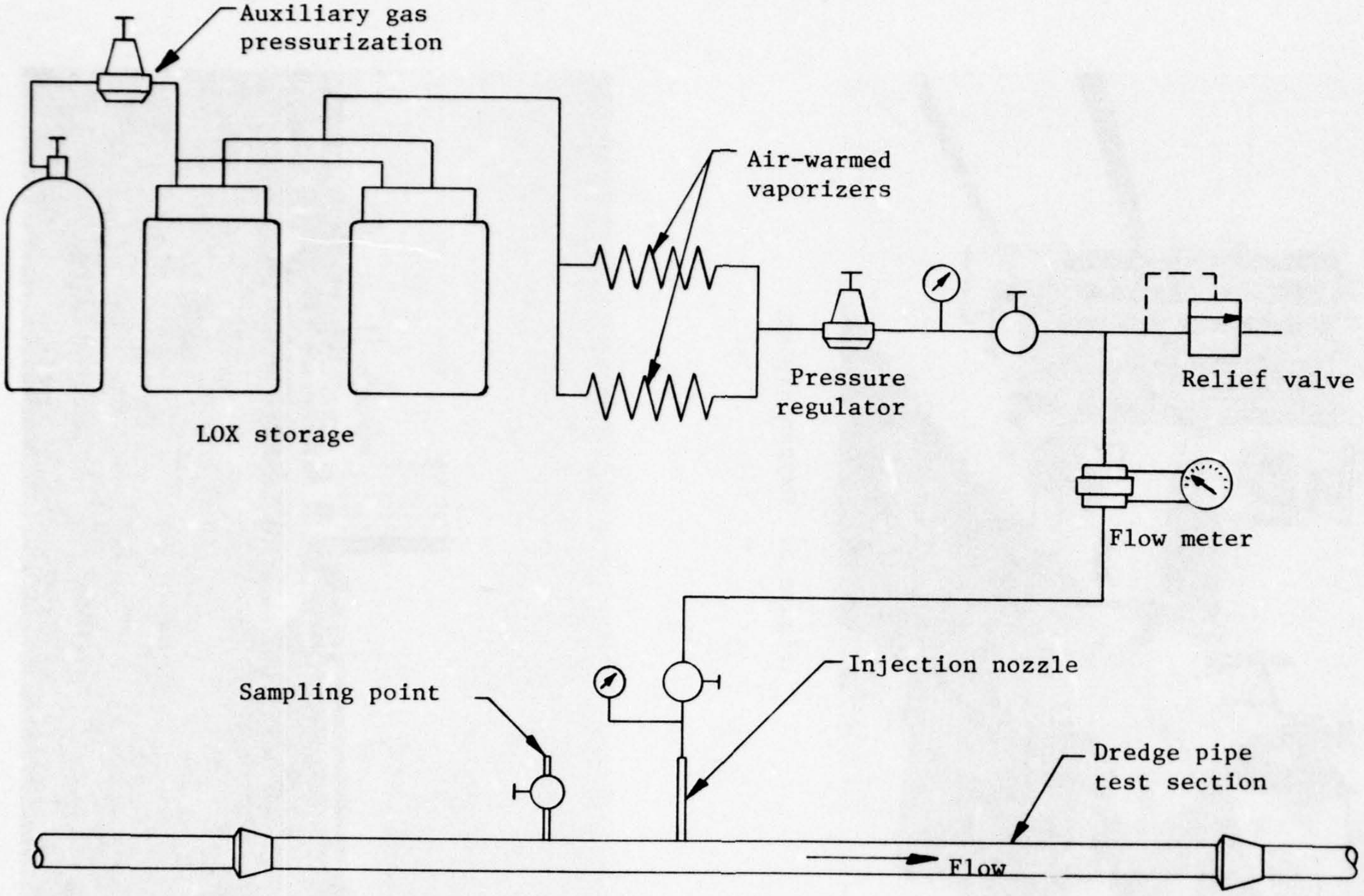


Figure 4. Oxygen injection system

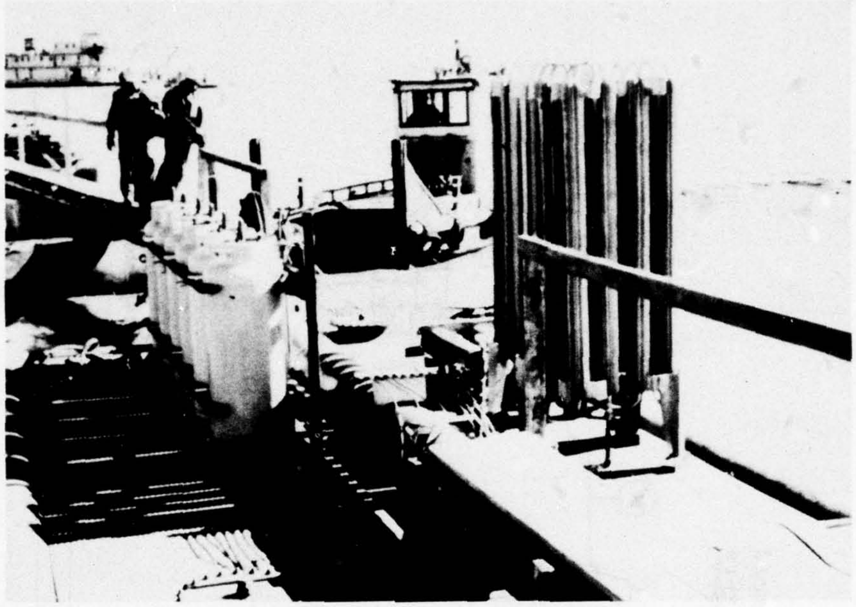


Figure 5. Oxygen system

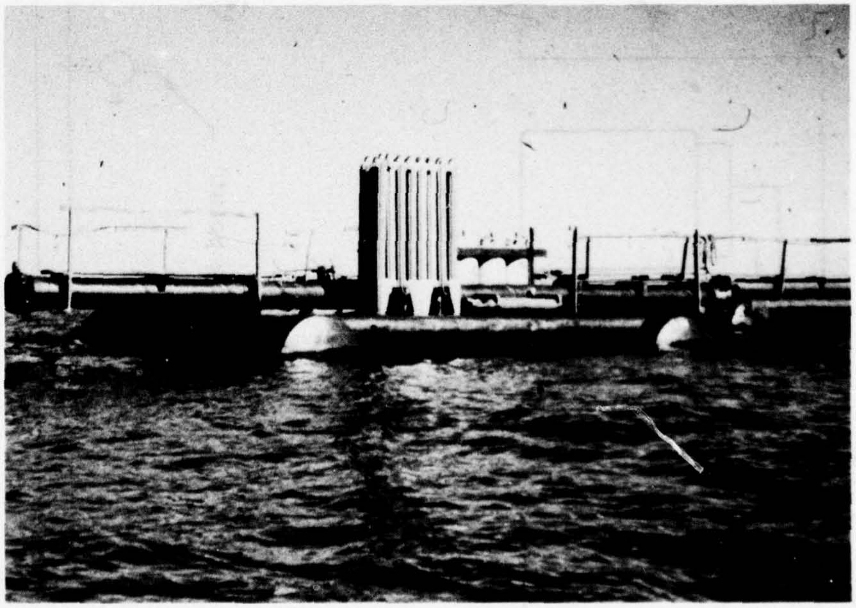


Figure 6. Oxygen system (side view)

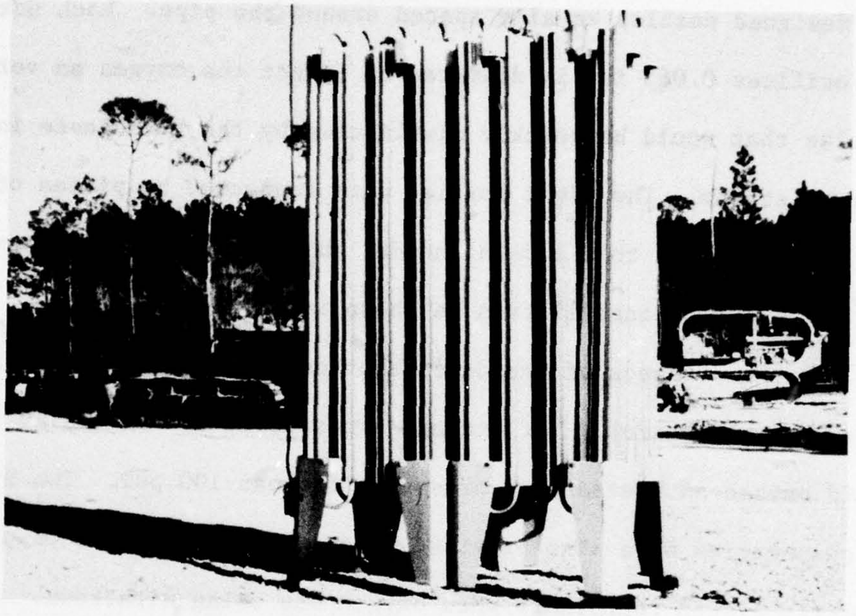


Figure 7. Liquid oxygen vaporizer

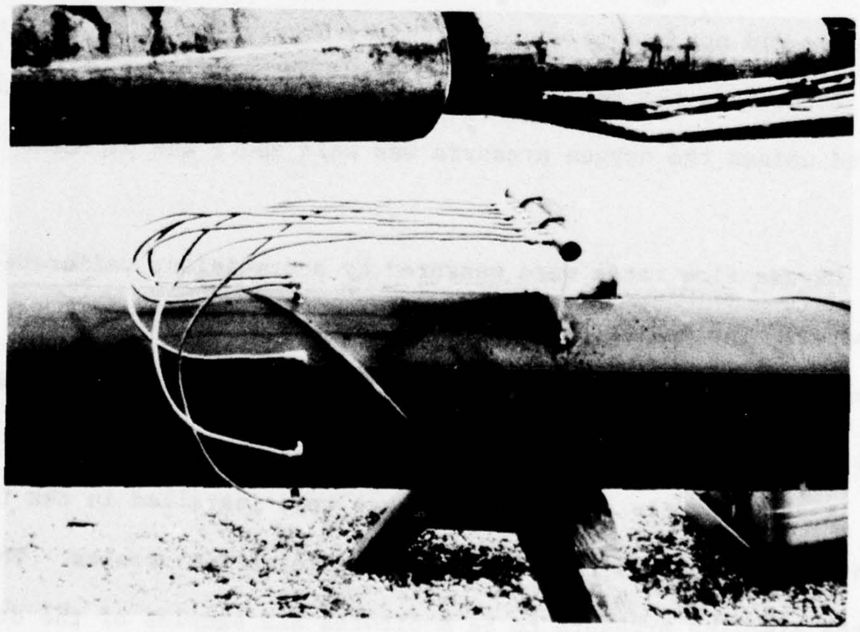


Figure 8. Oxygen-injector installation

specially designed nozzles equally spaced around the pipe. Each nozzle had seven orifices 0.063 in. in diameter to inject the oxygen as very small bubbles that would be quickly distributed by the turbulence in the discharge stream. The eight nozzles were connected by pieces of tubing of equal lengths to a 1.5-in. header into which the oxygen gas was fed. The injector installation is shown in Figure 8.

25. For the purposes of the demonstration, the system was designed for simple, manual control. The storage containers were initially filled with liquid oxygen saturated at a pressure of about 100 psi. Two high pressure gas bottles were also provided as an auxiliary source of pressurization for the liquid containers when oxygen was being withdrawn. Gas flow was controlled by a pressure regulator downstream of the vaporizer. This could be set at a pressure sufficiently above the pipeline pressure to inject the oxygen at the desired rate. In order to assure that the oxygen system did not become contaminated by dredged material, a shut-off valve was located on the injection nozzle header. This valve was always kept closed unless the oxygen pressure was well above the pipeline pressure.

26. Oxygen flow rates were measured by a precision, calibrated orifice meter. The indicated flow readings were adjusted by three correction factors: (1) upstream pipe diameter, (2) observed oxygen pressure, and (3) observed oxygen temperature.

27. A sampling tap and pressure gauge were installed in the test section pipeline about 15 ft upstream of the injection nozzles. This allowed the pipeline pressure to be monitored and samples of the dredged

material slurry to be withdrawn immediately upstream of the oxygen injection point.

Test operations

28. Time, location, and conduct of field measurements. The oxygenation tests consisted of measurements made prior to addition of oxygen to establish background conditions, and measurements made immediately prior to, during, and after oxygen addition. During the baseline measurements and oxygen injection, test personnel took samples and made measurements at a number of locations:

a. Bridge of the dredge. Data recorded were dredge pump speed, dredge pump discharge pressure, and dredge pump suction pressure (vacuum).

b. Oxygen barge. The test operation was directed from this location and the oxygen system was monitored and operated here. The following sampling and data recording were done: extract slurry samples from sampling tap upstream of injection nozzles; and record pipeline pressure and oxygen flow rate.

c. Pipeline discharge. At this location a man stationed on the discharge barge operated the sampling equipment to take slurry samples from the end of the discharge pipe and measured the DO concentration in the slurry.

d. Plume X. Plume X was located at a fixed point in the center of the plume approximately 60 ft downstream of the discharge point. DO concentration in the water column was measured and water samples were obtained.

e. Plume Y. Plume Y was located at a distance of approximately 120 ft from the discharge point and moved such that it was always in the center of the plume. Mobility was necessary since the plume meandered considerably even in a few minutes time. Aerial observations confirmed that Plume Y, as well as Plume X, was able to maintain a position in the center of the plume. Data recorded were values of DO, salinity, and temperature profiles. Samples were collected at mid-water depth for determination of suspended solids concentration.

f. Field laboratory. A laboratory was set up on the dredge. All water and sediment samples were delivered to this location where they were checked for proper identification and prepared for transfer to shore and shipment. The measurements performed in the field laboratory were IOD analysis of pipeline samples, turbidity of water samples, and pH of water samples.

g. Aircraft. The disposal area was overflown by a helicopter to aid in assuring that the boats were properly stationed in the plume and to provide a photographic record of the entire operation.

29. Operation Sequence. The sequence of operations followed during each of the oxygenation trials, including the dry run, was as follows:

a. Check oxygen injection system to assure that it is in readiness for the test.

b. Reduce the dredge pump from its normal speed of 390 rpm to 350 rpm.

c. Boats at locations Plume X and Plume Y assume their stations in the plume and begin taking readings and collecting water samples at approximately T-20 (T-0 was the time at which oxygen injection was to begin). Pipeline sampling also begins at this time.

d. At T-0 turn on the oxygen.

e. At T+20 (T+30 on the dry run), turn off the oxygen.

f. After readings return to normal (T+35 to T+45), cease monitoring the plume. Stop sampling pipeline at the same time.

30. Oxygen flow during tests. During the test runs a constant oxygen flow was maintained. This could not satisfy the variable demand from minute to minute. The primary source of this variability was the changing solids fraction in the dredge discharge line. Another source of

variability was an occasional fluctuation in the dredge line pressure. Because this reflected back to the oxygen system, it caused some variation in the oxygen flow rate. However, this was a relatively minor effect, and the average rate during each run is sufficiently representative for that entire run.

31. The oxygen flow rates achieved during the test runs are summarized in Table 2. The oxygen requirements are shown in two parts: that required to react with the sediment's immediate oxygen demand and that required to saturate the water. The amount of oxygen required to saturate the water has been calculated in two ways: one assuming that the liquid is in equilibrium with air, and the other assuming that it is in equilibrium with oxygen. Based on these calculations and the actual conditions occurring during the tests, the oxygen flow rates are shown as a percentage of the total that would have been required if the IOD were fully reacted and the water were fully saturated.

Table 2

Oxygen Rates and Requirements

	Run Number*			
	A-1	A-2	A-3	A-4
Oxygen flow rate:				
scfh	8459	8458	8378	9274
grams/min	5308	5307	5257	5819
lb/min	11.7	11.7	11.6	12.8
Oxygen rate required to satisfy IOD, grams/min	7784	6673	6112	5559
Oxygen rate required to saturate liquid in equilibrium with oxygen, grams/min	1284	1301	1309	1317

(Continued)

Oxygen rate required to saturate liquid in equilibrium with air, grams/min	257	260	262	263
Percent of total oxygen provided if in equilibrium with oxygen	59	67	71	85
Percent of total oxygen provided if in equilibrium with air	66	77	82	100

* For all runs: IOD = 1.12 mg/g
Flow rate of slurry = 8,147 gpm or 30,863 ℓ/min

32. The IOD of the sediments is taken as 1.12 mg/g for all test runs. This value is the mean of the IOD's measured for 49 slurry samples obtained when oxygen injection would not have affected the IOD value. IOD data were taken from all four runs and pooled because there was no significant difference between the means from one run to another. The measured values ranged from 0.82 to 1.51 mg/g, and the standard deviation of the data was 0.138.

Test results

33. Background data. Observations and measurements were made in the water column near the dredging operation (but outside its zone of influence) on several days prior to the actual oxygenation demonstration. Conditions were found to be quite uniform from location to location with the main variability with depth being a salinity stratification. A typical profile describing the water column is shown in Table 3. The location of this sampling point was in the disposal area 200 yd south of the discharge point. Dissolved oxygen values are seen to be at or near saturation, and salinity is very low at the surface and high at the bottom although the depth was less than 6 ft. The level of suspended matter was fairly

high. A curious observation, which was repeated at other background sampling stations, was that while the concentration of suspended solids increased with depth, the turbidity decreased. This was presumably due to differences in particle size with larger or denser particles predominating nearer the bottom. The speeds of the currents are seen to be low at the time of these observations.

Table 3

Background Measurements, Apalachicola Bay*

Depth ft	DO mg/ℓ	Salinity °/oo	Suspended Solids mg/ℓ	Transmissivity %	Turbidity NTU	Current knots
Surface	-	0.7	20	16	16	-
1	9.0	0.7	-	16	-	0.3
2	-	6.8	-	16	-	-
3	10.8	11.8	-	23	-	0.05
4	-	12.8	-	28	-	-
5	9.5	20.9	74	-	8	0.125
5.8 (Bottom)	-	20.9	-	-	-	-

*Air temperature, 16°C; water temperature, 16-18°C; date, 2 Dec 75; and time, 1400-1410 hr.

34. Slurry solids fractions. During each test run, samples of the dredged material slurry were withdrawn from the discharge line at a point immediately upstream of the oxygen injection nozzle. When the samples were taken (at intervals of about 5 min) there appeared to be a pronounced variability in the density or thickness of the slurry from one

sample to another. Some were quite watery while others were thick enough to mound up when poured onto a flat surface. The variability seemed quite random.

35. After the tests, the density of each slurry sample, P_s, was measured in the laboratory; for each run, the mean density and the standard deviation for the sample set were determined. These results are shown in Table 4. The table also shows the percent solids (both by weight and by volume) based upon the mean value of the measured slurry densities.

Table 4

Statistics of Slurry Densities

	Run Number*			
	A-1	A-2	B-1	B-2
Slurry Density, P_s, (g/cc)	1.15	1.13	1.12	1.11
Std. Deviation of P_s (Coeff. of Variation,%)	0.045 (3.9)	0.039 (3.5)	0.055 (4.9)	0.027 (2.4)
Number of Samples	12	11	11	15
Range of P_s (g/cc)	1.08-1.23	1.05-1.18	1.02-1.19	1.07-1.16
% Solids by Volume	8.5	7.3	6.7	6.1
% Solids by Weight	19.6	17.1	15.8	14.5

*For all runs: Density Solids = 2.66 g/cc; Density Seawater = 1.01 g/cc

36. One striking feature of these results is that there was a systematic variation superimposed upon the random variability in percent solids as the tests proceeded. This is further illustrated in Figure 9. The curves show the functional relationship between the solids fraction

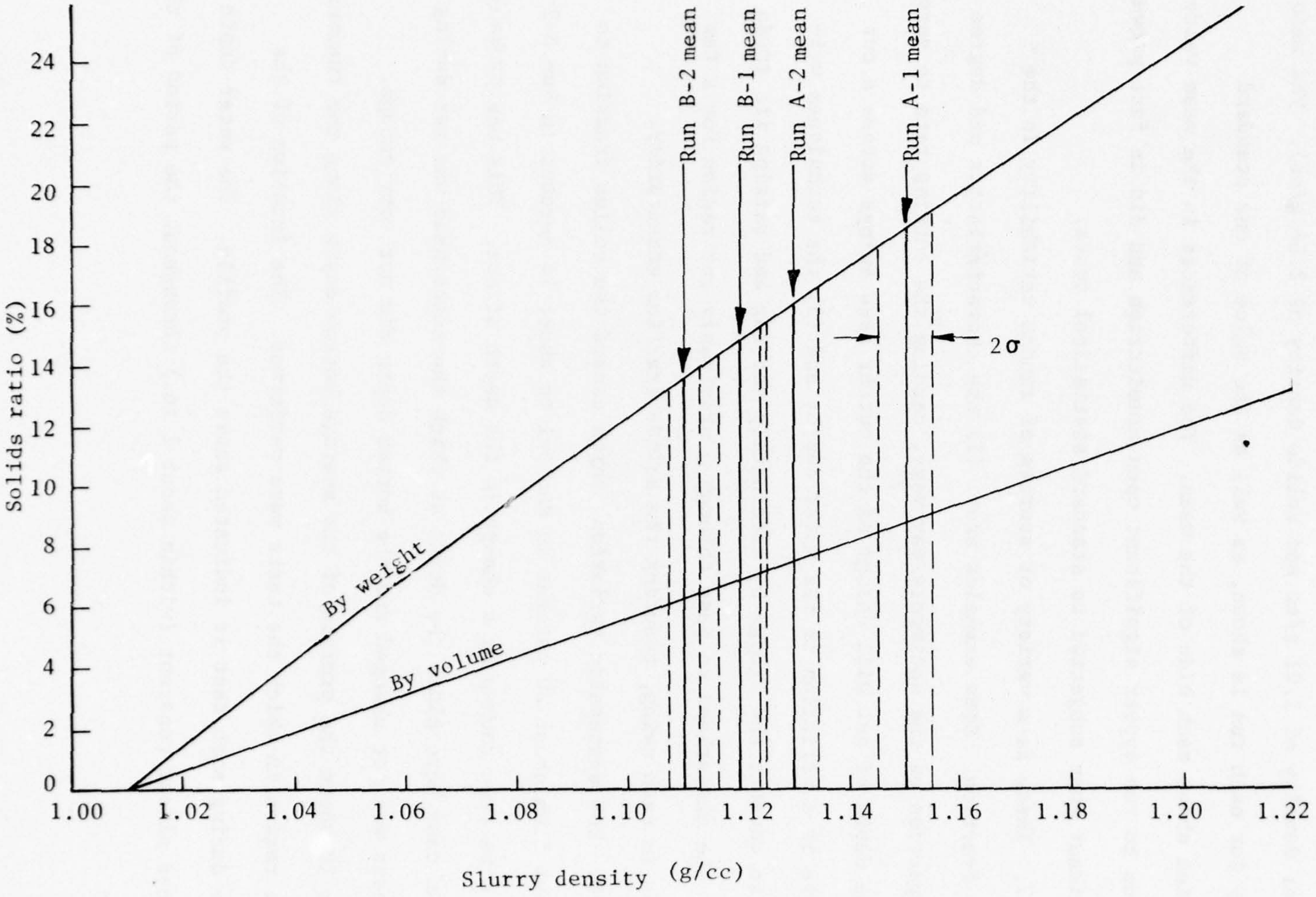


Figure 9. Percent solids vs. slurry density

in the slurry and the slurry density for the actual test conditions (i.e., seawater density of 1.01 g/cc and solids density of 2.66 g/cc). The mean density for each run is shown, as well as the value of one standard deviation about each side of the mean. The differences in the mean value from run to run appear significant upon examination and did in fact prove significant when subjected to standard statistical tests.

37. There is a variety of sources of random variability in the solids fraction. Some examples are: (1) the characteristics and degree of compaction of the sediments may vary, causing the cutting rate to vary; (2) the depth of cut will change as the cutter head swings across a cut if there is a variation in the water depth; and (3) the techniques utilized to advance the dredge by alternately setting and raising its spuds cause the cutterhead to pass through a previously cut region for a few degrees in each swing, reducing the solids fraction momentarily.

38. The systematic variation which caused the solids fraction to decrease from about 20 percent in Run A-1 to about 14 percent in Run B-2 could have been caused by a change in the depth of cut. This was probably not the case here since the depth at which the cutterhead was set during the tests was not changed and the bottom depth did not vary enough. Figure 10 shows the profile of the average bottom depth along the channel in the region in which the tests were performed. The location of the dredge during each test is indicated above the profile. The water depth remained almost constant (within about 1 in.) throughout the period of the tests.

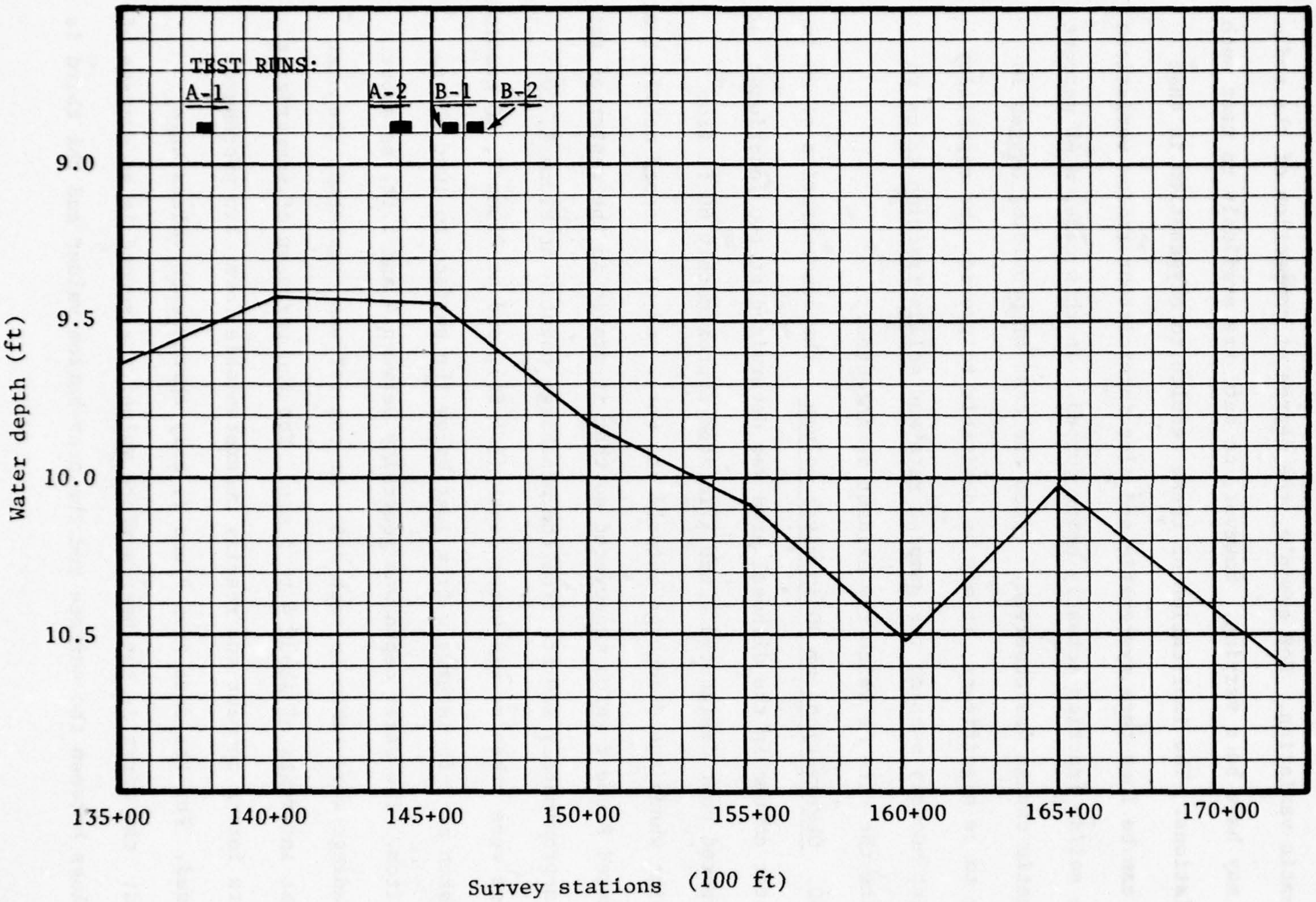


Figure 10. Bottom profile in vicinity of test runs

39. Other more speculative explanations may be sought for the systematic variation. For example, the degree of compaction of the sediments may have been varying. However, no data are available to test such speculations. The implication of these results to oxygenation is that there can be long-term systematic and also intermittent random variations in the solids fraction actually being pumped. In this case, a 40 percent systematic change was observed. Since the cost of providing oxygen is likely to be significant, it may be desirable to provide the capability for continuously sensing the pumping rate and solids fraction so as to modulate the rate at which the oxidant is injected.

40. Observations of DO in water column. The concentration of DO in the water column in the disposal area was determined at two locations: at an anchored boat designated Plume X located approximately 60 ft from the point where the discharge entered the water and at a second mobile boat designated Plume Y which maneuvered so that it stayed in the center of the plume approximately 120 ft. from the discharge point. At Plume X, DO readings were taken at mid-water depth (1.5 ft), and at Plume Y, DO readings were taken at 1-ft intervals from just below the surface to just above the bottom. The water depth was generally between 4 and 5 ft, so about six readings were taken in each set. As one set was completed, the next began at intervals of about 4 to 5 min. For the purposes of summarizing the data into a compact and readily understandable form, two procedures were used. For the data from Plume Y, only three depth values were plotted: the first is the near-surface value; the second is an average of all values between the surface and the near-bottom value; and the third is

the near-bottom value. For the Plume X data, the one value of mid-depth DO is plotted.

41. The second summarizing procedure was to use a time-averaging technique because of the high degree of variability observed from one set of readings to the next. To smooth out some of this variability and allow longer term trends to be more readily recognized, the value plotted at each time was an average of three values, the actual value and the value on each side of it in its time sequence.

42. The effect of oxygenation on DO levels in the water column at Plume X during Run A-1 is shown in Figure 11. Prior to oxygenation the DO level is seen to average 4.2 mg/ℓ . During oxygenation the average DO rose to 6.3 mg/ℓ and then rapidly fell again to preoxygenation levels. This clearly demonstrates the effect of oxygenation on the water column.

43. Dissolved oxygen levels at Plume Y during Run A-1 are shown in Figure 12. In this case the mid-depth value shown is the set of readings taken at the 3-ft level. Near the end of the oxygen injection period, the DO probe was held at the 3-ft level to observe the effect of ceasing oxygen injection. Once obvious effects were no longer noted at that depth, readings were resumed in the usual sequence.

44. Even at this location only about 120 ft from the discharge point, and although obviously in the turbid plume, the surface DO level is seen to be only slightly depressed from background values. At the 3-ft level a downward trend in DO levels is seen throughout this test period. That trend was apparently not affected by oxygen injection. Only near the bottom were DO levels seriously depressed when oxygen injection was

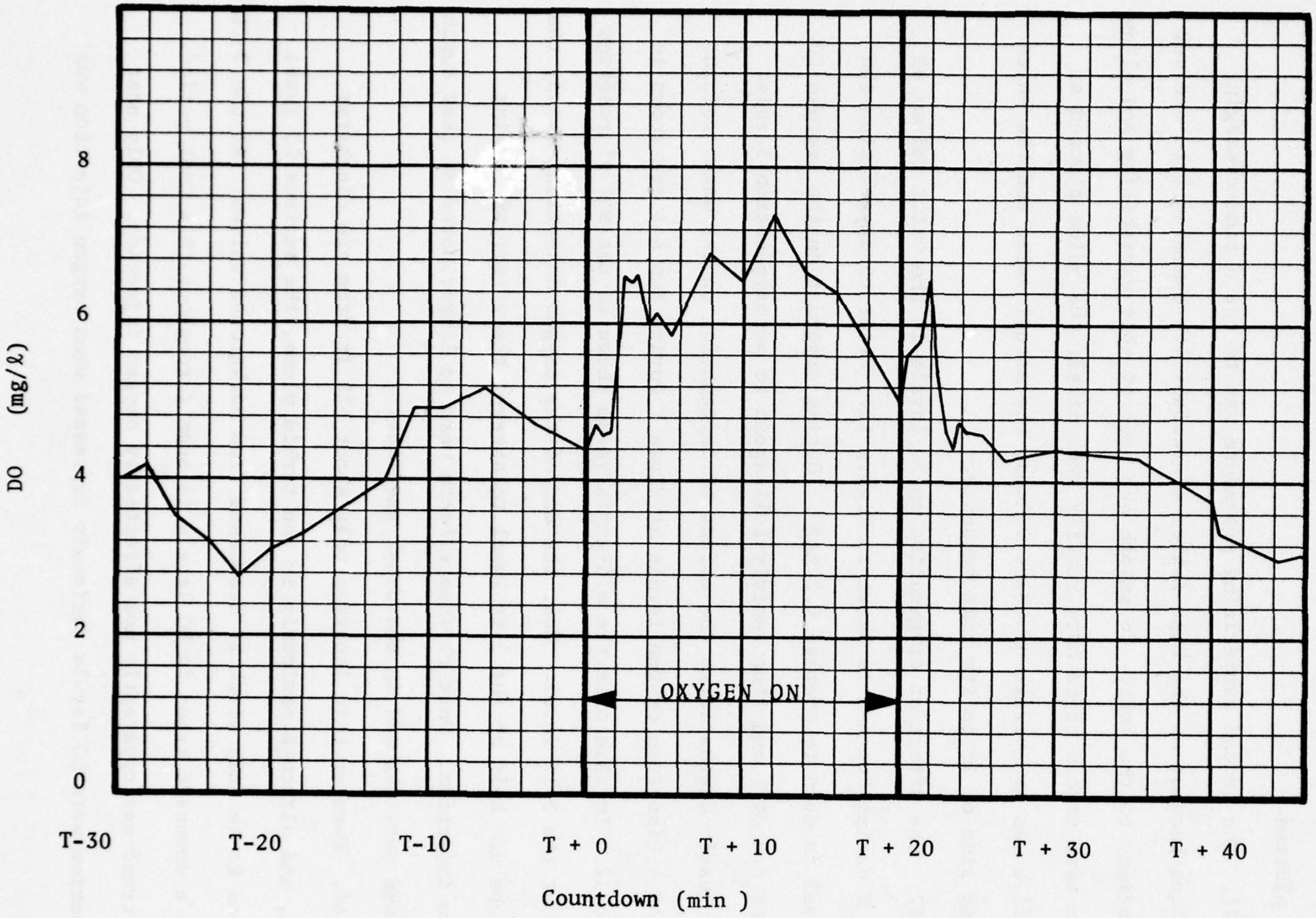
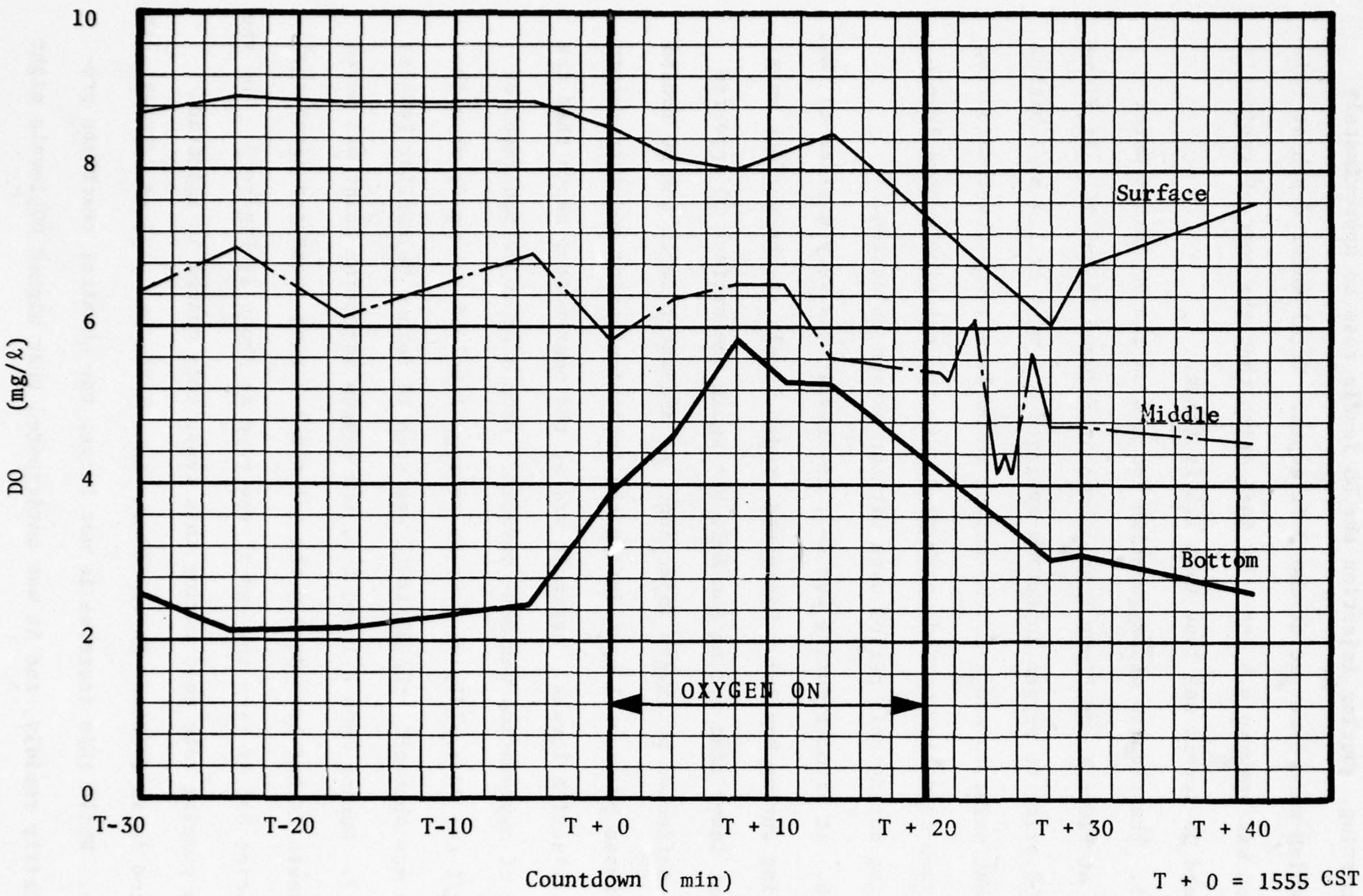


Figure 11. DO variation: Run A-1, Plume X

T + 0 = 1555 CST
3 Dec 1975



T + 0 = 1555 CST
3 Dec 1975

Figure 12. DO variation: Run A-1, Plume Y

not occurring. During injection the DO levels rose to approximately those which were observed at the 3-ft depth. Total water depth at this location was between 4.5 and 5 ft indicating that the zone of seriously depressed DO levels was less than 1.5 ft thick.

45. The results of oxygenation Run A-2 on the DO in the water column at Plume X and Plume Y are shown in Figures 13 and 14. At Plume X the DO prior to oxygen injection averaged 5.6 mg/ℓ or 1.4 mg/ℓ higher than that prior to Run A-1. No effect on DO levels was observed during the oxygen-injection period, perhaps due to the relatively high levels occurring during this period even without oxygen injection.

46. At Plume Y during Run A-2, the result was very similar to that occurring during Run A-1. Dissolved oxygen levels at the surface were somewhat lower than during Run A-1, but again the surface DO appeared to be unaffected by oxygen injection. At mid-water depth the DO tended to increase by about 1 mg/ℓ during the injection period and then return to preinjection levels. Again it was at the near-bottom depth that the effect of oxygenation was most obvious. From a preinjection level of 1.8 mg/ℓ the DO rapidly rose to an average level of 4.1 mg/ℓ; when the oxygen was shut off, the DO level was seen to return to earlier levels.

47. During Runs B-1 and B-2, the oxygen injection point was moved from where it had been during the A-1 and A-2 runs (near the discharge) to a point 835 ft from the end of the pipe as shown in Figure 3. For the dredge pumping rate used during this test, this change in injection resulted in an increase in residence time within the pipe of approximately 45 sec. While this increase is not large, the chemical reactions proceed fairly rapidly, and it was anticipated that higher DO levels might be observed in the disposal area.

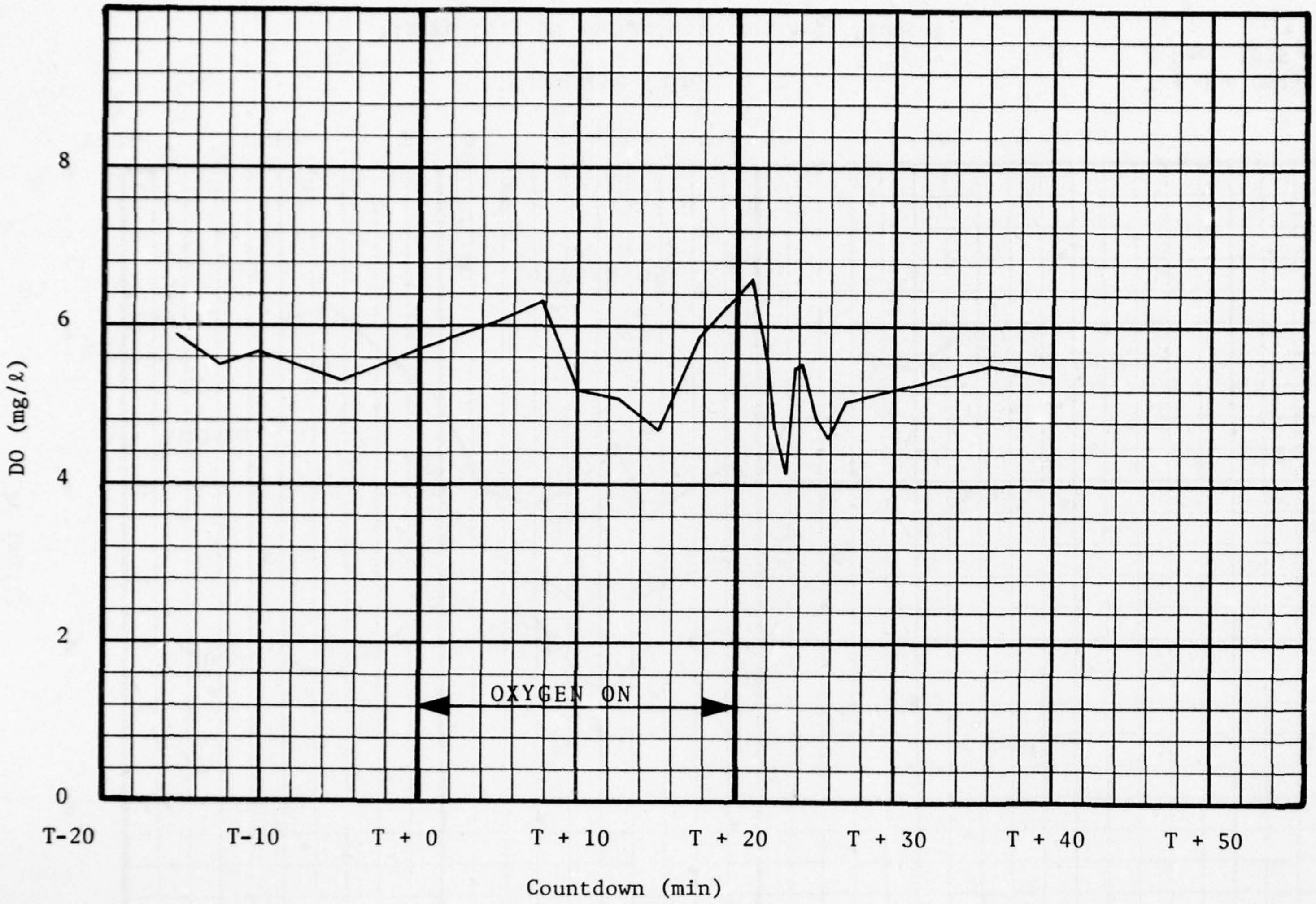
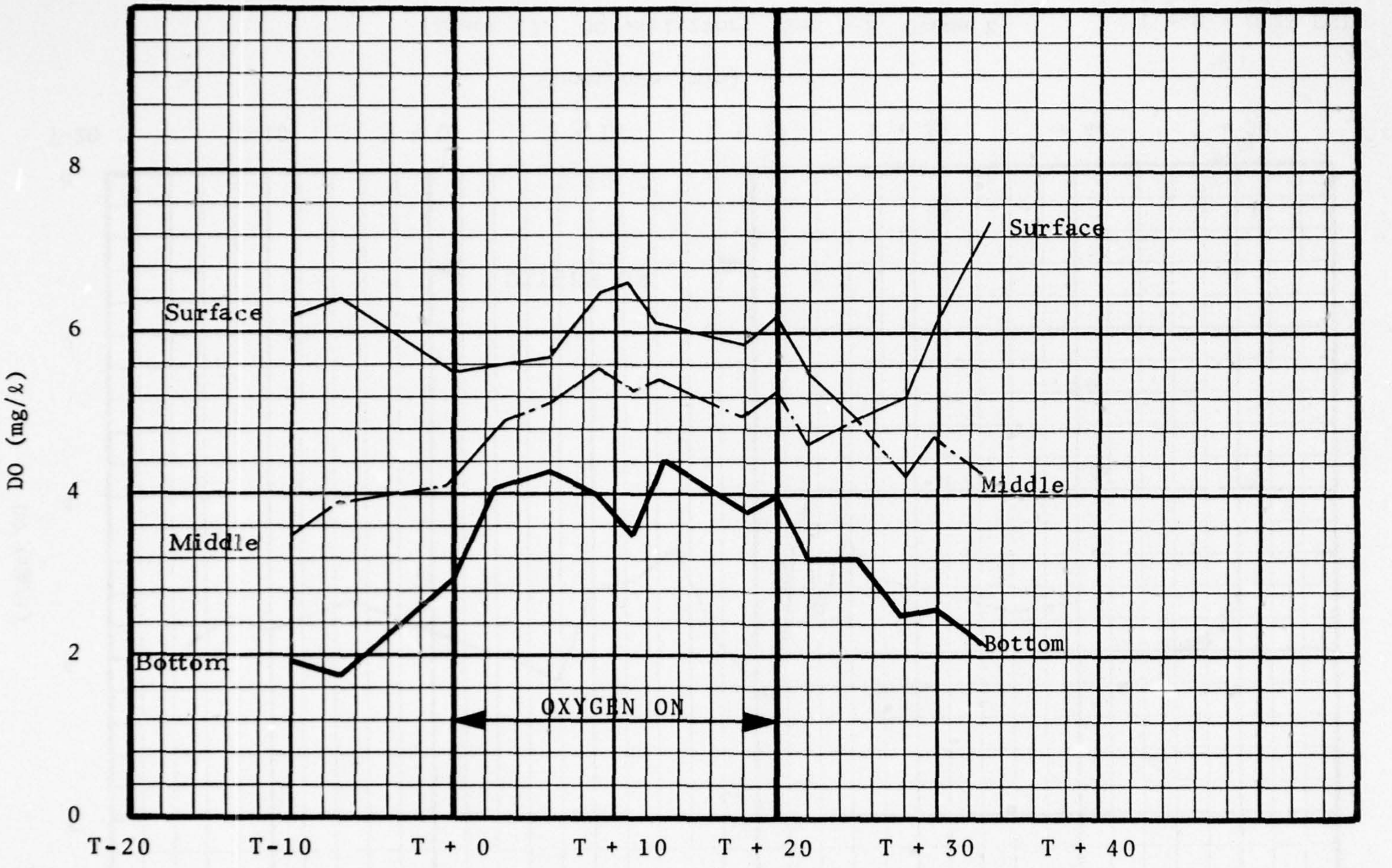


Figure 13. DO variation: Run A-2, Plume X

T + 0 = 0945 CST
4 Dec 1975



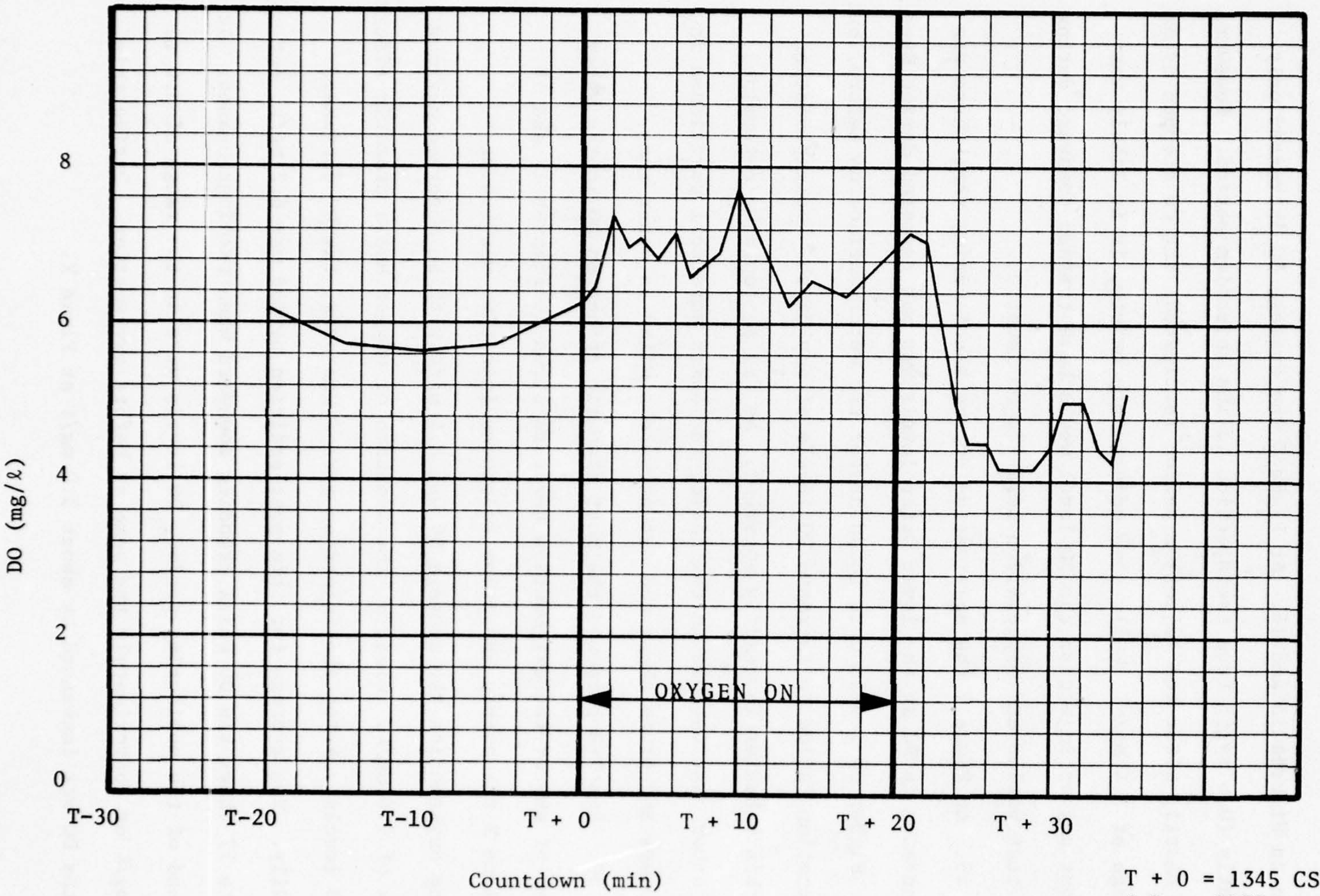
T + 0 = 0945 CST
4 Dec 1975

Figure 14. DO variation: Run A-2, Plume Y

48. The observed DO levels at Plume X and Plume Y for Run B-1 are shown in Figures 15 and 16. At Plume X the average DO increased only slightly (0.6 mg/ℓ) from preinjection to the injection period. However, very shortly after the injection period terminated, the DO dropped by an average of 2.4 mg/ℓ. While some uncertainty exists, it is likely that without oxygen injection the DO level would have trended downward during this test period and oxygenation held the DO level up.

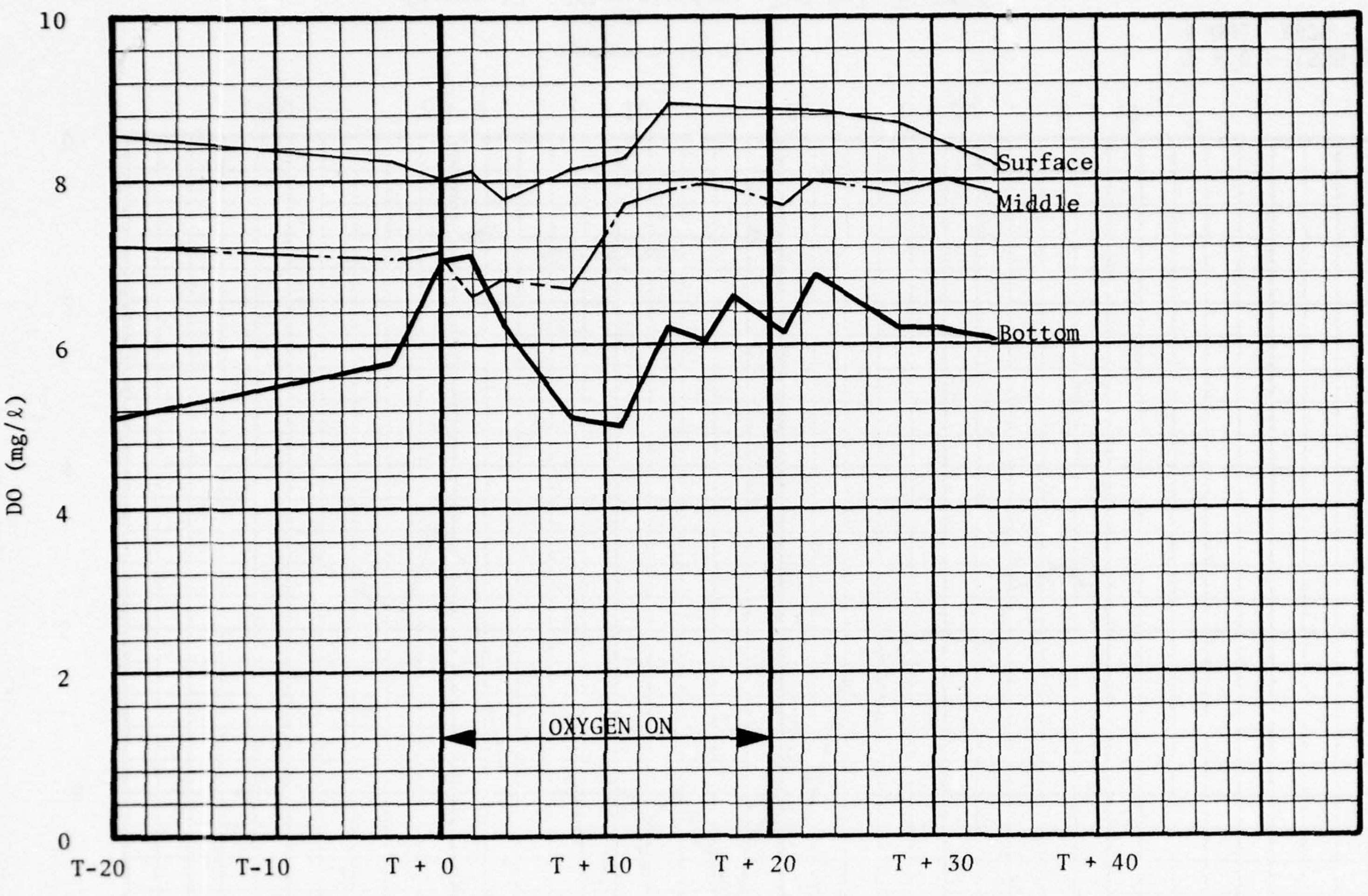
49. At Plume Y the observation during the A-series that there was an increase in DO at the lower water levels was not repeated during Run B-1. Higher DO levels were found nearer the water surface as before, but oxygenation failed to increase DO levels at any depth. No explanation for this behavior is readily apparent. As far as could be determined from other observations in the field, the boats were well positioned in the plume and plume shape and extent were similar to other runs.

50. Run B-2 produced the most dramatic effect on DO in the water column of any of the oxygenation tests as shown in Figures 17 and 18. At Plume X the average DO prior to oxygen injection was 5.4 mg/ℓ. During oxygenation the average DO was 8.4 mg/ℓ with an observed maximum value of 9.6 mg/ℓ. Clearly, the addition of oxygen had a dramatic effect on DO levels. After the injection period was over, the DO decreased steadily. The average for this post-addition period was 6.2 mg/ℓ, but Figure 17 shows the DO still trending downward when readings ceased. At the end of the monitoring period, DO levels were in the range of 5.0 to 5.5 mg/ℓ or approximately the same as before oxygenation. During this run the DO was increased by about 3.0 mg/ℓ at Plume X.



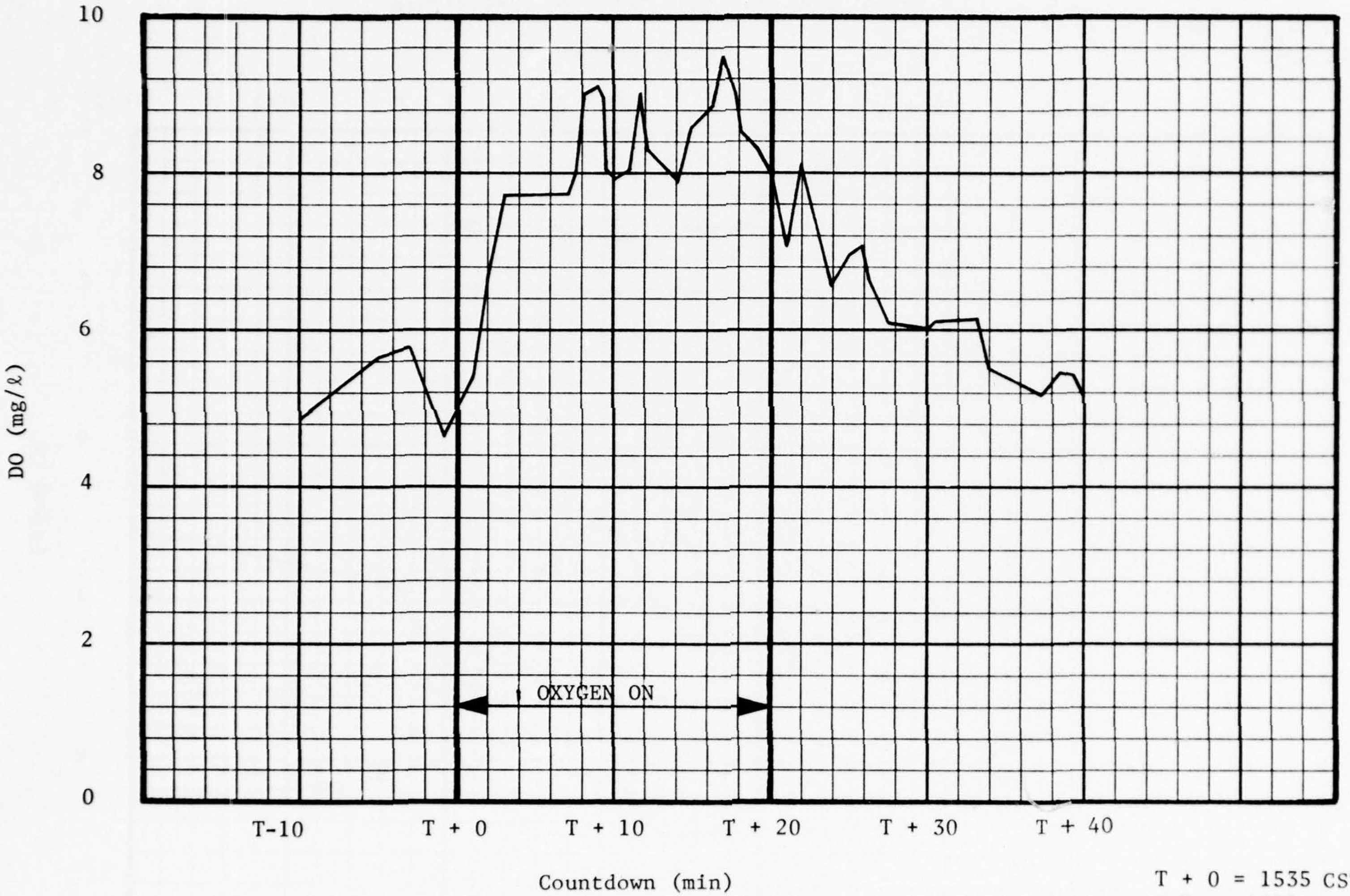
T + 0 = 1345 CST
4 Dec 1975

Figure 15. DO variation: Run B-1, Plume X



T + 0 = 1345 CST
4 Dec 1975

Figure 16. DO variation: Run B-1, Plume Y



T + 0 = 1535 CST
4 Dec 1975

Figure 17. DO variation: Run B-2, Plume X

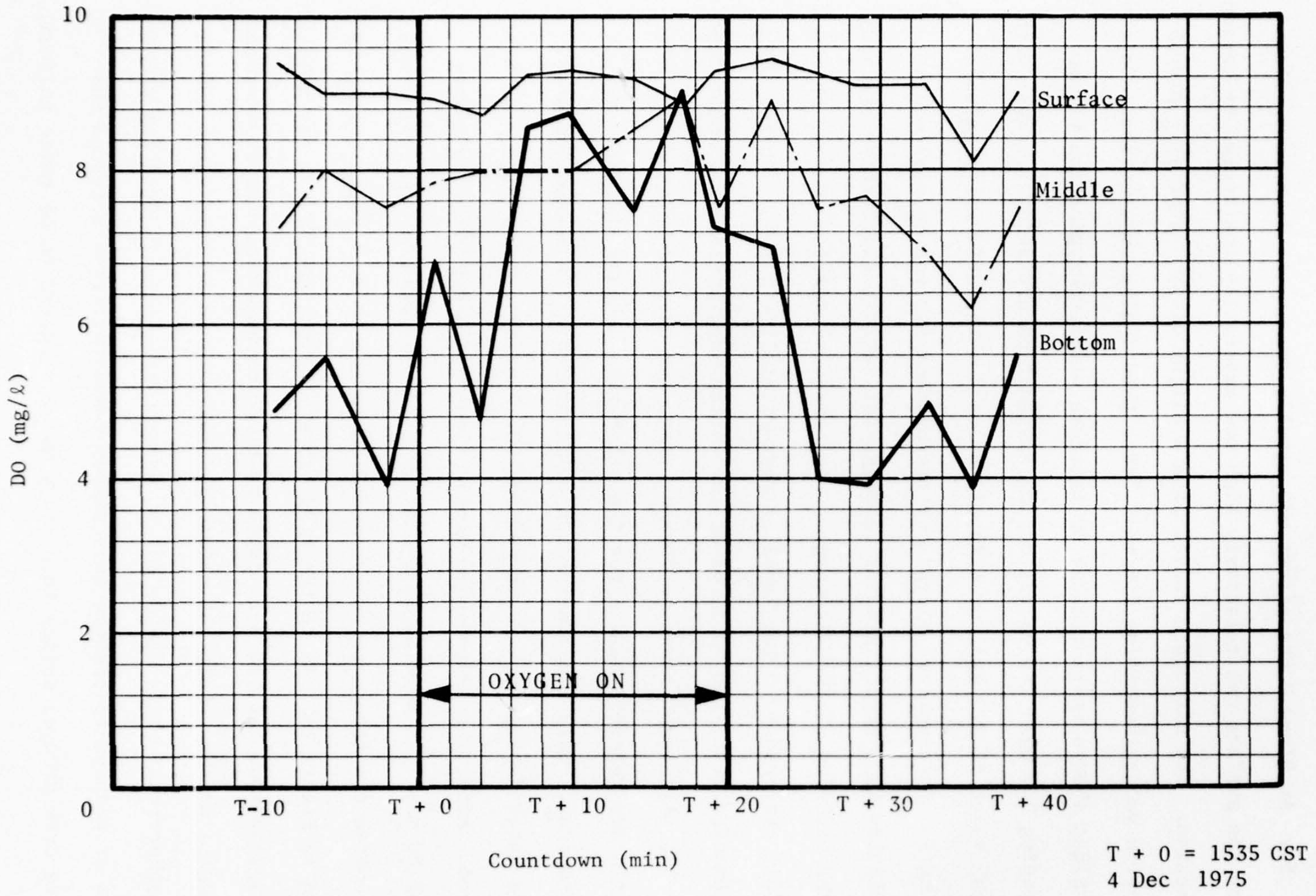
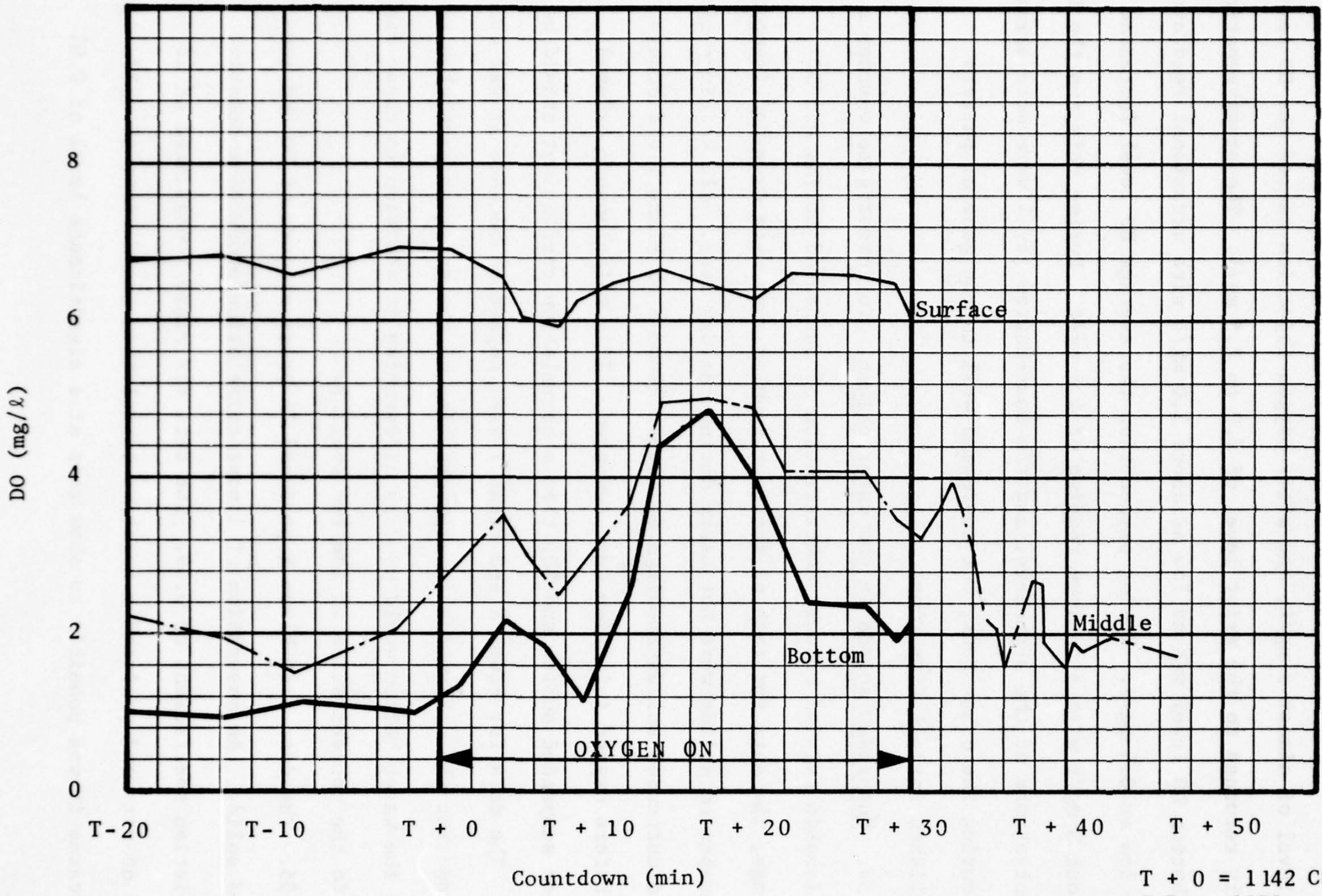


Figure 18. DO variation: Run B-2, Plume Y
(unadjusted)

51. At Plume Y the effect was equally dramatic. As before, the DO at the surface was relatively high and apparently unaffected by oxygen injection. The mid-depth values show a slight upward trend with preoxygenation values averaging 0.6 mg/ℓ lower than during oxygenation. Bottom DO values show a very dramatic DO increase with preoxygenation values averaging 5.3 mg/ℓ and values during oxygenation averaging 7.7 mg/ℓ with a peak value of 9.0 mg/ℓ or slightly exceeding the saturation value of 8.7 mg/ℓ. The apparent slight supersaturation may not be real due to difficulty in correcting meter readings for rapidly fluctuating salinity in the vicinity of the discharge. When oxygen injection ceased, the DO rapidly returned to a low level of approximately 4.5 mg/ℓ. During this oxygenation test, the DO level at the bottom was increased by about 3 mg/ℓ.

52. Although it was performed first, the data gathered during the dry run are reported here after the other runs because the data are not as complete. Only the observation point at Plume Y was used and only three water depths were monitored for DO: surface, 3-ft depth, and near bottom. After the oxygenation period (lasting 30 min rather than the usual 20 min) was over at T+30, the DO probe was held at the 3-ft level to observe the return to unoxygenated DO levels at that depth. This is shown in Figure 19. As in the other runs, the surface DO was not affected by oxygenation. At the 3-ft depth prior to oxygenation, the DO averaged 2.0 mg/ℓ, or about half the values generally found at this depth during the other runs. This may be due to normal variations in dredging operations or perhaps to changes in sediment characteristics although the entire area dredged during this study was considered to be quite uniform.



T + 0 = 1142 CST
3 Dec 1975

Figure 19. DO variation: Dry run, Plume Y

53. Once oxygenation began, the DO at the 3-ft level was seen to rise to a level of almost 5 mg/ℓ, and after oxygen injection ceased the DO level rapidly returned to the prior level of 2.0 to 2.5 mg/ℓ. The preoxygenation near-bottom DO level was as low as about 1.0 mg/ℓ with occasional readings of as low as 0.4 mg/ℓ. During oxygenation the average DO level increased to about 3 mg/ℓ with a maximum reading of 4.8 mg/ℓ. During this run the DO concentrations at the 3-ft level and the near-bottom level were more erratic than during the other runs, but conformed well to the general pattern established for all five runs.

54. Suspended solids in the water column. To investigate whether a relationship existed between concentration of suspended solids and DO readings, the data for each of the four regular runs were examined (samples for suspended solids were not taken during the dry run). All pairings of DO and suspended solids readings at either Plume X or Plume Y and occurring before oxygen injection were compared. If a relationship existed between suspended solids and DO, then a correlation coefficient should be high. The data for Plume X and Plume Y were separated because it was considered that the difference in exposure time of the sediment particles to DO in the water column would produce differences in addition to those due only to the concentration of the two species.

55. The data from Plume X produced 16 pairs of data of DO and suspended solids. An assumption of linear correlation produced a negative correlation coefficient of 0.69. The data for Plume Y consisted of 13 pairs of data and produced a negative correlation coefficient of 0.77. In both cases it was possible to show that at a significance level of 0.01

the population correlation coefficient differed from zero. In other words, it was shown statistically that there was a relationship between DO level and the level of suspended solids. As DO levels increased, the concentrations of suspended solids decreased.

56. An indication of the effect of dilution and settling of suspended solids from the discharge plume may be obtained by comparing the level of suspended solids observed at Plume X and Plume Y with the concentration of suspended solids in the discharge pipe. Because it has been shown that oxygenation did not significantly affect the level of suspended solids, all suspended solids data for a single run have been averaged. Plume X data are still separated from Plume Y data as shown in Table 5. In the table are shown the data from each run and the respective dilution factors. For Plume X, at a distance of approximately 60 ft from the discharge, the average dilution factor was about 14. For Plume Y, at a distance of approximately 120 ft, the average dilution factor was about 27. Thus, at the farther point, which was twice as far from the discharge as the nearer point, the dilution was twice as great. If the discharge plume was in the shape of a cone, then a difference of four times (or more when sedimentation is considered) would be expected, rather than two times as observed. The most likely explanation for the difference would be that the data were inconsistent and highly variable. This can be seen by comparing dilution factors at Plume X and Plume Y. For example, during Run B-2 the dilution factor at Plume X was the lowest for any run while the dilution factor at Plume Y was the highest for any run. Therefore, the suspended solids values and dilution factors derived

during the oxygenation test runs serve only as general indicators of values likely to be found and should not be used as definitive data. Unplanned variability due to wandering of the plume and other factors probably is as important as distance from the source.

Table 5

Dilution Factors at Plume X and Plume Y

	Suspended Solids, mg/ℓ			Dilution Factor	
Run	Pipeline Discharge	Plume X	Plume Y	Plume X	Plume Y
A-1	19.6	1.76	0.64	11.1	30.6
A-2	17.1	1.05	0.89	16.3	19.2
B-1	15.8	0.92	0.61	17.2	25.9
B-2	14.5	1.47	0.47	9.9	30.9
AVG	--	--	--	13.6	26.7

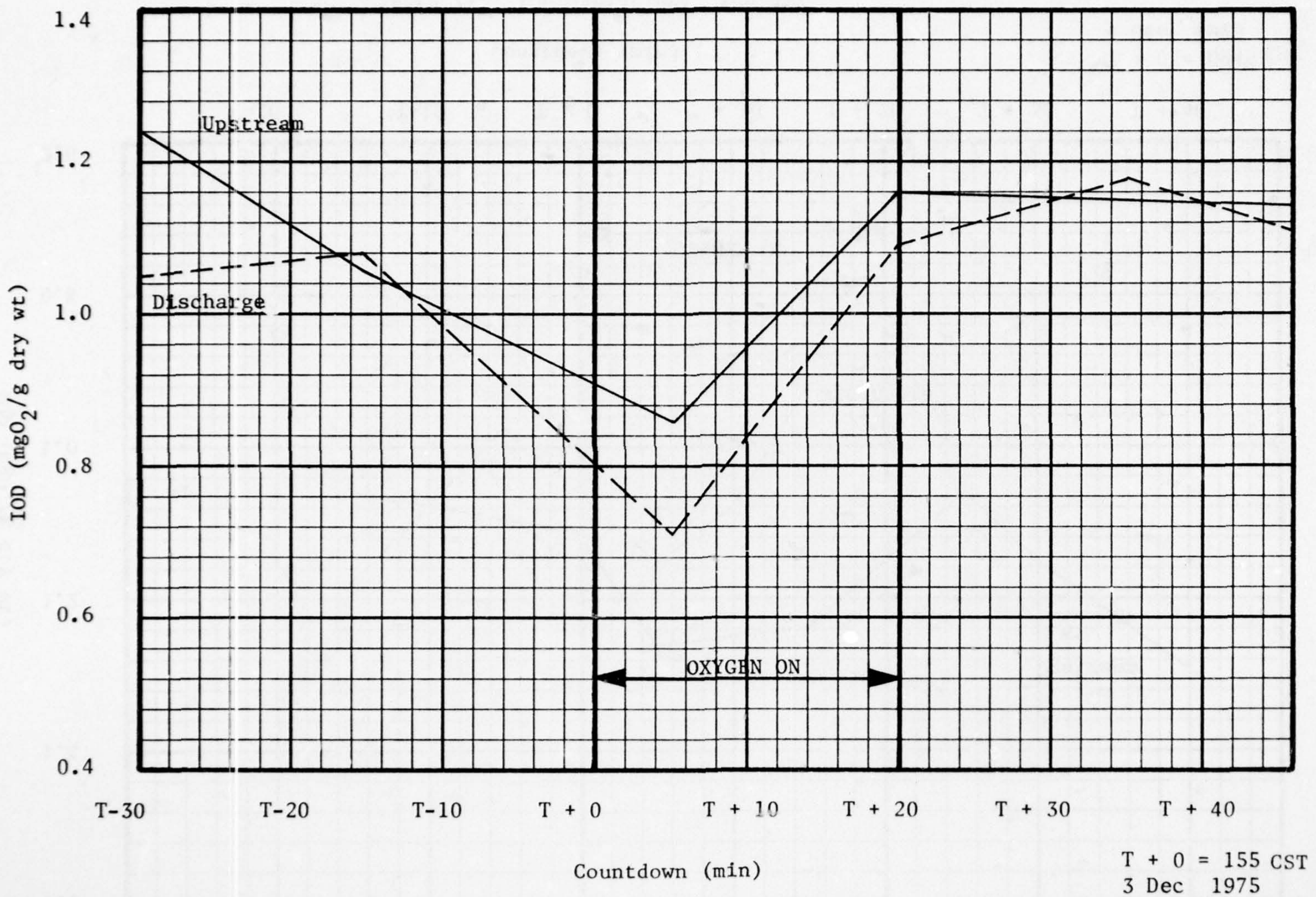
57. An investigation was undertaken to determine if the process of oxygenation increased the concentration of suspended solids in the plume. An increase was considered possible due to increased turbulence caused by oxygen bubbles and/or by precipitation of insoluble ferric iron from soluble ferrous iron. In this case for each oxygenation run the mean of the suspended solids values prior to oxygenation was compared to the mean of the values during the oxygenation period. Once again the suspended solids values for Plume X were evaluated separately from those of Plume Y. Values of suspended solids after oxygenation were not included.

58. Statistical evaluation of the eight sets of data (four oxygenation runs with two sampling points for each) showed that in no case was the mean of the suspended solids values prior to oxygenation different at the 0.01 level of significance from the similar values during oxygenation. In one case (Run B-2 at Plume Y), the difference between the means was found to be significant at the 0.05 level. Based on all this evidence, it is concluded that oxygenation did not materially affect the concentration of suspended solids in the plume. The one case of the statistical test indicating that the concentration increased is considered to be a chance happening and does not reflect true differences in the field. This conclusion is supported by the fact that, with the exception of Plume Y in Run B-2, in no case was the difference significant even at the 0.20 level. Thus, oxygenation did not affect the level of suspended solids observed.

59. Immediate oxygen demand of pipeline samples. During each test run, samples of the discharge slurry were obtained at the sample port immediately upstream of the oxygen-injection point and also at the end of the discharge pipe. The IOD of these samples was determined by measuring the oxygen uptake of sample aliquots in the field. Later in the laboratory the amount of solids which had been added to each bottle was determined. Although the procedures followed were identical to those recommended in the laboratory studies (Chapter III), the pressures caused by working in the field (numerous samples, limited time, inadequate laboratory facilities, etc.) prevented the field laboratory technician from maintaining the necessary 40 to 70 percent oxygen depletion in all cases. As a rule, only one dilution was run on each slurry sample.

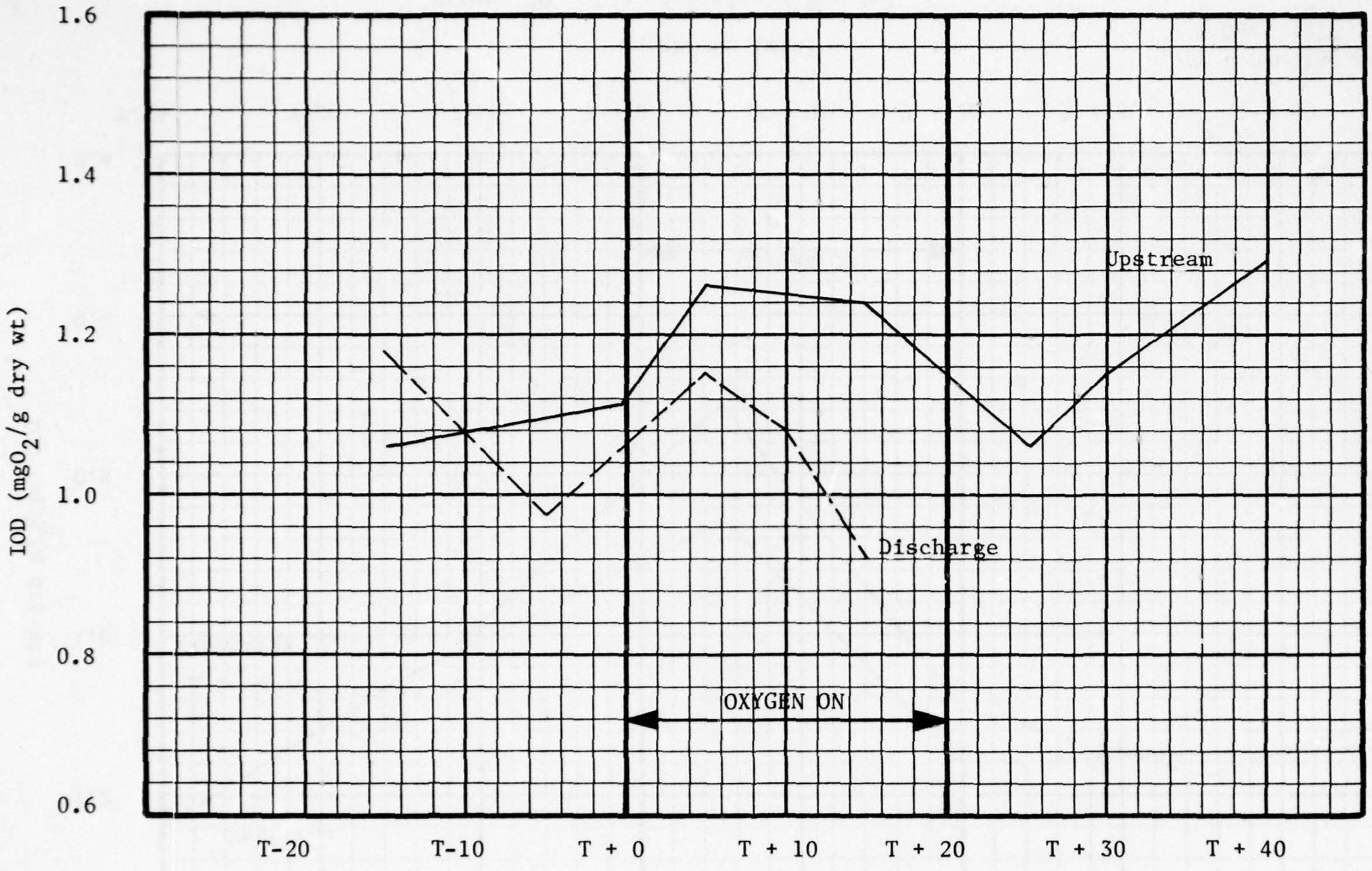
60. Because oxygen was being added to the dredge discharge slurry during each oxygenation run and because a significant effect was observed in the level of DO in the water in the disposal area as a result of oxygen injection, it should be possible to detect a difference in the IOD of pipeline samples between those oxygenated and those which were not. Figures 20 through 23 show the values of IOD found at the sample port upstream of the oxygen-injection point and the IOD values found at the point of discharge. In each case the effect of oxygenation is relatively small. For Runs A-1, A-2, and B-2, it appears that during the oxygenation period the IOD values at the discharge point were somewhat lower than the upstream values. For Run B-1 visual observation did not indicate any obvious effect of oxygenation.

61. To further determine the effect of oxygenation on the IOD of pipeline samples, the average value for each run of IOD for all nonoxygenated samples was calculated. The average IOD of all oxygenated samples was also determined. These values are shown in Table 6. The nonoxygenated values are seen to be quite similar for each run. The oxygenated values are generally lower, but with greater variability from one run to the next. In three of the four cases (Runs A-1, A-2, and B-2), the average oxygenated IOD value was less than the corresponding value without oxygenation. The differences in these cases were found to be significant at the 0.05 level, but not at the 0.01 level. In the case of Run B-1, the oxygenated value was slightly greater than the nonoxygenated value. When data from all the runs were lumped together, the oxygenated IOD values were significantly different from the nonoxygenated values at the 0.05 level, but not at the



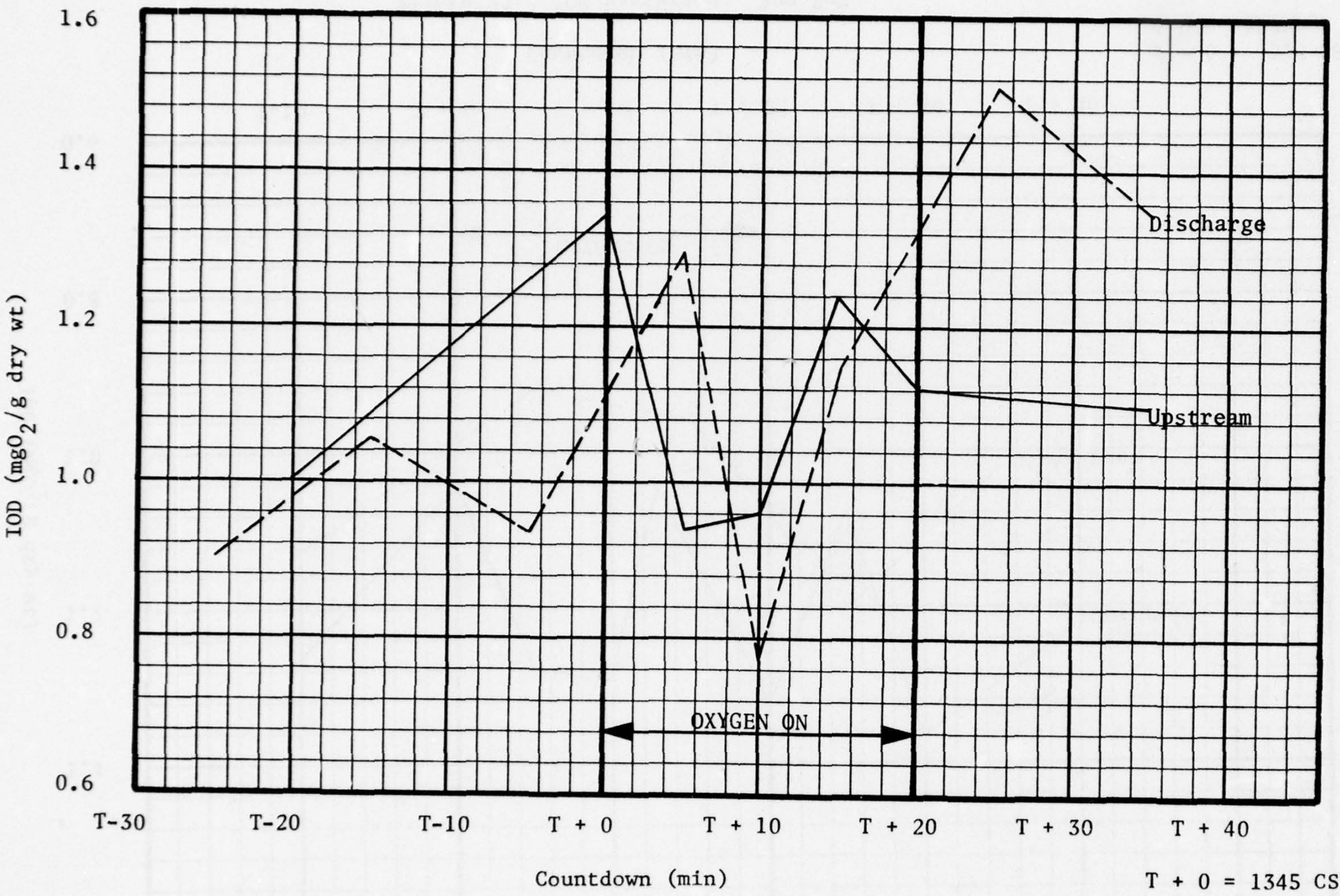
T + 0 = 155 CST
3 Dec 1975

Figure 20. IOD variation: Run A-1



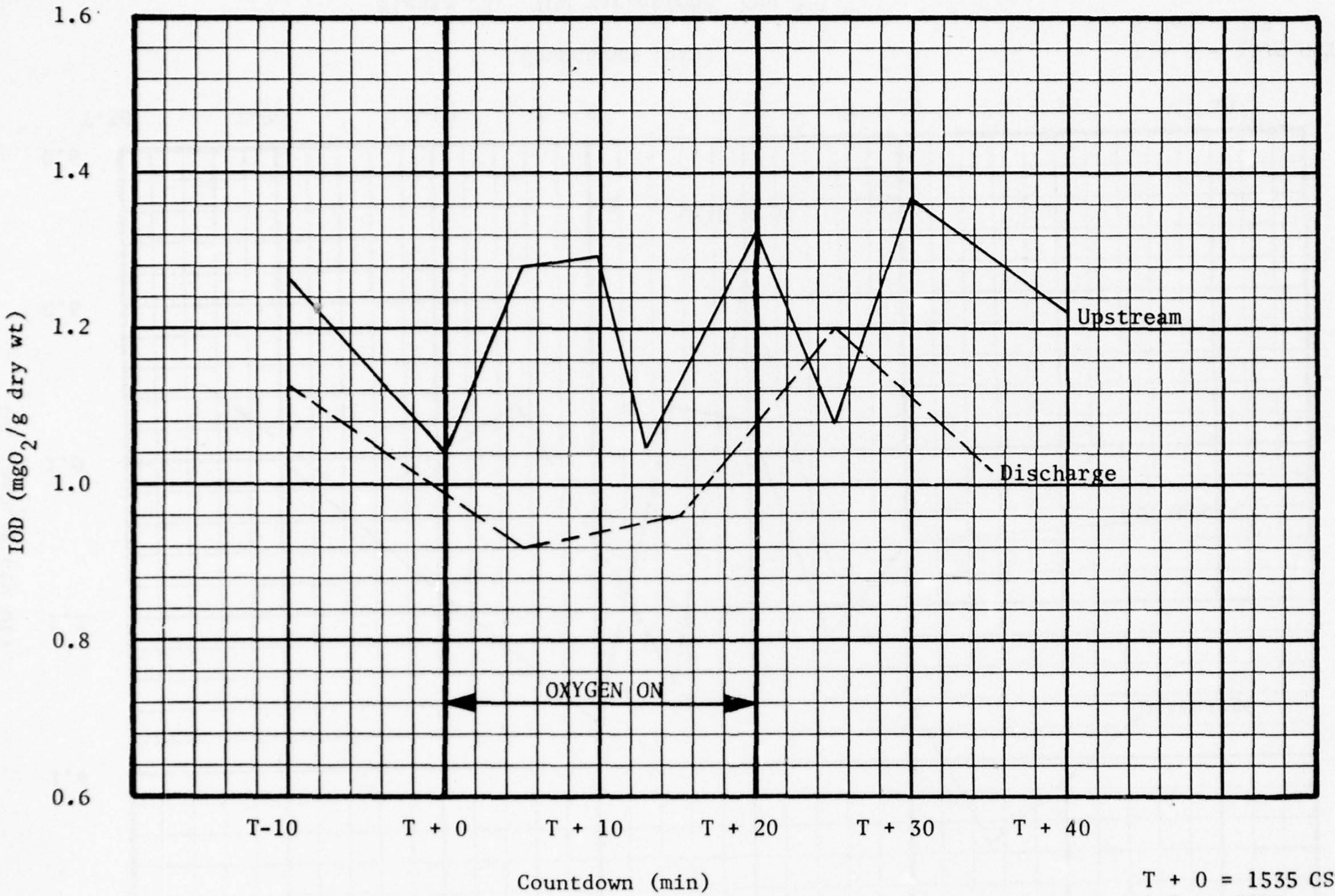
T + 0 = 0945 CST
4 Dec 1975

Figure 21. IOD variation: Run A-2



T + 0 = 1345 CST
4 Dec 1975

Figure 22. IOD variation: Run B-1



T + 0 = 1535 CST
4 Dec 1975

Figure 23. IOD variation: Run B-2

0.01 level. Therefore, it was concluded that the oxygenated values were probably lower than the nonoxygenated values. Variability introduced by rapidly changing conditions in the pipeline and by uncertainties in the IOD test itself prevented any conclusive finding that the anticipated IOD reduction due to oxygenation was actually observed.

Table 6

Immediate Oxygen Demand of Pipeline Samples*

Run	IOD, mg/g Nonoxygenated	 Oxygenated
A-1	1.10 ± 0.09	0.91 ± 0.19
A-2	1.12 ± 0.11	1.03 ± 0.14
B-1	1.10 ± 0.19	1.11 ± 0.20
B-2	1.16 ± 0.13	0.95 ± 0.01

*The value shown is the mean value ± one standard deviation.

Aeration Demonstration

Experimental design

62. A maintenance dredging project in the Mobile Bay ship channel, scheduled for completion in August 1976, was selected as the best opportunity for performing a field demonstration of air injection. The project was being supervised by the U.S. Army Engineer Area Office in Mobile. Owned and operated by OKC Dredging, Inc., Metairie, Louisiana, the dredge was the PAUL F. JAHNCKE, a 24-in. hydraulic cutterhead dredge with ball and socket discharge pipeline. The positions of the dredge when the air injection tests were performed are indicated in Figure 24.

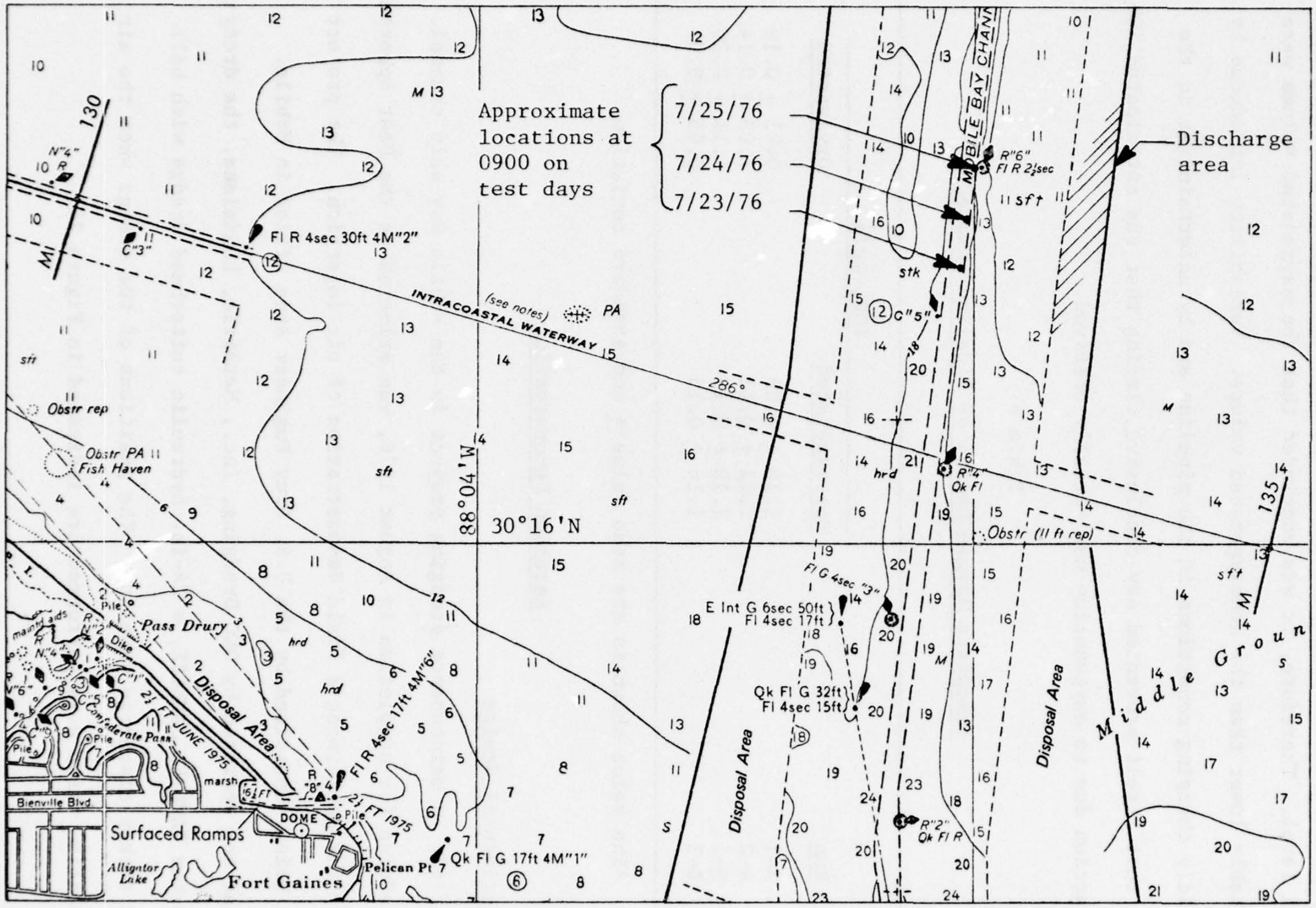


Figure 24. Air injection field demonstration locations

63. The experiment was designed to utilize a commercially available leased air compressor in combination with the injection manifold, nozzles, and controls already built and available from the previously conducted oxygen-injection demonstration. Except for miscellaneous services and supplies, all support for installing and servicing the equipment and conducting the tests was provided by dredge personnel.

64. The maximum air flow rates for the experiment were fixed primarily by the available injection equipment and air compressor. However, experience with oxygen injection had shown that for residence times of the order of 1 to 2 min, very little of the IOD of the sediments would react in the pipeline. The effectiveness of the oxygen injection appeared to be associated primarily with maintaining a fully saturated condition in the slurry water. Therefore, the air injection tests were planned so as to maintain an air flow rate well in excess of that required to saturate the water.

65. Figure 25 shows the amount of air flow required to saturate the water in a 24-in. pipeline as a function of the line velocity. The calculated rates are based on the conditions that prevailed during the tests, i.e., water temperature 25°C and salinity $31^{\circ}/oo$. The range of flow rates actually achieved is indicated in the figure. The amount of air in excess of that required for saturation was approximately 150 percent.

66. During all tests the dredge pump was operated at its normal speed of 290 rpm, which produces a velocity in the discharge line of approximately 18 fps. It was not practical to vary or reduce the pump speed for

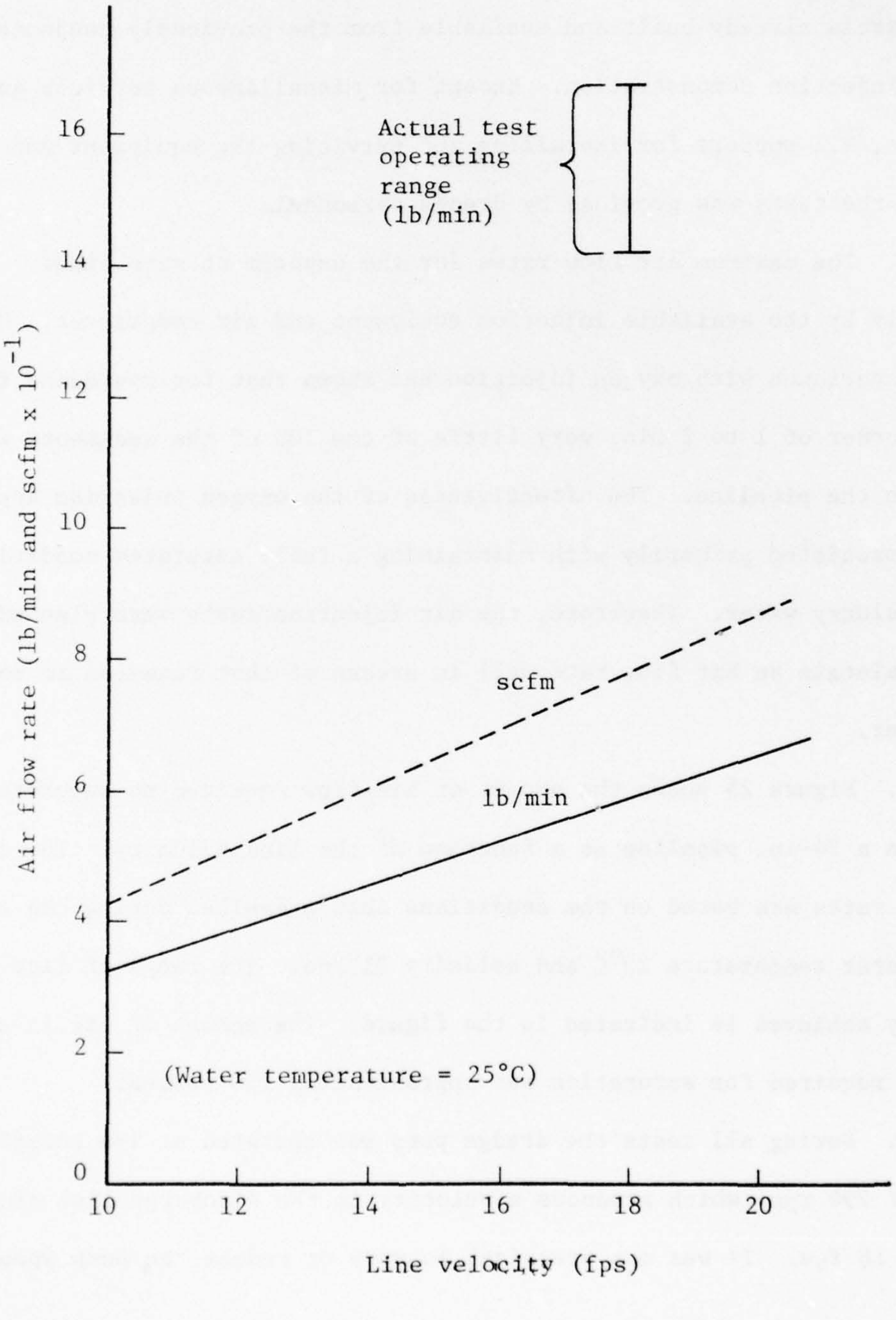


Figure 25. Air flow required to saturate water in a 24-in. pipeline

the tests because the pump is directly connected to a diesel engine which is limited to a narrow speed range for satisfactory operation. The Reynolds number in the pipeline was approximately 3.6×10^6, which is well into the turbulent region, ensuring good mixing of the injected air.

67. During the tests, the JAHNCKE was operating with a total pipeline length of 3000 ft. Two series of tests were run: one with the air injection point 1500 ft upstream of the discharge and the other 2300 ft upstream. The positions of the test points are shown schematically in Figure 26.

Test facilities and equipment

68. For the air injection demonstration, environmental measurements were made in the discharge area and in the channel ahead of the dredge. These included water temperature, salinity, water current, and pH. Samples taken for laboratory analysis included undisturbed sediments from the channel, slurry samples at the injection point and at the discharge, and water samples in the discharge plume. The sampling and measurement equipment utilized were the same as that for the oxygenation demonstration. Descriptions of these were given in the previous section and need not be repeated here.

69. The air supply used for the demonstration was a diesel powered portable air compressor of the type commonly used in construction work (Figures 27 and 28). The machine was rated at 600 scfm; however, this rating was specified only to ensure that a flow rate of 200 scfm could be obtained at maximum delivery pressure of 150 psi.

70. The injection nozzles and sampling tap were installed on a standard 40-ft section of the dredge's 24-in. discharge line. The eight

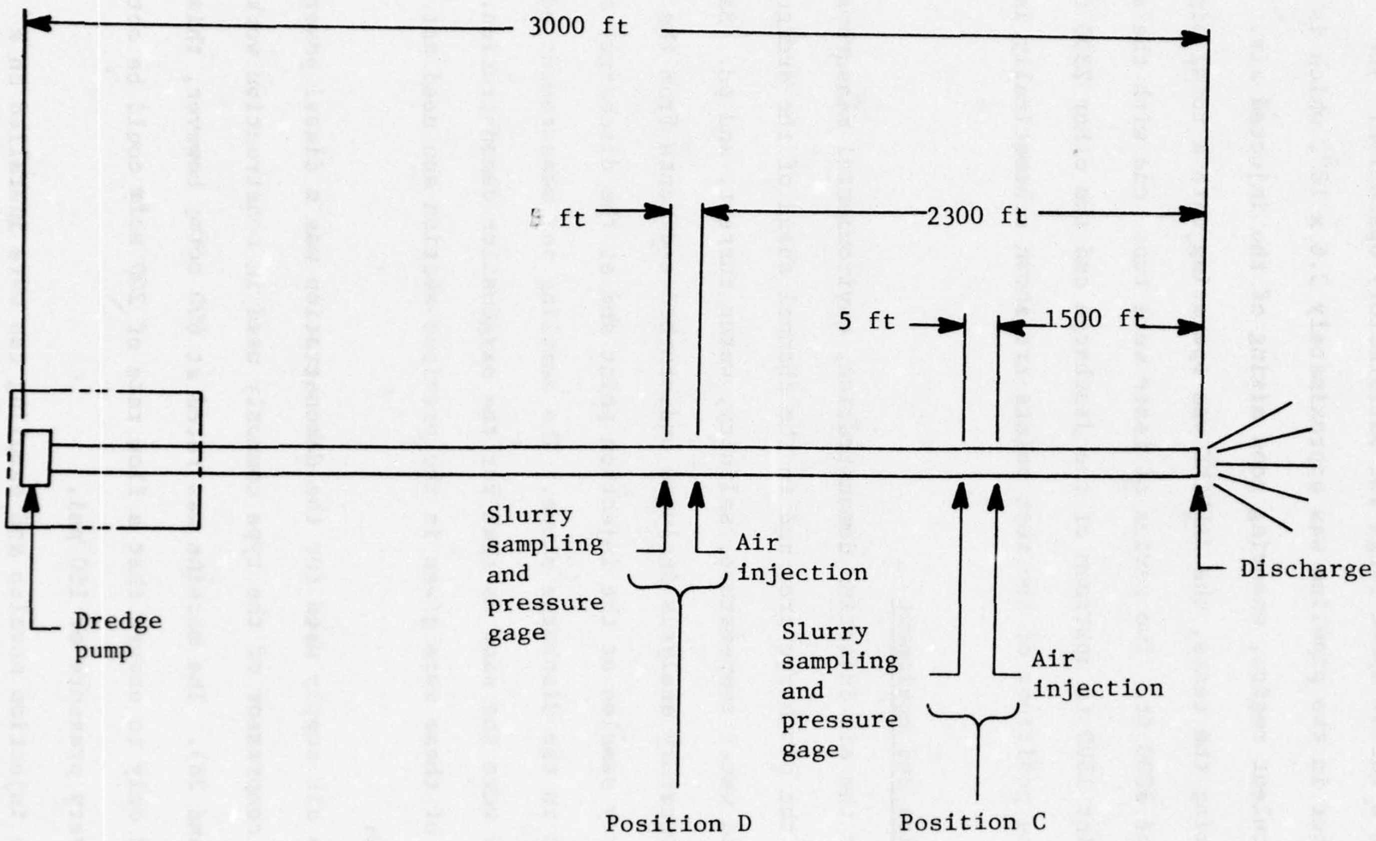


Figure 26. Positions of test points in pipeline (air injection)

Figure 27. Air compressor on barge

Figure 28. Air compressor at air injection point

injection nozzles and header, the orifice flow meter, and the control valves previously used for oxygen injection were used for the air tests with some modifications to adapt to the air connections. In order to provide more flow area, four of the nozzles, which had been made with seven orifices each of 0.063 in. diameter, were replaced with nozzles having only one orifice 0.297 in. in diameter. Thus, four nozzles had a flow area of 0.069 sq in. each and four had an area of 0.022 sq in. each. The injection air flow was therefore divided in proportion to the areas. The nozzles were located and spaced around the pipeline so as to ensure uniform injection into the stream.

71. The orifice flow meter was originally calibrated for pure oxygen flow. In order to use it for the air injection, a calibration curve for air was obtained from the manufacturer. The indicated air flow readings were adjusted by four correction factors: (1) the air calibration, (2) upstream pipe diameter, (3) observed air pressure, and (4) observed air temperature.

72. A sampling tap and pressure gage were installed in the test section about 5 ft upstream of the air injection nozzles. Pipeline pressure at the point of injection was monitored and slurry samples were extracted periodically during each test. In addition, periodic measurements of DO in the slurry were also made.

73. A schematic of the air injection system is shown in Figure 29, and the system is illustrated in the photos, Figures 30 and 31. For the test operations air flow was controlled by a throttling valve upstream of the flow meter. The air compressor ran continuously during the tests, automatically maintaining a constant pressure in the receiver of the unit. The throttling valve was manipulated to maintain a constant flow rate, and

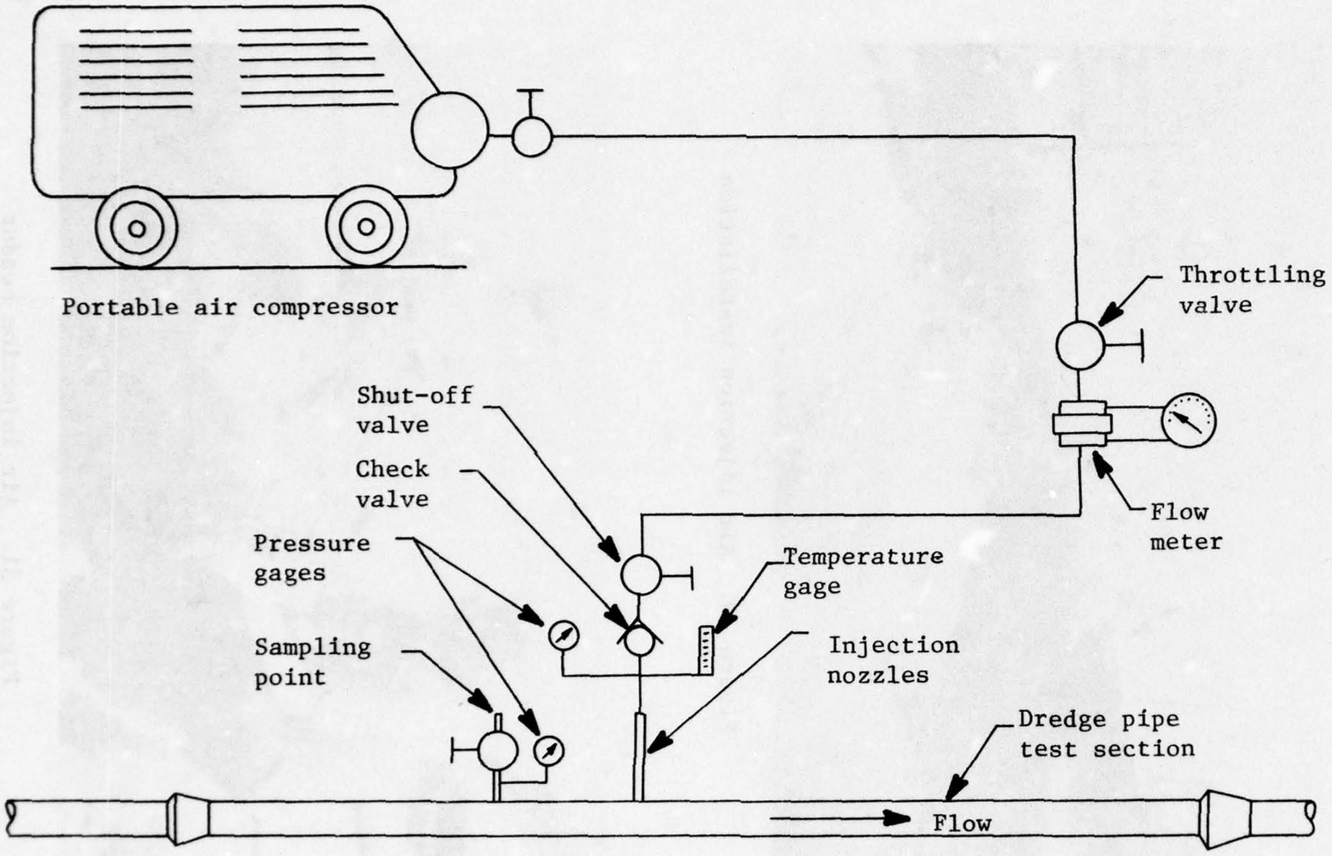


Figure 29. Air injection system

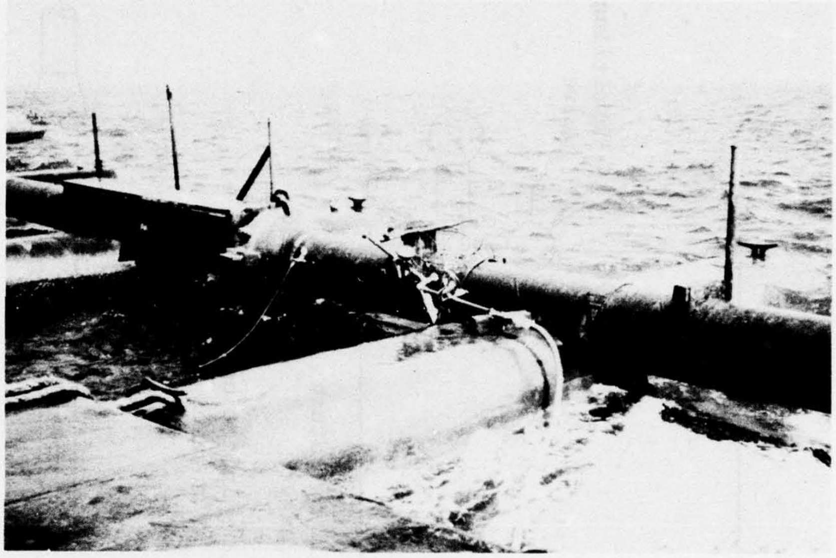


Figure 30. Air injection installation

Figure 31. Air injection header

the air pressure upstream of the injection nozzles simply established a level equal to the pressure in the pipeline plus the pressure drop across the nozzles.

Test operations

74. The tests using compressed air were similar to those described previously for oxygenation. Measurements were made before air injection to establish background conditions, and intensive sampling and measurement efforts took place immediately before, during, and after pipeline aeration. Several stations were used for sampling and measurements. These were similar to those described previously for oxygenation, as noted below:

a. Bridge of the dredge

b. Aeration barge

c. Pipeline discharge

d. Plume - Only one plume station was used, because the oxygenation tests had indicated that more useful data could be obtained by intensively studying one location than by less intensively observing two.

e. Field laboratory - in motel

75. The sequence of operations for each aeration test was the following:

a. Check aeration system to ensure its readiness for the test.

b. Sampling boat assumes its station in the plume and begins to take readings and collect water samples at approximately T-20 (T-0 was the time of beginning air injection). Begin taking pipeline samples at the same time.

c. At T-0 begin air injection.

d. At T+30 turn off air.

e. After readings return to normal (T+45 to T+50), cease monitoring the plume and the pipeline.

76. Although a constant air flow rate, as measured on an orifice meter, was maintained during each test, fluctuations in pressure and temperature of the injected air yielded minor fluctuations in the actual mass rate of air injected during each run. Another source of variability in the balance between oxygen supply and demand was, as in the oxygenation tests, an occasional change in discharge line pressure. Calculations to convert meter readings to true air flow on a mass basis showed that the supply of air was quite consistent. Accordingly, the average rate is a valid measure of air supply for each run.

77. The air flow rates achieved during the test runs in Mobile Bay are summarized in Table 7. Because IOD was not strongly decreased in the previous oxygenation tests and because time constraints limited the size of air supply equipment which could be procured, air supply was planned to be certain to saturate the water, but not to attempt satisfaction of IOD. Therefore, Table 7 does not consider IOD. Based on the average conditions which occurred during each test, the oxygen supply rates are shown as a percentage of the total that would have been required to saturate the water.

Test results

78. Background data. Observations and measurements made in Mobile Bay near the dredging operation but outside its zone of influence produced a quantitative description of background conditions. This site was similar to the Apalachicola Bay site in that conditions were fairly uniform in the horizontal, with a vertical salinity stratification. A typical water column profile is shown in Table 8. Ambient suspended solids appear relatively high, and DO is at or near saturation.

Table 7

Air Flow Rates and Requirements

	Run Number*			
	C-1	C-2	C-3	C-4
Air Flow Rate:				
scfh	13,076	12,096	12,266	11,426
lb air/min	16.7	15.4	15.6	14.4
lb O_2/min	3.9	3.6	3.6	3.3
g O_2/min (1)	1,771	1,634	1,634	1,498
O_2 Rate Req'd to Saturate Liquid in Equil. with Air (g O_2/min) (2)	623	631	609	612
% of Total O_2 Provided Relative to Equil. with Air: $\frac{(1)}{(2)}$ X 100	284	259	268	245

	Run Number*			
	C-5	D-1	D-2	D-3
Air Flow Rate:				
scfh	11,141	13,051	12,854	12,645
lb air/min	14.2	16.7	16.3	16.1
lb O_2/min	3.3	3.9	3.8	3.7
g O_2/min (1)	1,498	1,771	1,725	1,680
O_2 Rate Req'd to Saturate Liquid in Equil. with Air (g O_2/min) (2)	585	635	631	630
% of Total O_2 Provided Relative to Equil. with Air: $\frac{(1)}{(2)}$ X 100	256	279	273	267

For all runs:
Flow Rate of Slurry = 24,330 gpm

Table 8

Background Measurements, Mobile Bay*

Depth, ft	Oxygen mg/ℓ	Water Temp. °C	Salinity °/oo	Suspended Solids mg/ℓ	Turbidity NTU	Current knots
Surface	8.0	31	13	56	5	--
3	8.1	30	13	--	--	0.4
6	8.1	30	14	140	12	0.5
10	8.2	28	19	--	--	0.1
(Bottom depth 11 ft)						

* Air temperature 30°C; date, 7/23/76; time, 1300 hr.

79. Slurry solids fractions. Samples of the material passing through the pipeline were taken immediately upstream of the air-injection point in a manner similar to the sampling during the oxygenation trials. The field demonstration in Mobile Bay was different from that in Apalachicola chiefly in the high frequency of traffic in the channel causing periods during which the dredge was pumping water with little or no bottom sediment. Chiefly because of the many periods of watery discharge, the slurry densities in Mobile, shown in Table 9, were generally lower than those in Apalachicola. Several other characteristics of the pipeline materials, together with some statistical data, are shown in Table 9.

Table 9

Statistics of Slurry Densities, Air Barge Samples

	Run Number							
	C-1	C-2	C-3	C-4	C-5	D-1	D-2	D-3
Slurry Density P_s (g/cc)	1.09	1.07	1.12	1.13	1.18	1.06	1.07	1.08
Std. Deviation of P_s	0.039	0.045	0.081	0.059	0.070	0.026	0.044	0.046
(Coeff. of Variation, %)	(3.5)	(4.2)	(7.2)	(5.3)	(5.9)	(2.4)	(4.1)	(4.2)
Number of Samples	5	9	9	10	10	7	7	6
Range of P_s (g/cc)	1.03- 1.19	1.03- 1.17	1.04- 1.30	1.04- 1.24	1.03- 1.27	1.04- 1.11	1.03- 1.14	1.03- 1.16
% Solids by Volume	5.0	3.8	7.2	6.8	10.9	3.3	3.9	4.0
% Solids by Weight	12.0	9.2	16.3	16.7	23.7	7.9	9.3	10.2

For all runs:
Density of solids = 2.66 g/cc; density of seawater = 1.01 g/cc

80. No systematic trends from run to run are apparent in Table 9 although Runs C-3, C-4 and C-5 appear to have higher solids fractions than earlier and later runs.

81. Dissolved oxygen in the water column. Observations of DO content in the disposal area water column were made from a single boat which was anchored for each run in the center of the plume approximately 50 ft from the discharge. Dissolved oxygen was measured at 5-min intervals beginning 20 min before the start of aeration and ending 15 to 20 min after the end

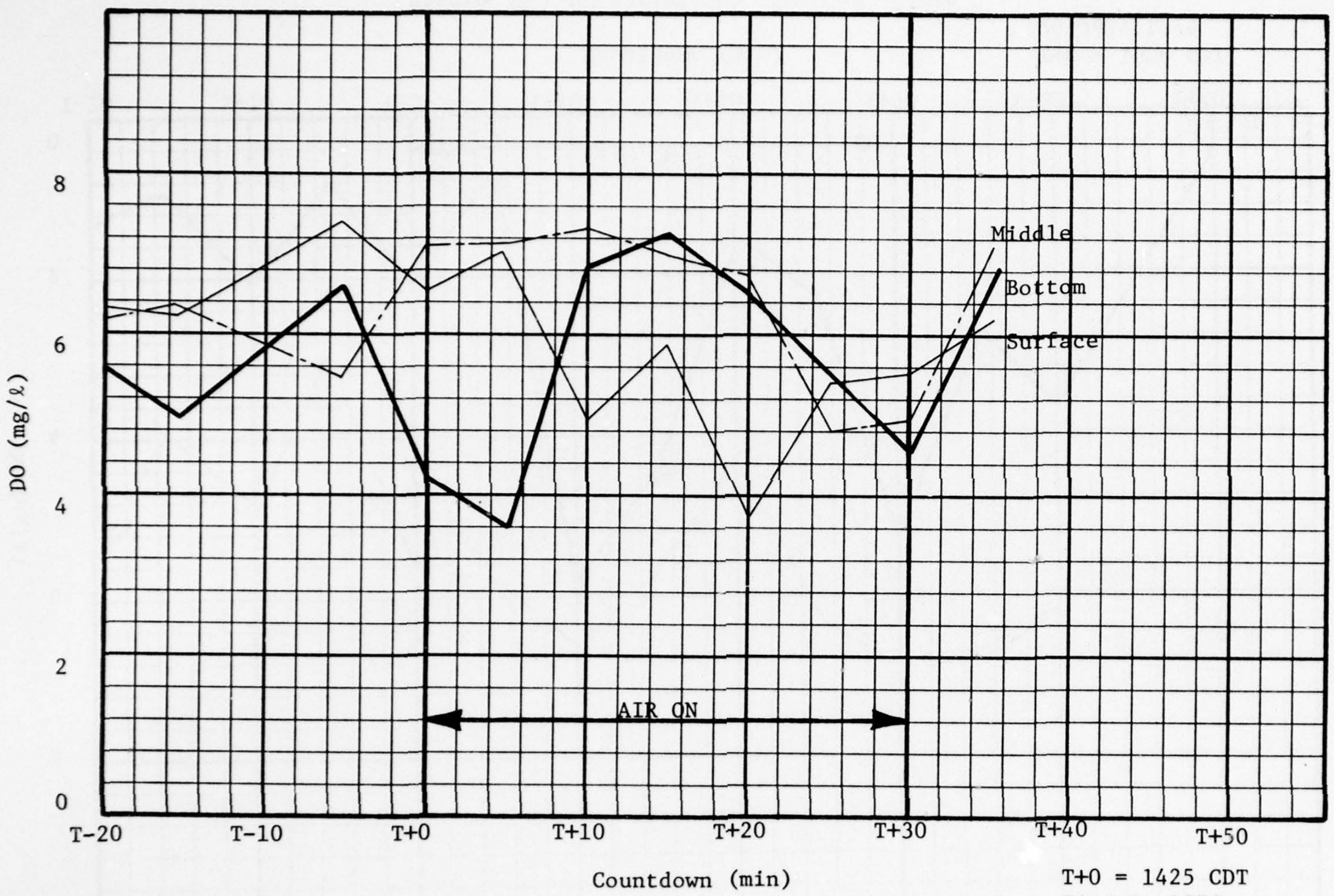
of aeration. Measurements were taken at three depths at each time interval: 3 ft below surface, 6 ft below surface, and 1 ft above the bottom. Water depths were 11 to 13 ft in the discharge area.

82. Figure 32 shows the effect of aeration on DO in the water column for Run C-1. It is difficult to infer from this graph any benefit from aeration; the average DO at all three depths appears not to have changed while the air was on. The rise in bottom DO at T+5 is encouraging until one notes the subsequent fall while the air was still on and the rise in DO at all levels after the air was turned off.

83. Run C-2, Figure 33, is slightly more promising in that the bottom DO appears higher during the aeration period. The average bottom DO before aeration was 1.4 mg/ℓ ; during aeration the average rose to 3.2 mg/ℓ and returned to lower values after aeration.

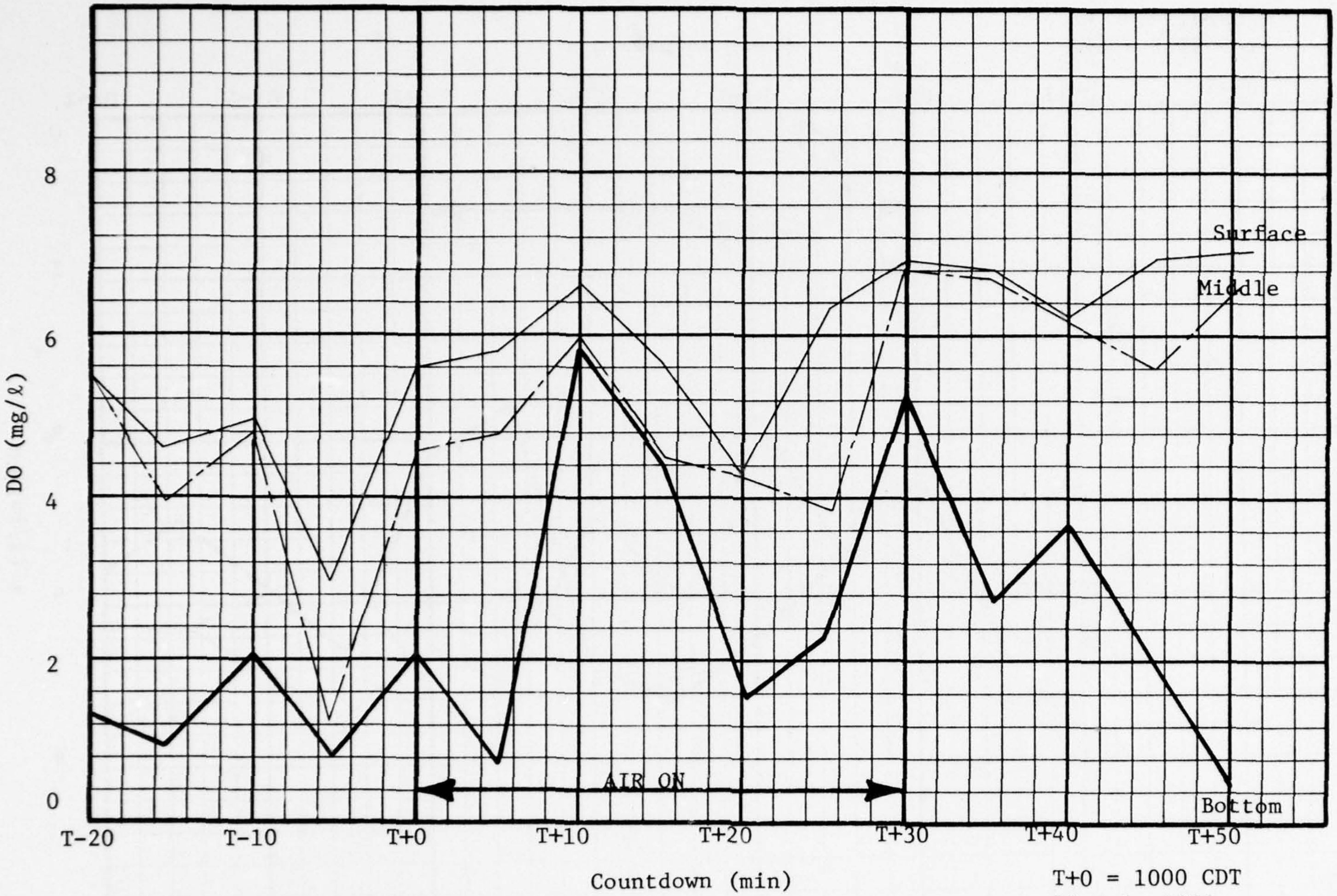
84. No apparent effect of aeration is observable for Run C-3, Figure 34. Run C-4, however, shows an apparent increase in bottom DO during aeration (Figure 35). Before aeration, average DO was 2.9 mg/ℓ , and during aeration the average was 4.4 mg/ℓ despite one very low value. A confident assessment of improvement is hindered here, however, by the rise in DO after the air was turned off. It should also be noted that pipeline samples taken at T+25 were quite watery, and this factor may have had some effect in raising DO levels.

85. Runs C-5, D-1, and D-2 (Figures 36, 37, and 38) provide little or no evidence of benefit from air injection. The difference between runs prefixed C and D is that on C runs the air barge was 1500 ft from the discharge, while on D runs, the distance was 2300 ft. Valid interpretation of



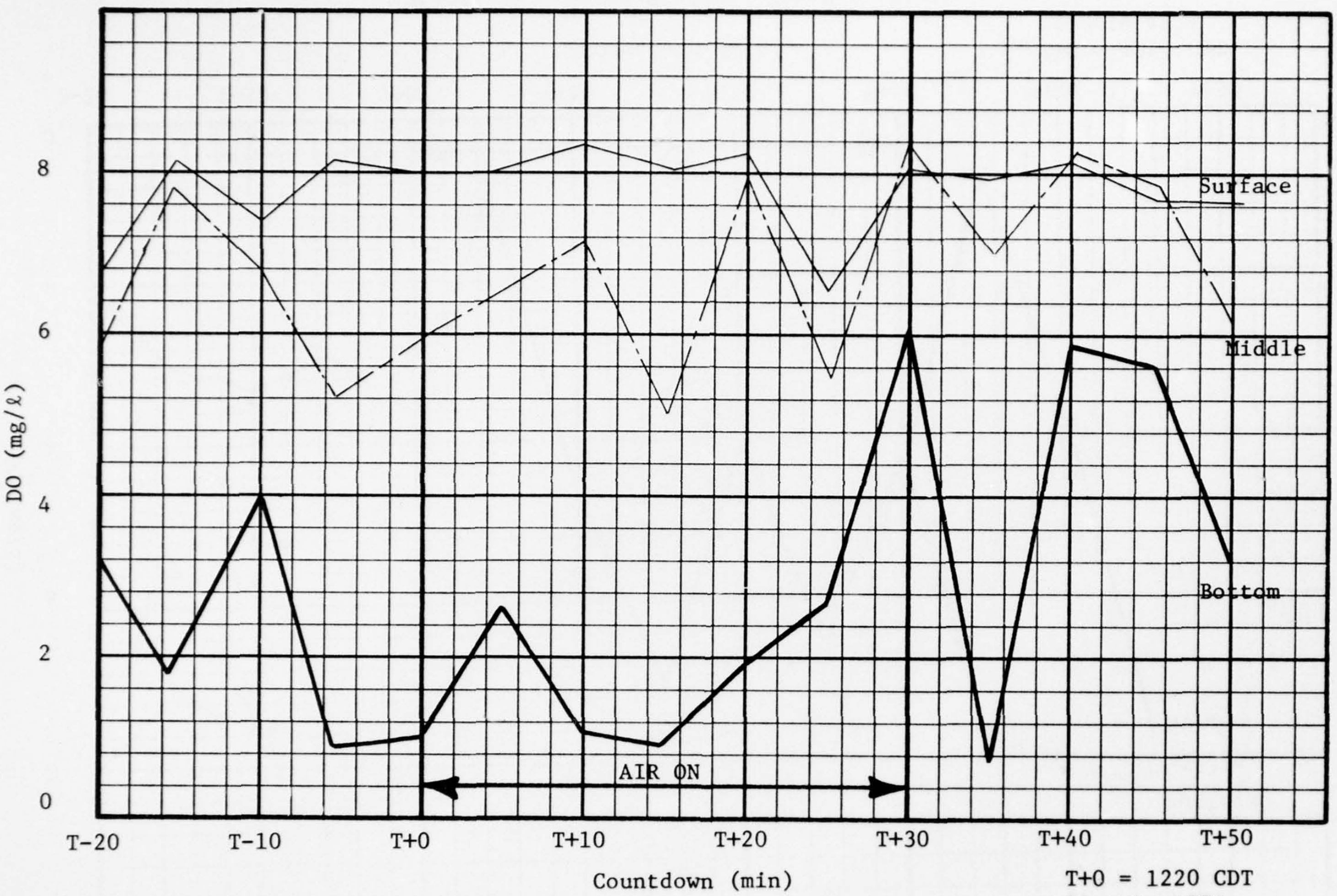
T+0 = 1425 CDT
23 July 1976

Figure 32. DO variation: Run C-1, Plume



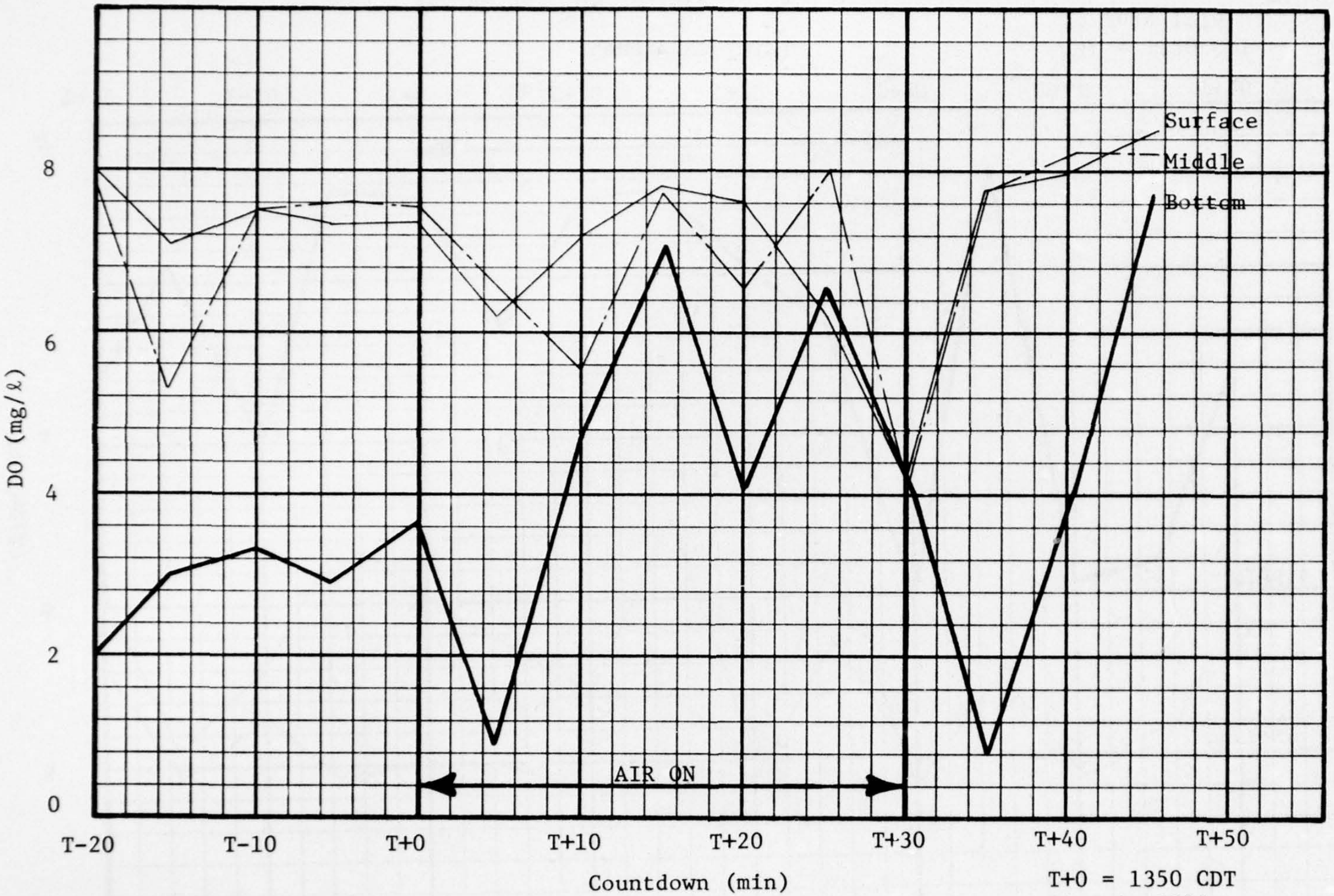
T+0 = 1000 CDT
24 July 1976

Figure 33. DO variation: Run C-2, Plume



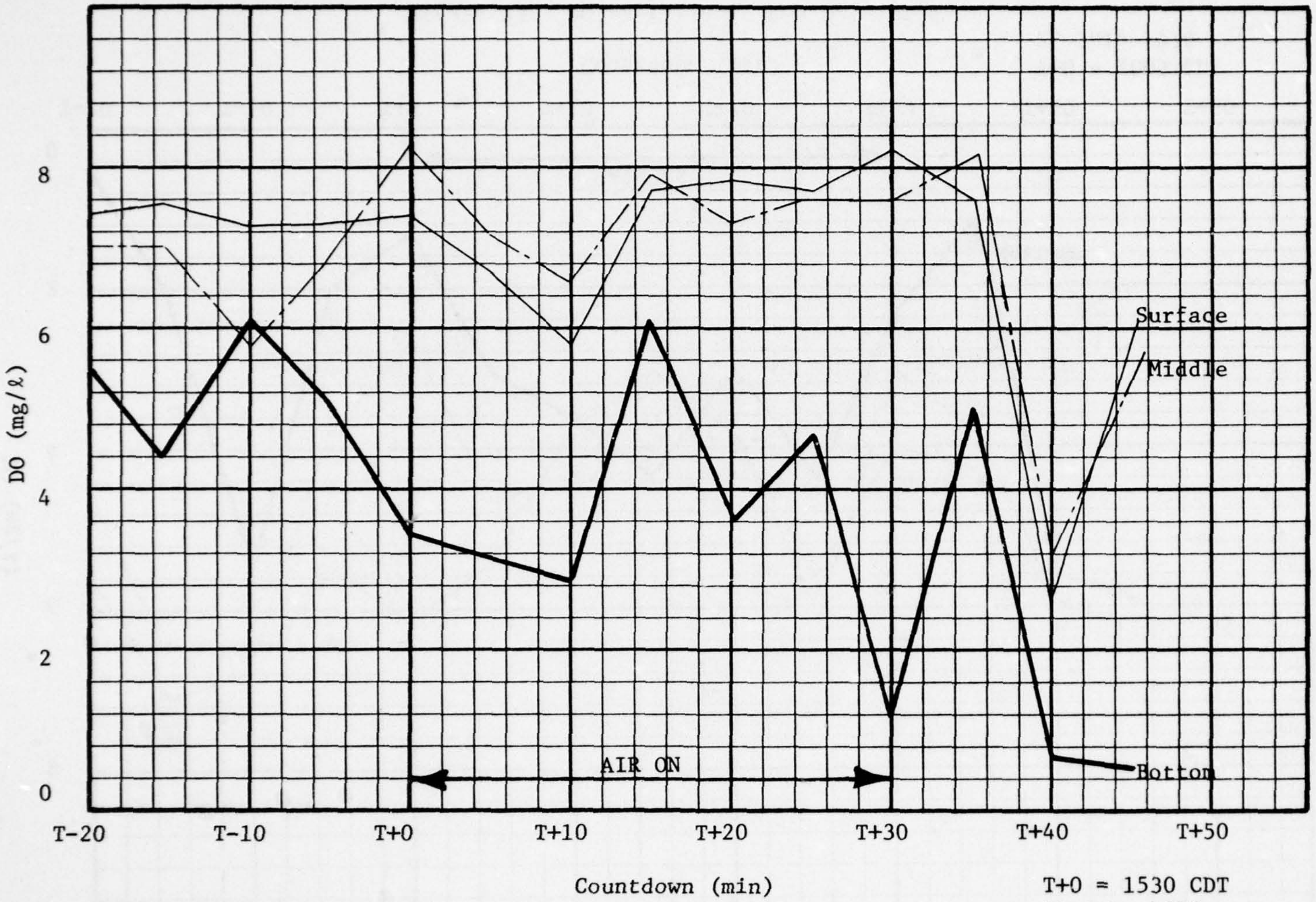
T+0 = 1220 CDT
24 July 1976

Figure 34. DO variation: Run C-3, Plume



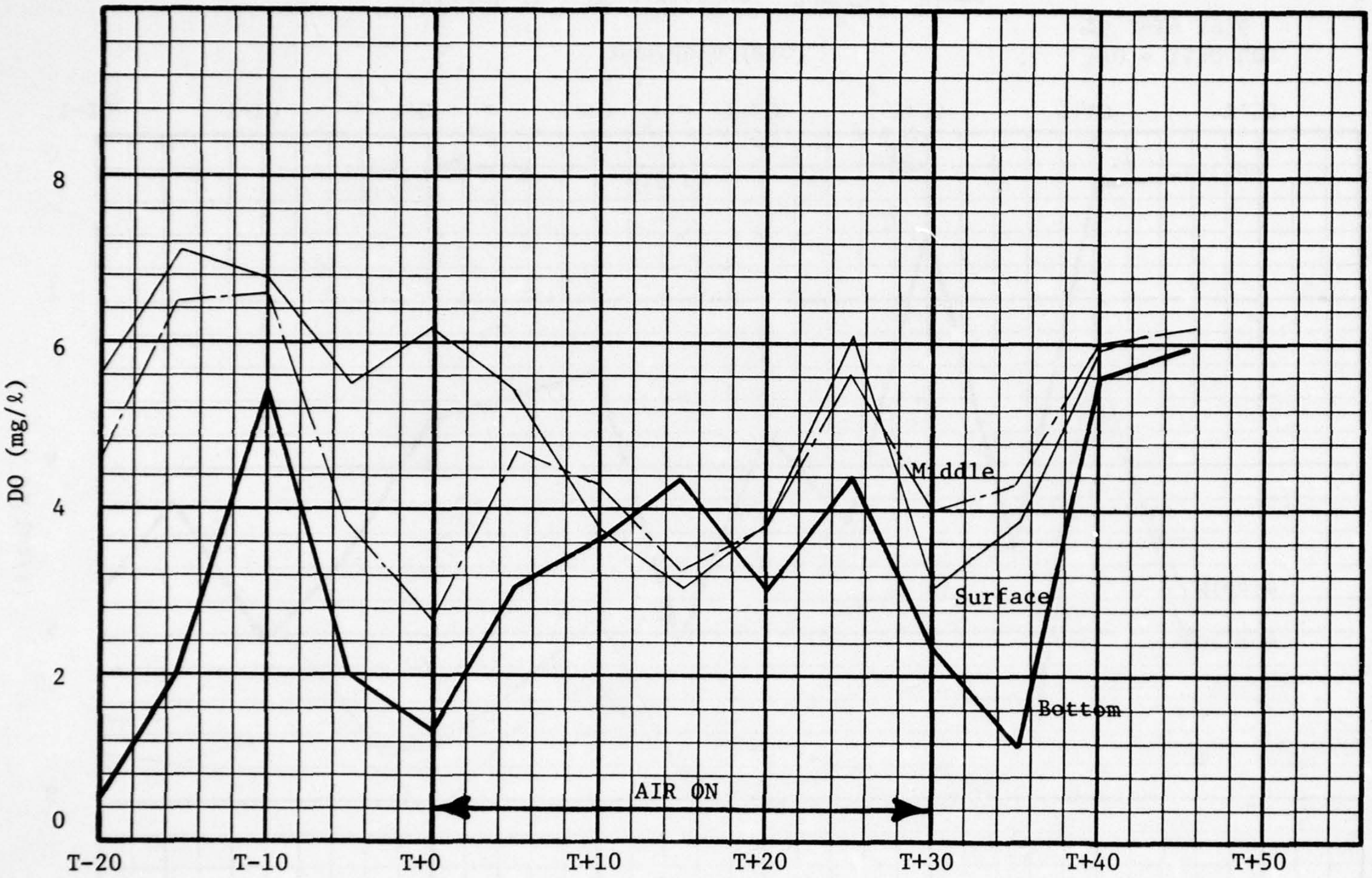
T+0 = 1350 CDT
24 July 1976

Figure 35. DO variation: Run C-4, Plume



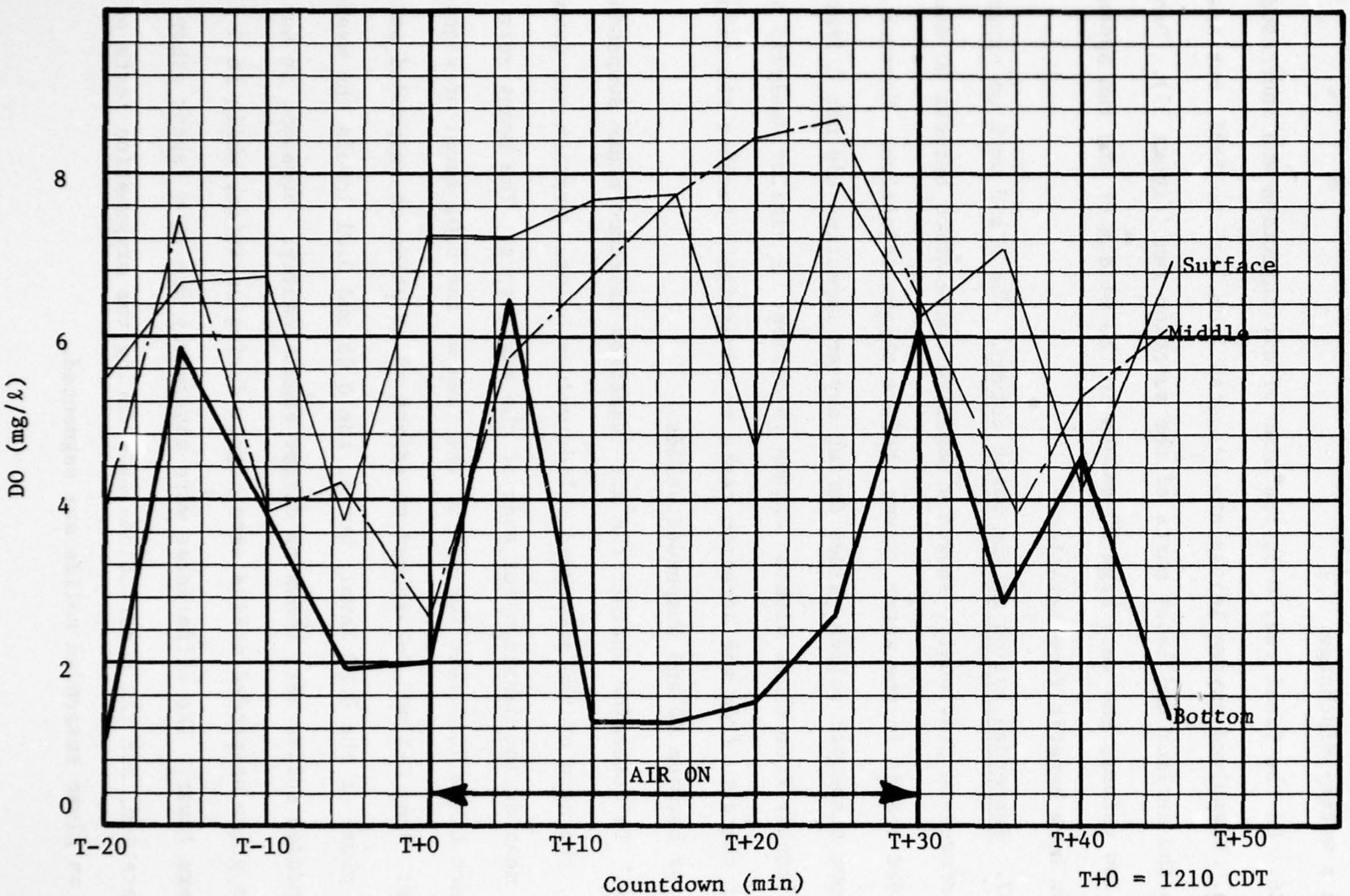
T+0 = 1530 CDT
24 July 1976

Figure 36. DO variation: Run C-5, Plume



T+0 = 1005 CDT
25 July 1976

Figure 37. DO variation: Run D-1, Plume



T+0 = 1210 CDT
25 July 1976

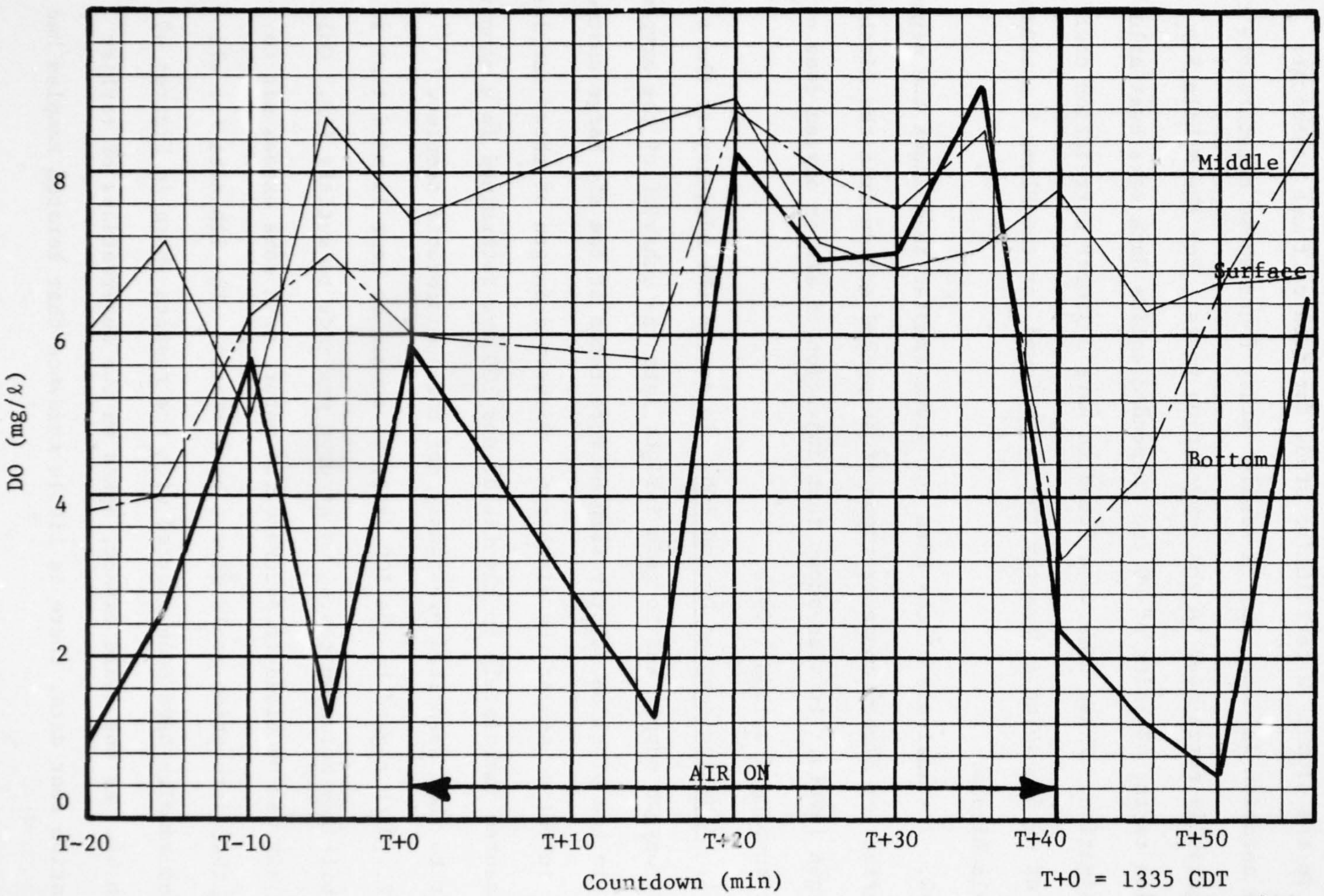
Figure 38. DO variation: Run D-2, Plume

Run D-1 is confounded by the field observation that much of this run involved a watery discharge.

86. On the final run, D-3, the time of air injection was increased to 40 min. Dissolved oxygen levels are elevated from T+15 to T+35, but are low in the earlier and later parts of the aeration run (Figure 39). Despite these low values, the very high DO values in the middle of the run appear to show some benefit from aeration.

87. Suspended solids in the water column. The field work on oxygenation, discussed previously, showed a negative correlation between DO and suspended solids in the water column, before oxygen injection. However, the plume suspended solids values during oxygen injection did not differ significantly from those without oxygen injection. A similar analysis was made of the data from the aeration tests to investigate further the relationships between DO and suspended solids.

88. To determine whether the air injection affected plume suspended solids, the mean of the suspended solids values before aeration was compared to the mean during aeration for each of the eight runs. The means were found not to be different for six of the runs at the 0.01 level of significance. Runs C-1 and C-2 showed no effect of aeration on suspended solids in the plume at the 0.20 level, but at the 0.05 and 0.01 levels the means of suspended solids were shown to differ significantly. However, in Run C-1 the plume suspended solids were higher during aeration, while in C-2 they were lower. The differences were apparently due to a factor other than aeration, and the observations made during the oxygenation tests of no effect on plume suspended solids are augmented.



T+0 = 1335 CDT
Date: 25 July 1976

Figure 39. DO variation: Run D-3, Plume

AD-A046 482 J B F SCIENTIFIC CORP WILMINGTON MA F/G 13/2
OXYGENATION OF DREDGED MATERIAL BY DIRECT INJECTION OF OXYGEN A--ETC(U)
OCT 77 R W NEAL, R B POJASEK, J C JOHNSON DACW39-75-C-0105
UNCLASSIFIED WES-TR-D-77-15 NL

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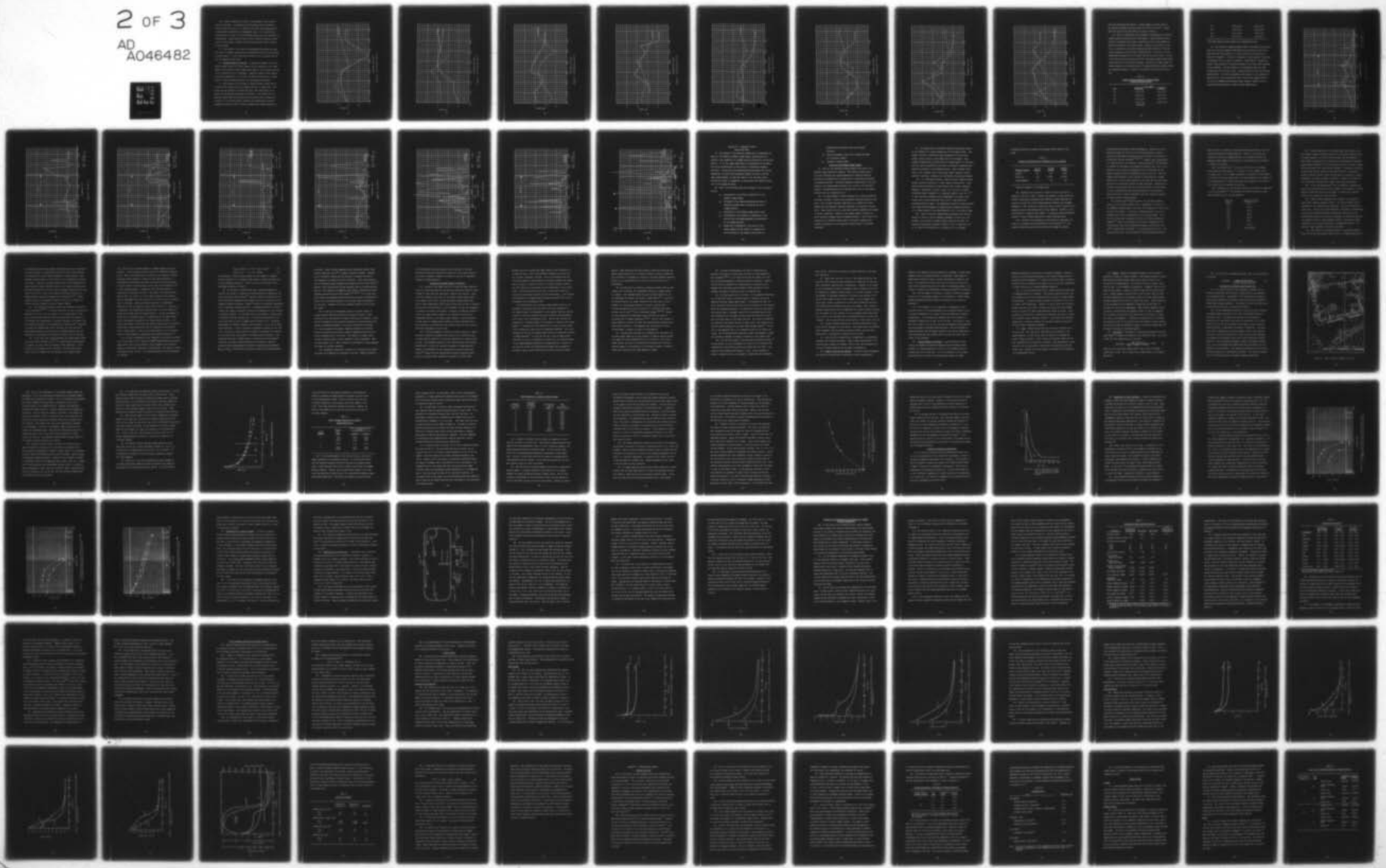
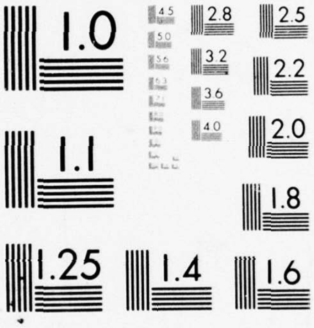




MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

89. Another examination was made of DO-suspended solids relationships in the plume: a correlation study for data on these parameters before aeration in each run. A similar study found these constituents to be negatively correlated in the oxygenation tests. For the Mobile Bay aeration tests, 48 pairs of DO and suspended solids data were available for investigation. These data were found to have a linear correlation coefficient of -0.69, which is exactly the value found for the Plume X station at Apalachicola.

90. The analysis of the data for plume samples thus shows the negative effect of higher concentrations of suspended solids from the discharge on oxygen levels. It also shows that injection of air or oxygen does not affect suspended solids levels.

91. Pipeline samples DO and IOD. To assess the adequacy of the air-induced oxygen supply and to gain insight into the behavior of the oxygen demand in the pipeline, slurry samples were taken at the air barge upstream of air injection and at the discharge. Dissolved oxygen of these samples was measured immediately in the field, and IOD was determined in a manner similar to that described previously for the Apalachicola samples.

92. With regard to the IOD data, it should be kept in mind that in the Mobile Bay aeration tests, no attempt was made to satisfy IOD. Only enough air was provided to saturate the water, with some excess air to ensure that saturation would always be achieved. The IOD data for all pipeline samples have been plotted with the results shown in Figures 40 through 47. As one would expect, based on the observations of earlier oxygenation test data, there is little evidence that aerated samples had

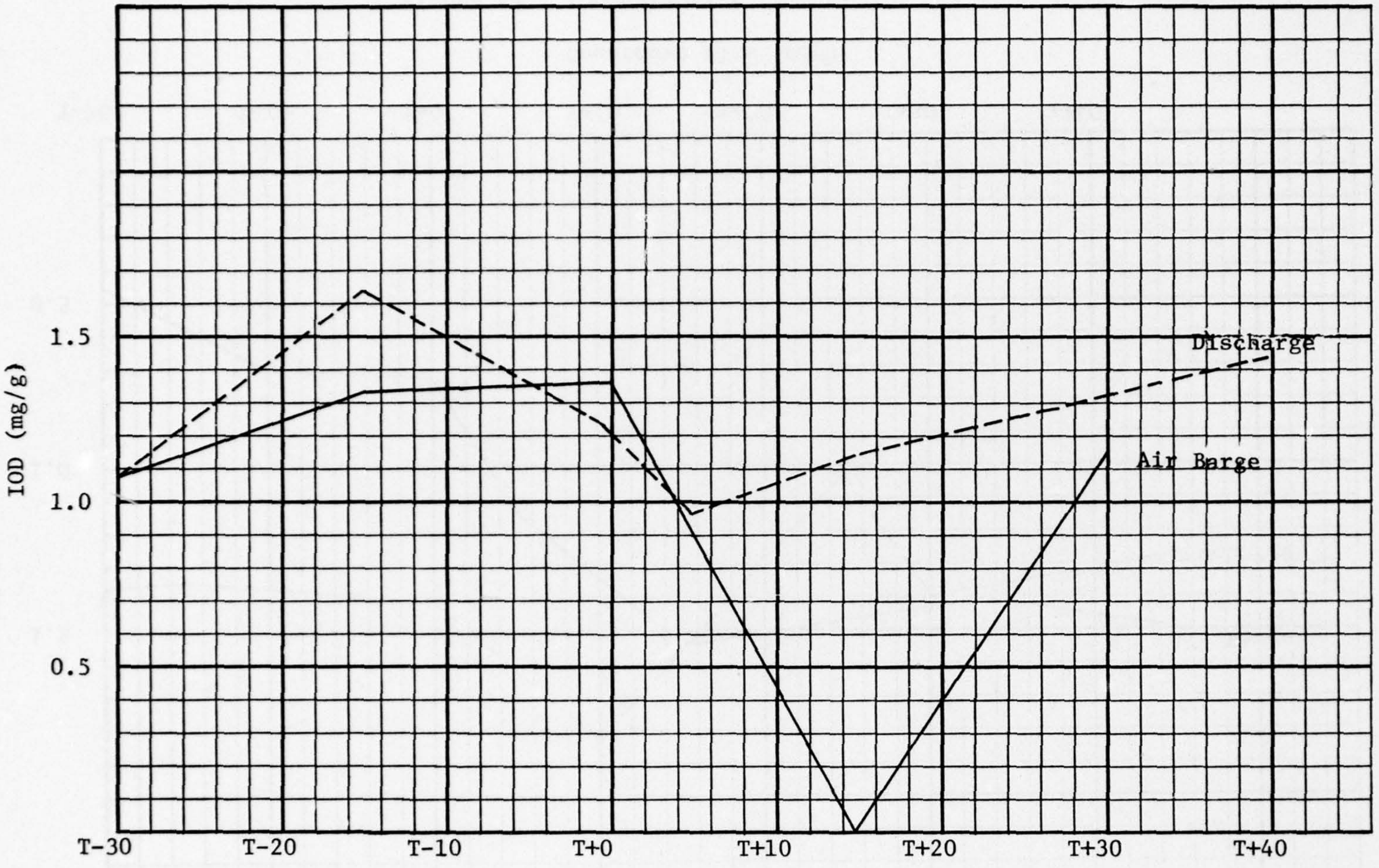


Figure 40. IOD variation, Run C-1

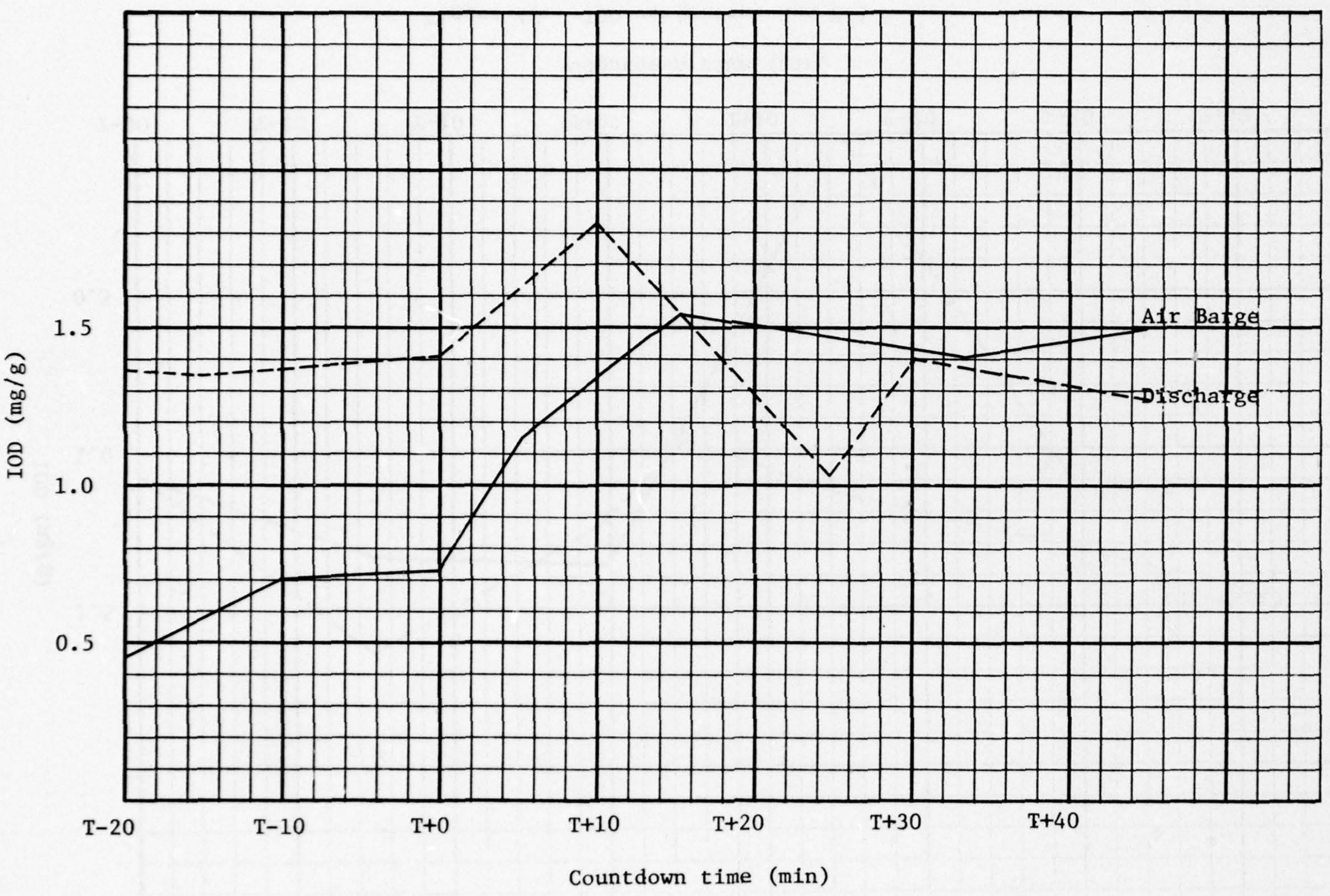


Figure 41. IOD variation, Run C-2

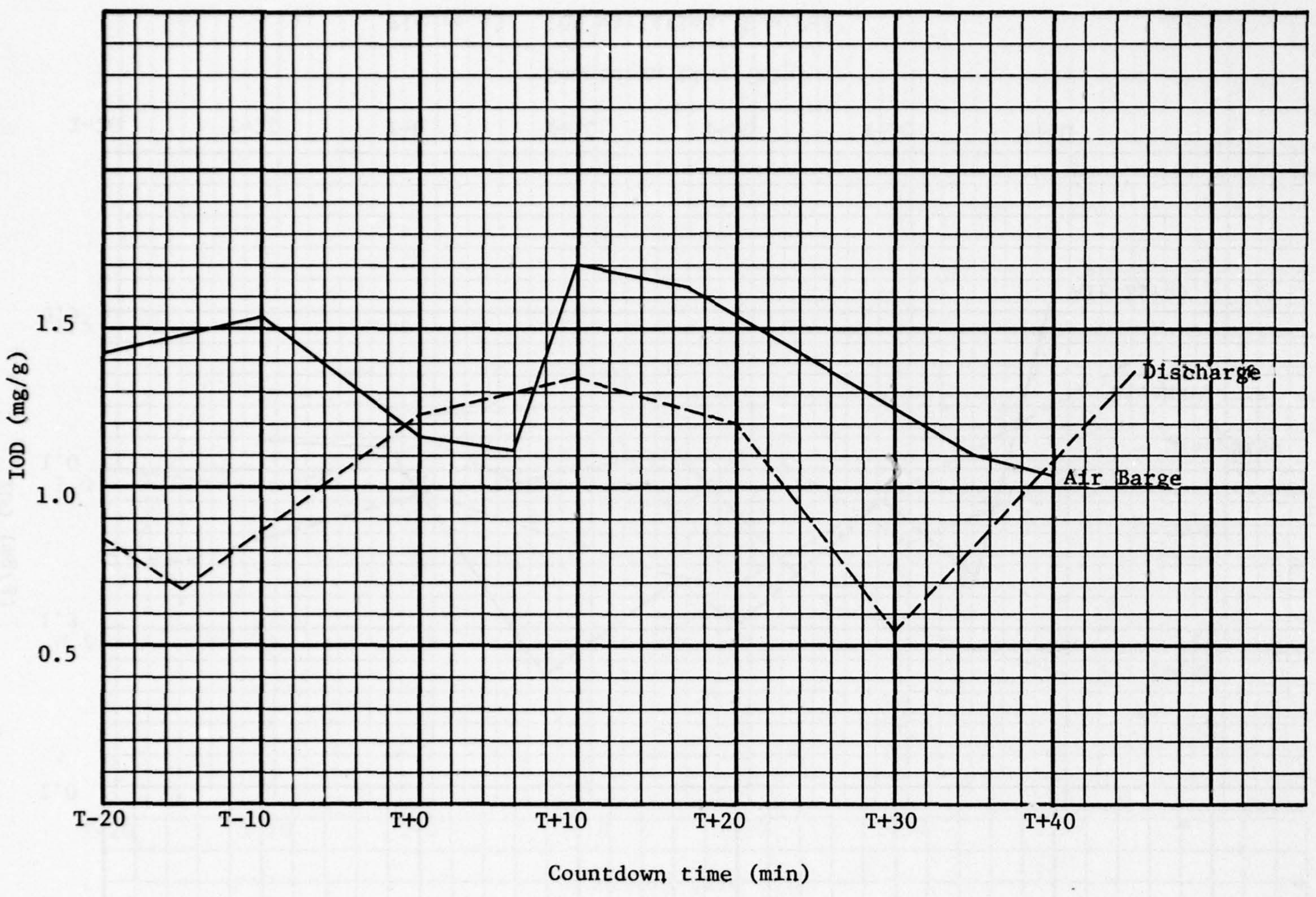


Figure 42. IOD variation, Run C-3

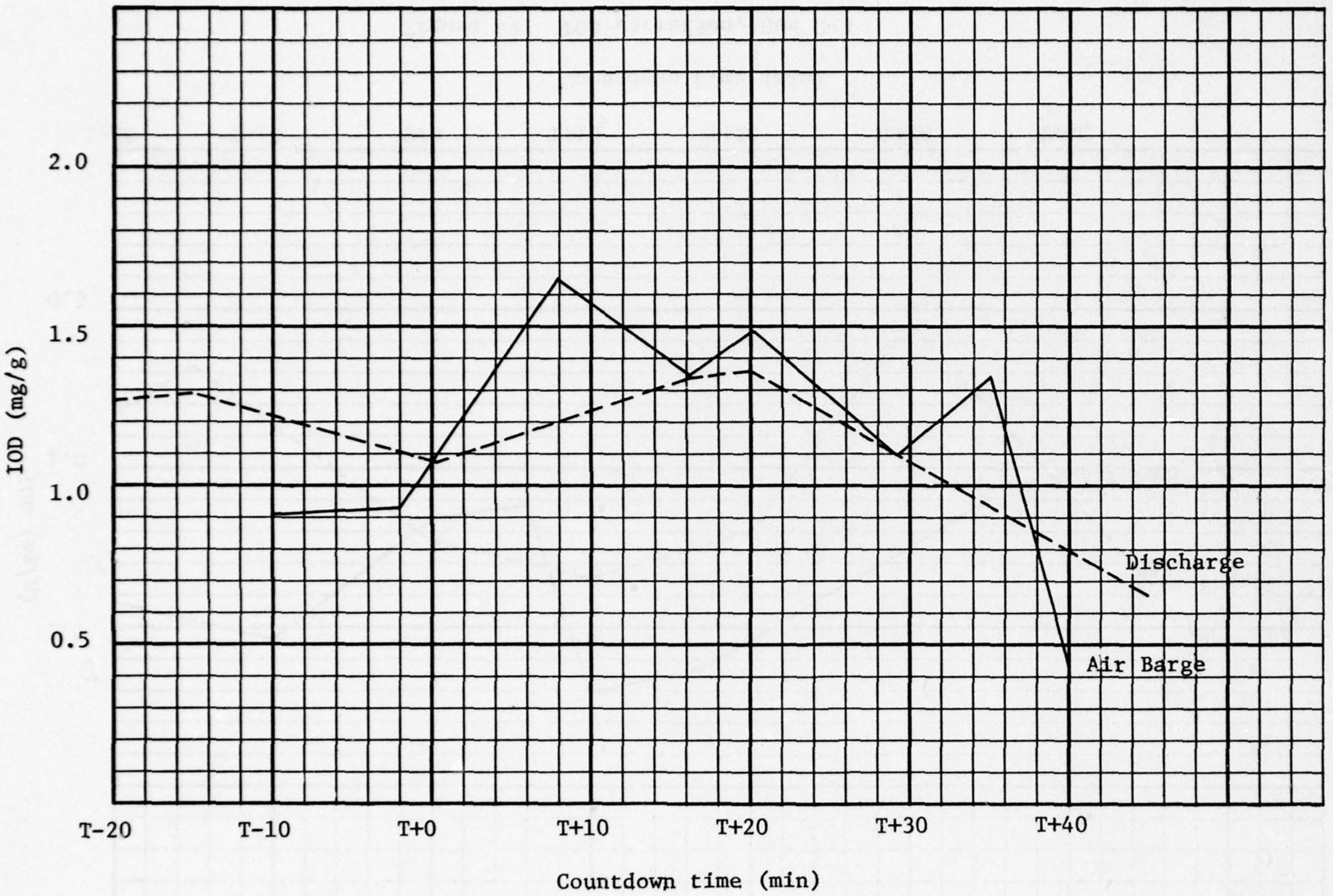


Figure 43. IOD variation, Run C-4

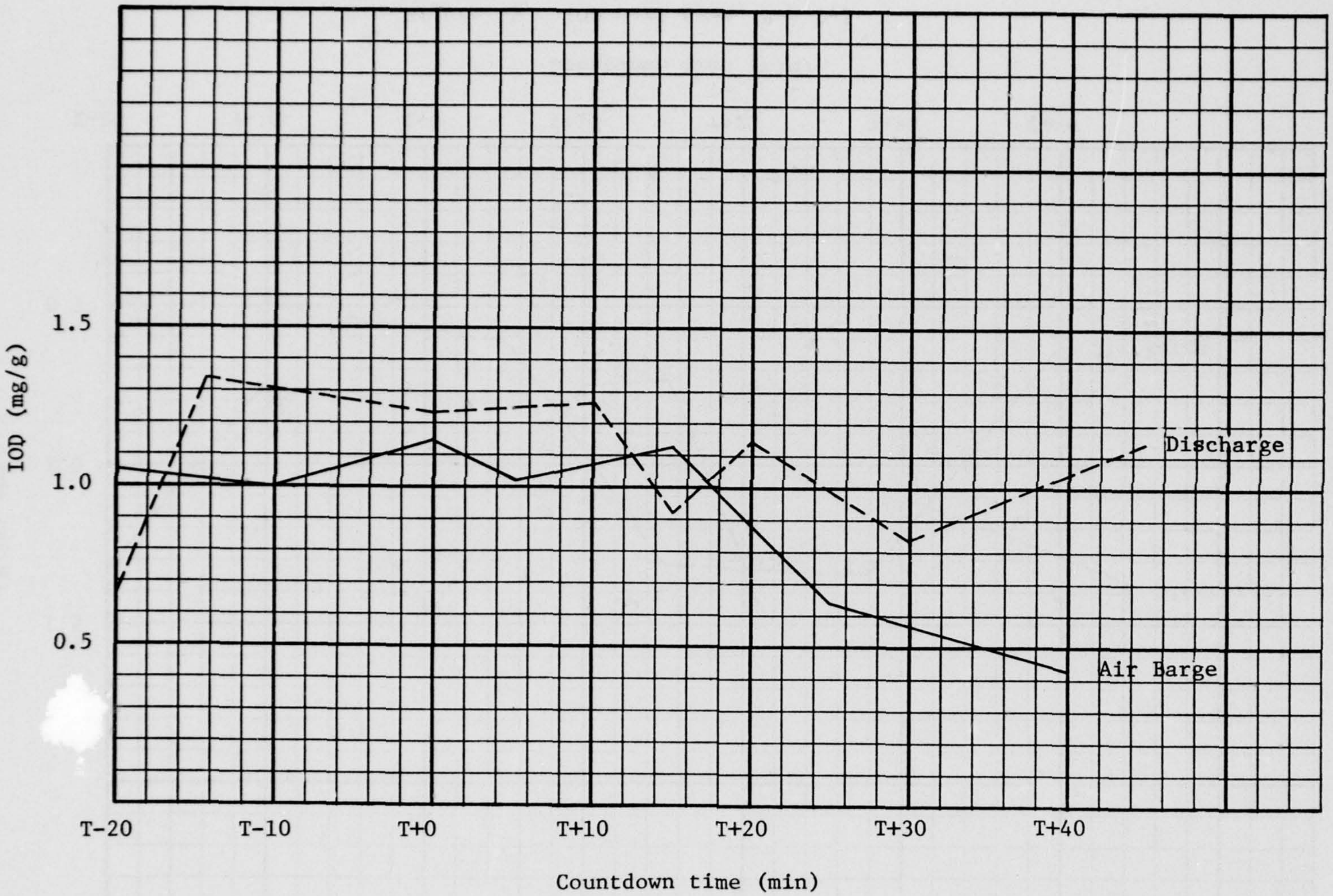


Figure 44. IOD variation, Run C-5

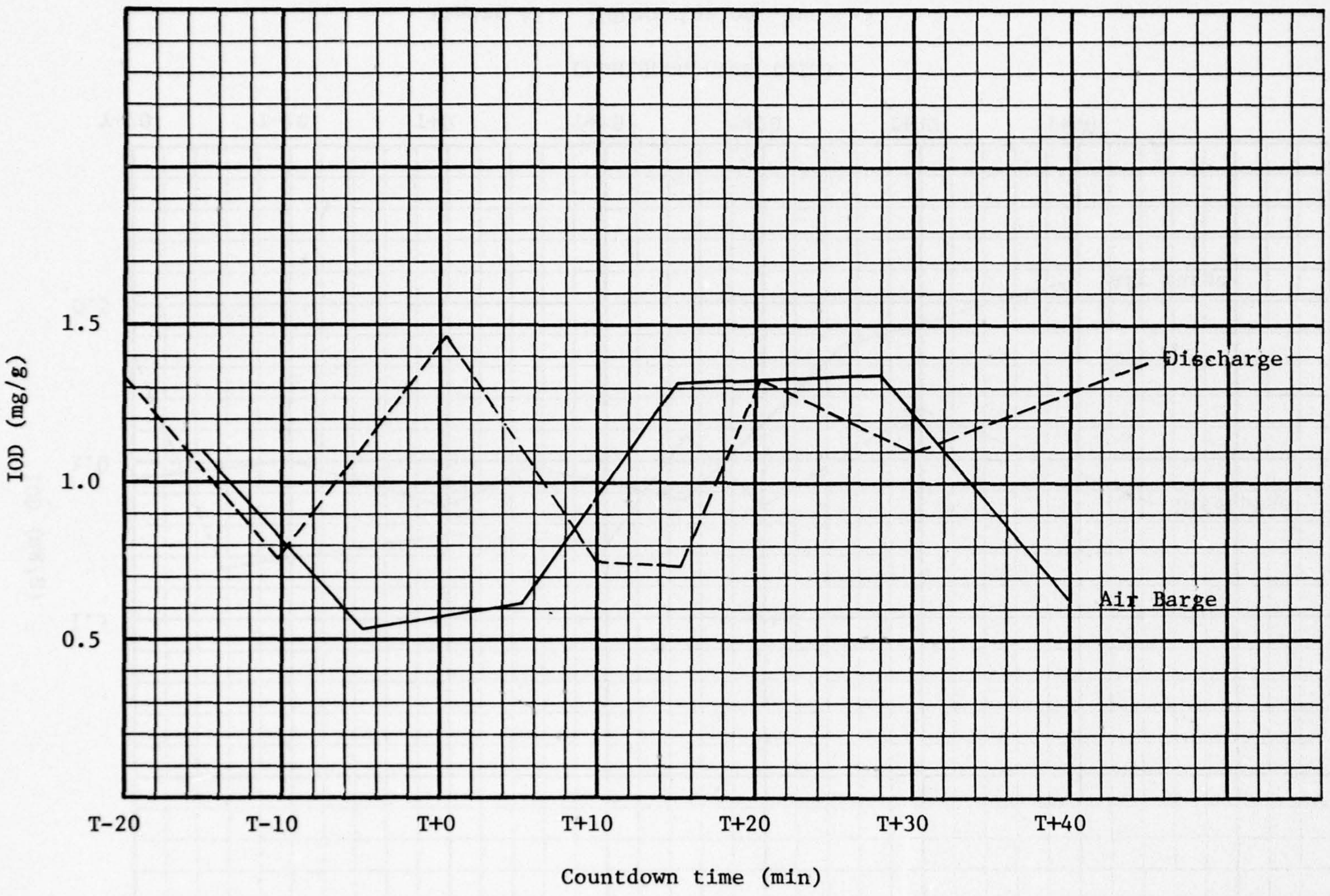


Figure 45. IOD variation, Run D-1

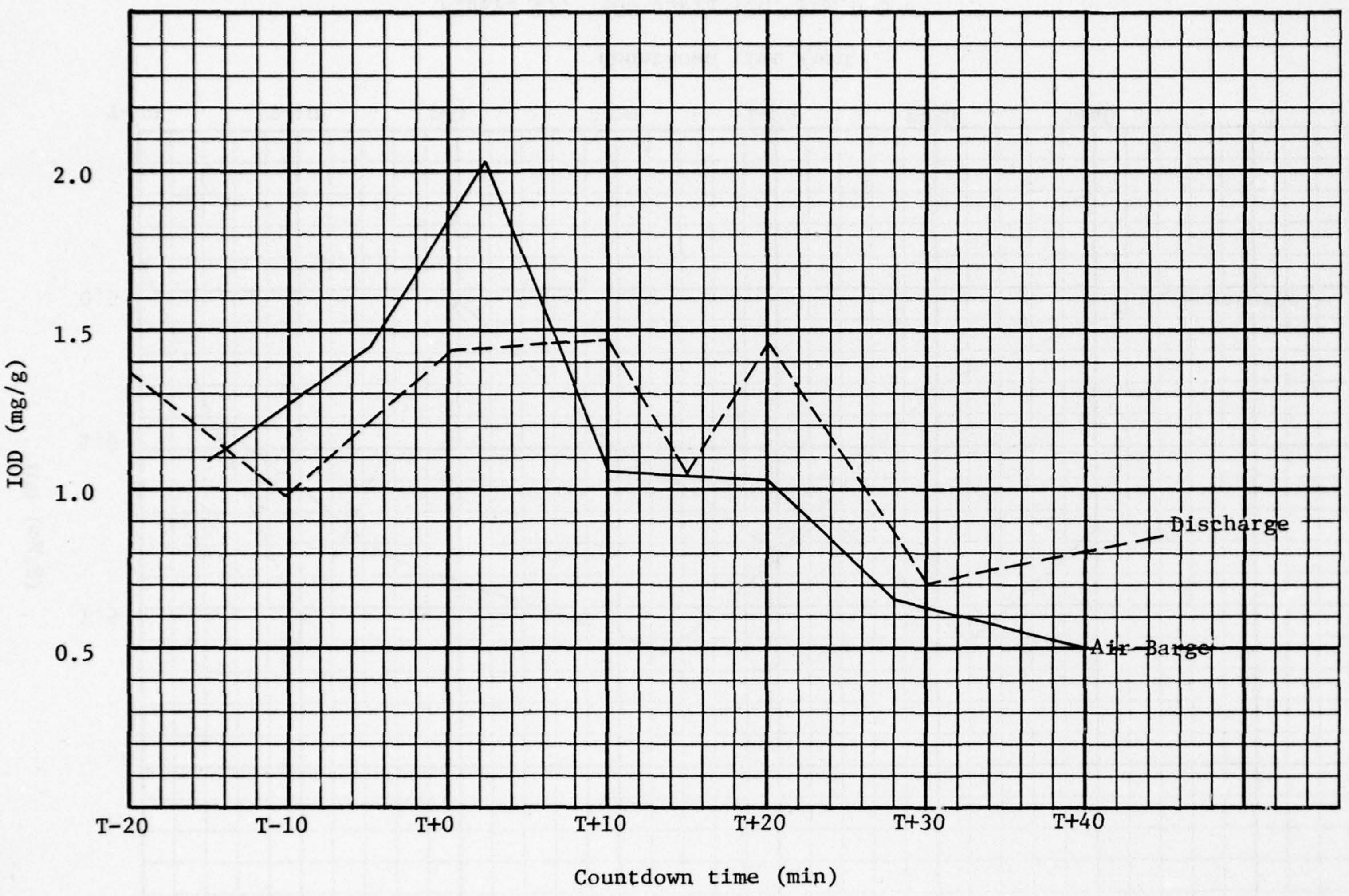


Figure 46. IOD variation, Run D-2

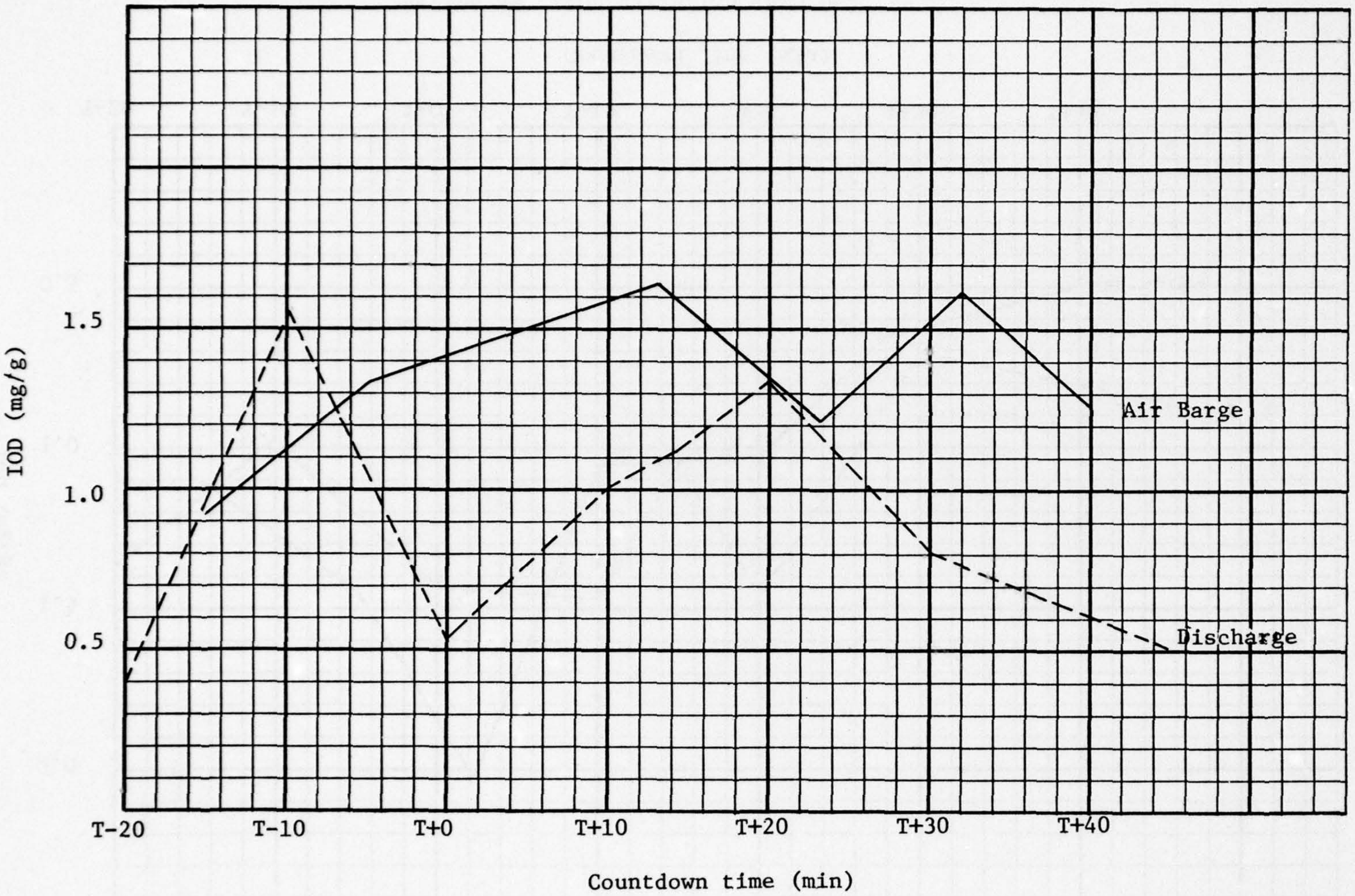


Figure 47. IOD variation, Run D-3

lower IOD than nonaerated samples. Aerated samples are those taken at the pipeline discharge between T+0 and T+30 (T+40 for Run D-3). Average IOD's for each run were determined, as shown in Table 10.

93. Tests of significance were performed to determine more rigorously whether aeration affected IOD in these samples. These statistical tests should be interpreted with caution, because only four or five samples in each run represented the aeration period. However, in two runs (C-3 and D-3), the mean IOD of the aerated samples was lower than that of the nonaerated samples at the 0.01 level of significance. In Run D-1, the same observation was made at the 0.05 level, but not at the 0.01 level. In none of the other five runs was the mean IOD of the aerated samples significantly lower than that of the nonaerated samples. Because of the small number of aerated samples and the inconsistency of finding differences between aerated and nonaerated samples, it cannot be concluded that air had any effect on IOD.

Table 10

Immediate Oxygen Demand of Pipeline Samples
Mobile Bay Aeration Tests

	IOD, mg/g*	
Run	Nonaerated	Aerated
C-1	1.14 ± 0.47	1.06 ± 0.12
C-2	1.18 ± 0.37	1.41 ± 0.16
C-3	1.17 ± 0.35	1.09 ± 0.38
C-4	1.16 ± 0.34	1.18 ± 0.28

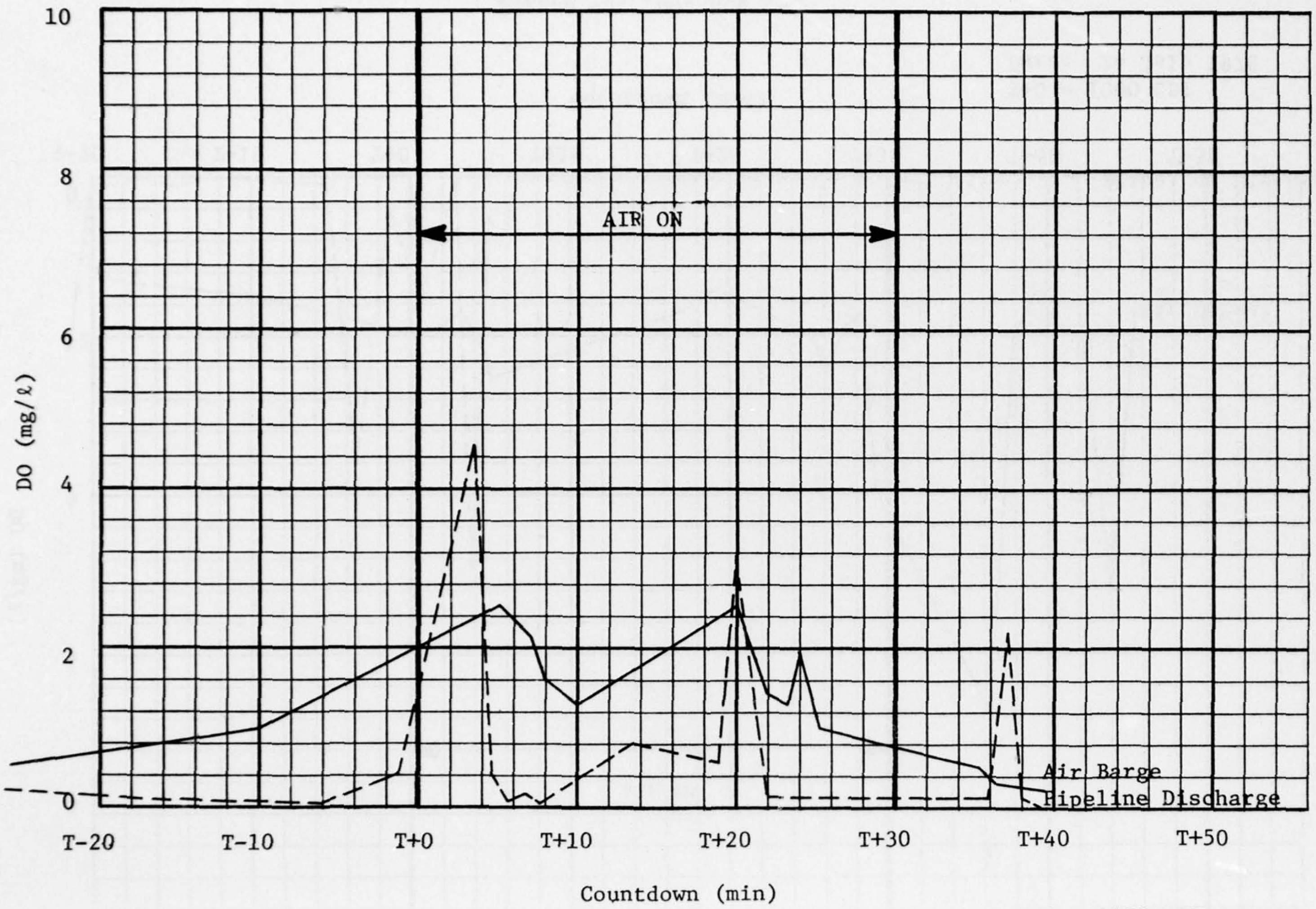
(Continued)

C-5	0.98 ± 0.29	1.05 ± 0.21
D-1	1.07 ± 0.37	0.98 ± 0.30
D-2	1.14 ± 0.42	1.15 ± 0.42
D-3	1.11 ± 0.49	1.05 ± 0.27

---

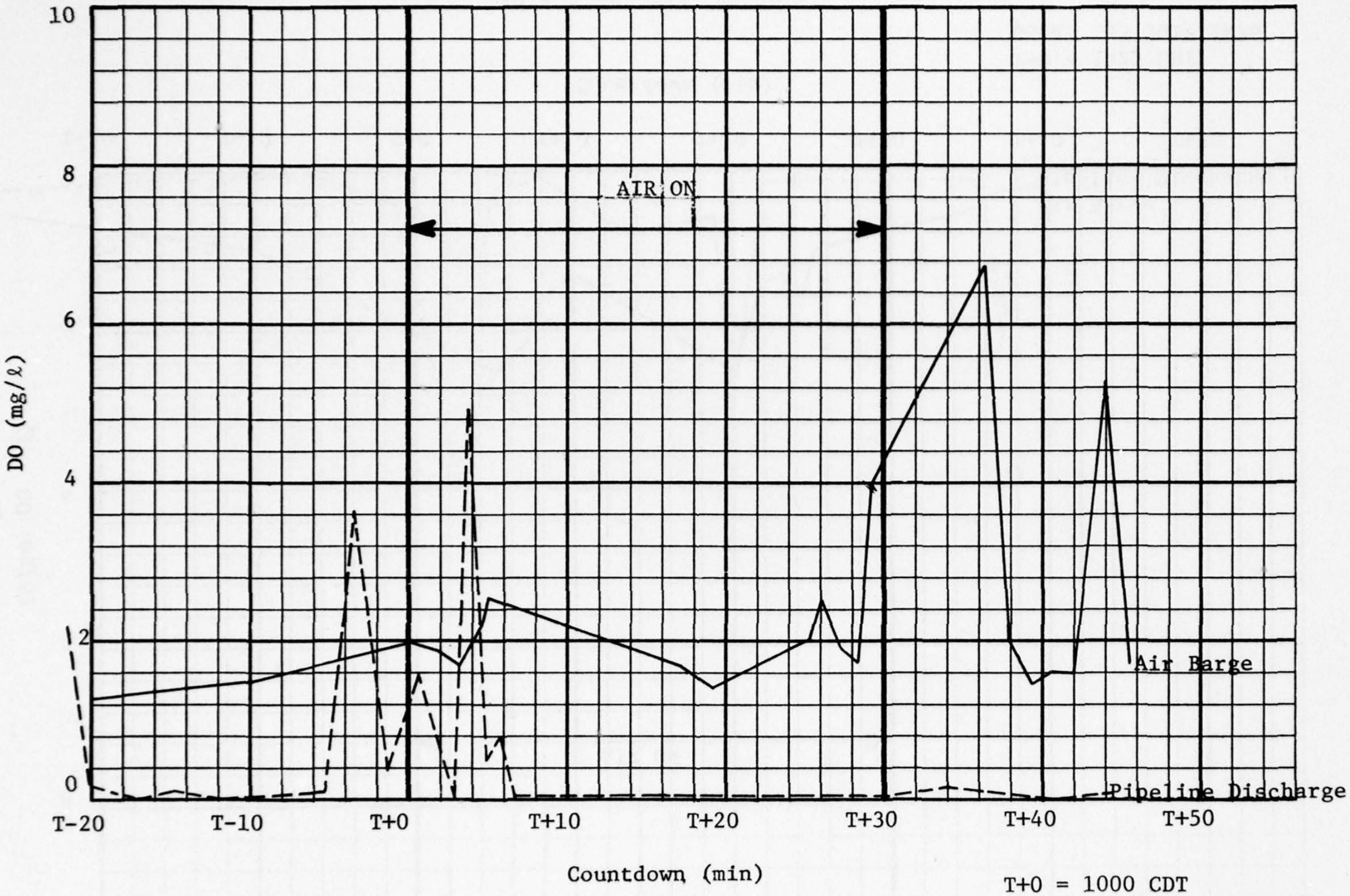
* The values shown are mean values ± one standard deviation.

94. The DO data for pipeline samples taken in the Mobile Bay aeration tests were far more extensive than those for the Apalachicola Bay tests. These data have been plotted, in a manner similar to the IOD data, in Figures 48 through 55. On Runs C-1 through C-5, there appears to have been no increase in DO as a result of aeration. During Runs D-1 through D-3, however, there appeared a noticeable increase in very high, spiky readings at the discharge. The test observer at the discharge noted very high readings when the fluid was watery, indicating that the water was becoming supersaturated. The IOD was apparently being exerted by the sediments in Mobile Bay at a rate exceeding the rate of air-carried oxygen injection. In both the oxygenation and aeration tests, however, oxidation was not being exerted sufficiently to reduce the IOD significantly.



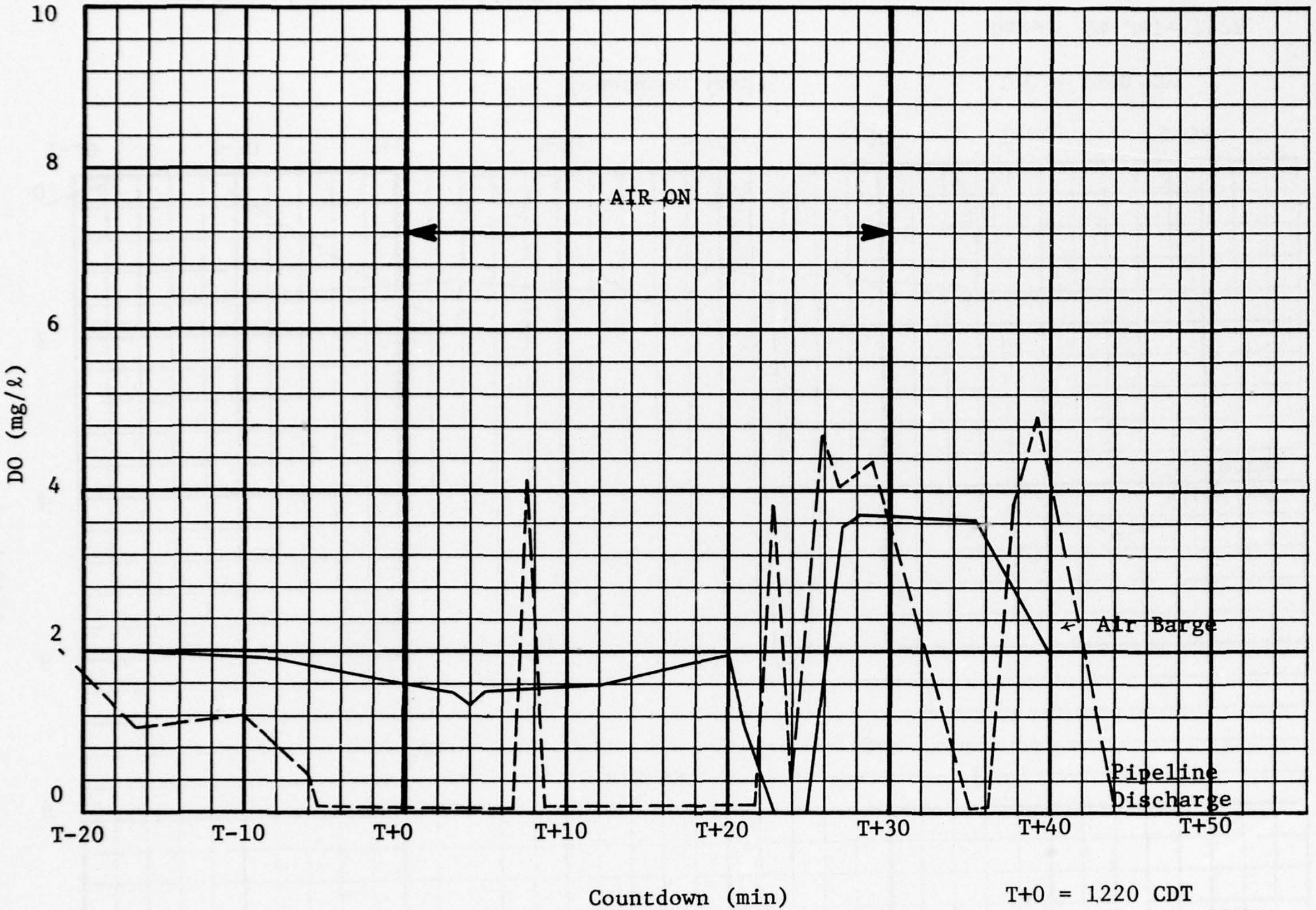
T+0 = 1425 CDT
Date: 23 July 1976

Figure 48. DO, Run C-1



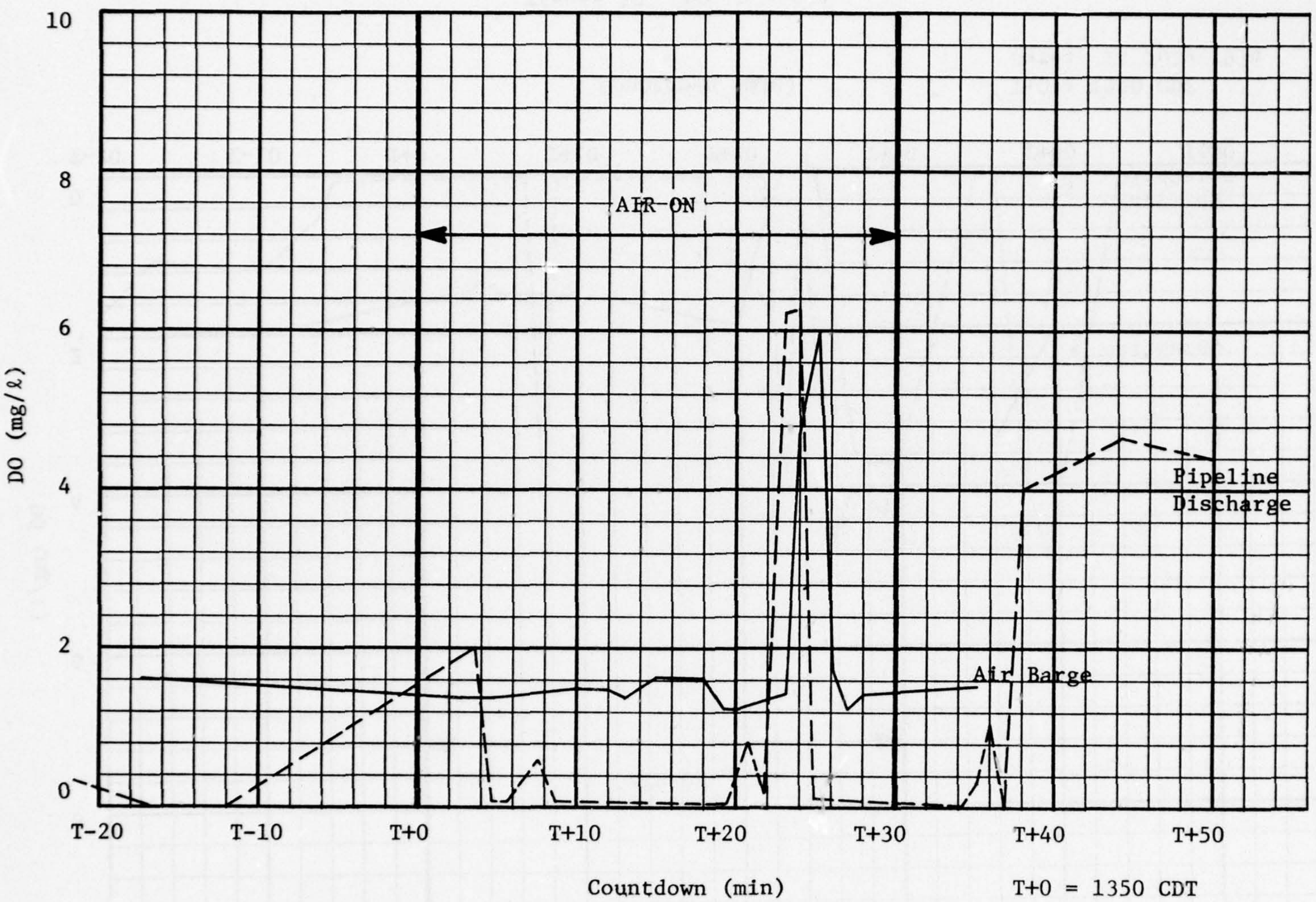
T+0 = 1000 CDT
Date: 24 July 1976

Figure 49. DO, Run C-2



T+0 = 1220 CDT
Date: 24 July 1976

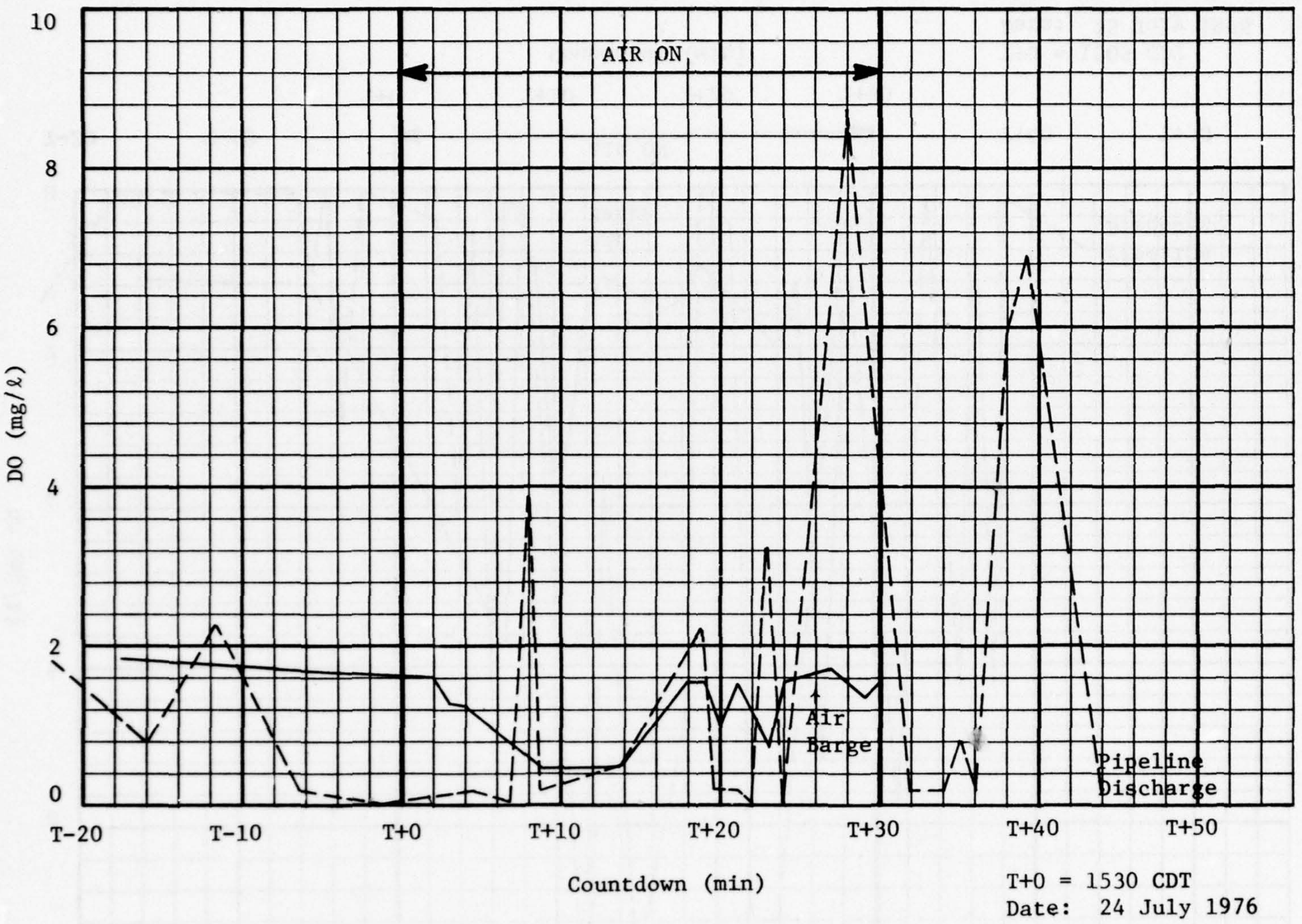
Figure 50. DO, Run C-3



T+0 = 1350 CDT

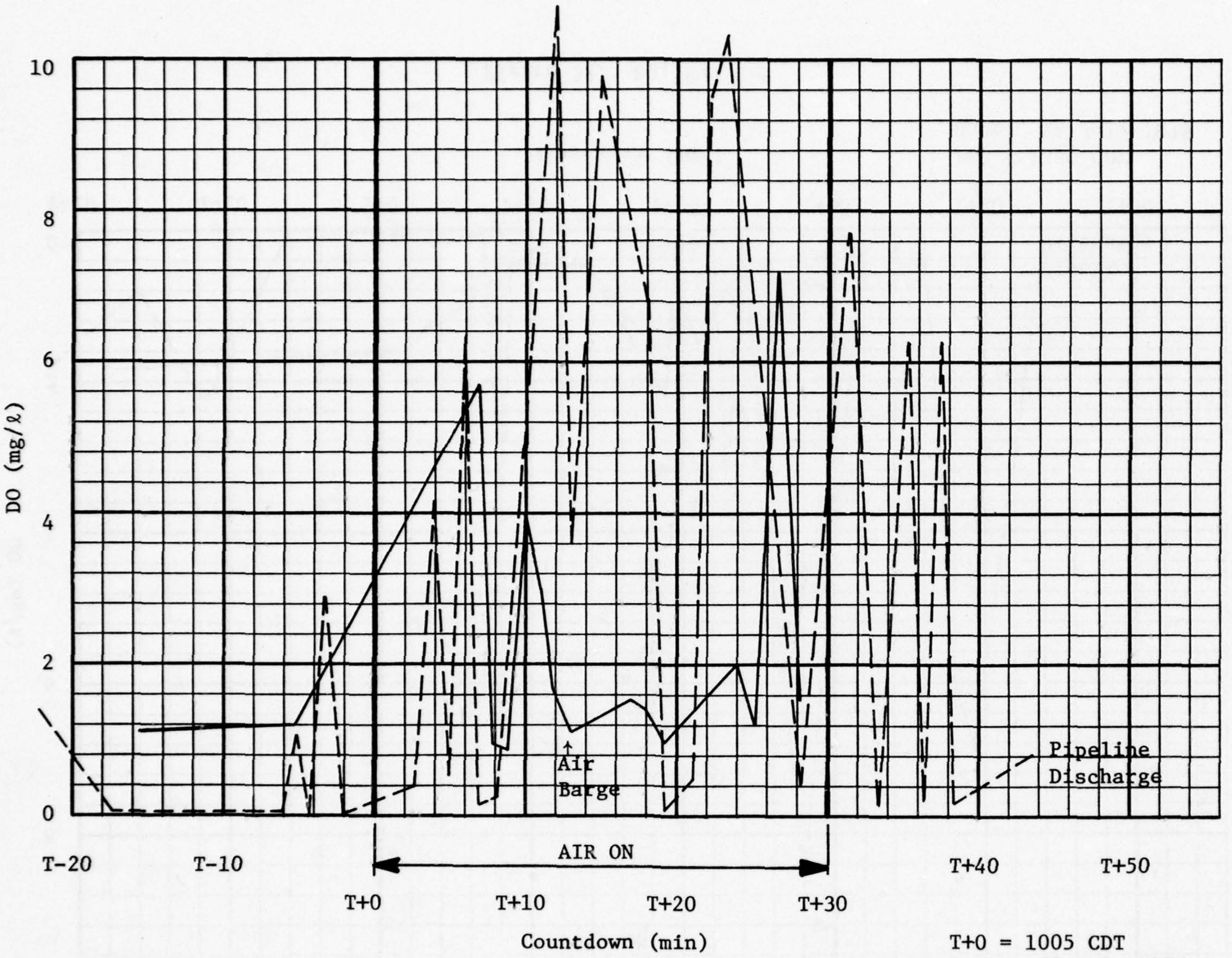
Date: 24 July 1976

Figure 51. DO, Run C-4



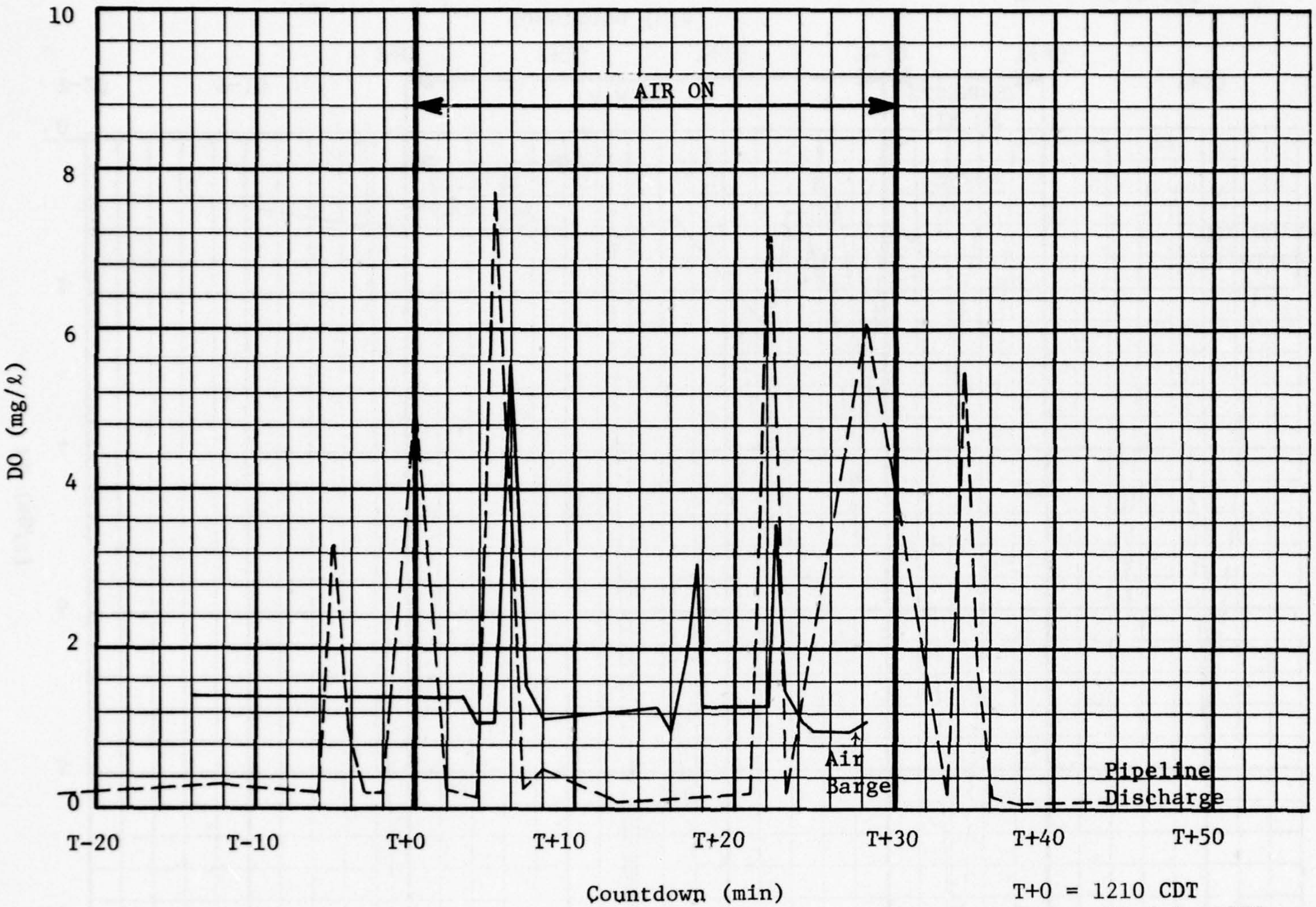
T+0 = 1530 CDT
Date: 24 July 1976

Figure 52. DO, Run C-5



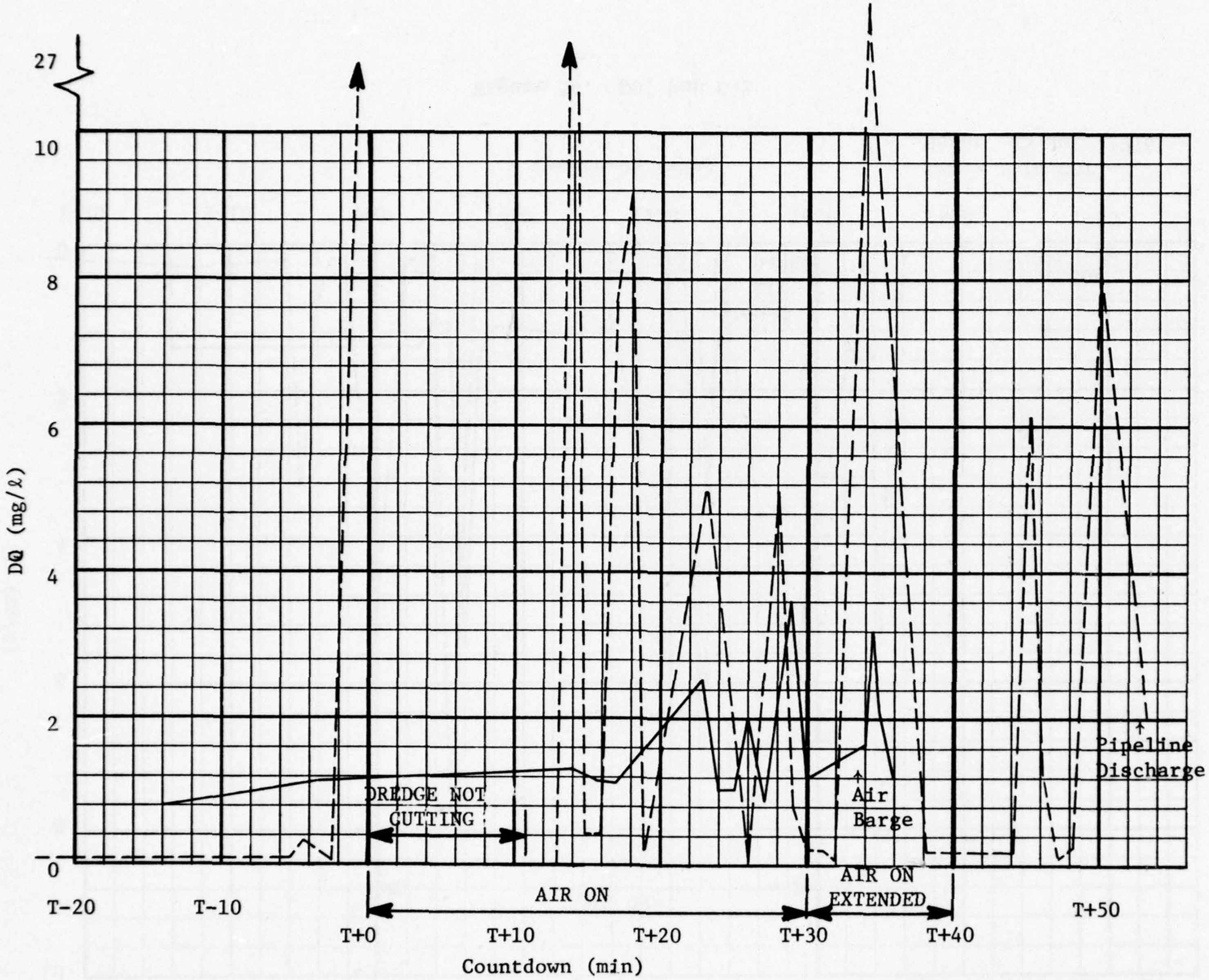
T+0 = 1005 CDT
Date: 25 July 1976

Figure 53. DO, Run D-1



T+0 = 1210 CDT
Date: 25 July 1976

Figure 54. DO, Run D-2



T+0 = 1335 CDT
Date: 25 July 1976

Figure 55. DO, Run D-3

CHAPTER III: LABORATORY STUDIES

Purpose and Scope

95. The purpose of the laboratory studies was to investigate the nature of the immediate sediment oxygen demand, specifically as it relates to the oxygenation of dredged material described in the previous chapter. It is this oxygen demand which is responsible for the depression of DO concentrations in the vicinity of maintenance dredging operations. Because the field demonstrations investigated the in-pipe oxygenation of hydraulically generated sediment slurries to satisfy these oxygen demands, an important aspect of the laboratory study involved the effect of oxygenation on the physical and chemical properties of the dredged materials.

96. Each of the following items were addressed in the laboratory studies:

a. Investigation of the factors responsible for the sediment oxygen demand.

b. Refinement of the sample handling methods and the laboratory methods used to determine the IOD for dredged material.

c. Description of the sediment oxygen uptake rates.

d. Investigation of the effects of oxygenation on the particle size and oxygen-demanding characteristics of the dredged material.

e. Comparative investigation of the nature of the oxygen demands and the effects of oxygenation on the elutriation of the chemical constituents in dredged material obtained from three separate locations.

f. Limited assessment of the use of hydrogen peroxide as an alternate oxidant.

g. Laboratory column studies.

Nature of the Sediment Oxygen Demands

97. Early in the laboratory studies program, the nature of the sediment oxygen demands was examined. This section reviews some of the theory describing the oxygen-demanding and oxidation-reduction properties of sediments and how these relate to conditions encountered in dredging operations. Particular emphasis has been placed on the discussion of the oxygen-demand phenomenon that occurs in the open-water disposal of dredged material and an examination of some of the chemical processes that are responsible for it.

98. The oxygen demand of aquatic sediments is a complex phenomenon involving a variety of chemical and biochemical oxidation-reduction reactions. Each of these reactions takes place at a variable rate which depends upon environmental conditions existing at a particular time and place. These reactions tend to occur when anaerobic sediments are exposed to aerobic conditions. Generally, less oxygen demand is exerted by a static anaerobic sediment than by suspended sediment. This is due to the formation of an oxidized surface layer on the static sediment which inhibits the exposure of the chemically reduced species to oxidizing conditions.[7]

99. The largest pool of oxidizable substances generally present in the sediments at a given dredging site is the organic matter. This organic fraction is continually being decomposed by bottom-living animals, fungi, bacteria, and perhaps also by free enzymes. These biogenic decomposition activities exert an oxygen demand at a relatively slow rate which is governed by the level of biological respiration and metabolic activities of the indigenous biota. Under favorable conditions, static sediments with a high oxygen demand frequently become anaerobic, creating a chemically and biologically reducing environment.

100. In a reducing environment, many multivalent chemical species undergo reduction reactions to a lower chemical valence state. These reduced species potentially include ferrous iron, sulfide, manganous manganese, thiosulfate, sulfite, nitrite, and a variety of readily oxidizable organic compounds (i.e. aldehydes, phenols, urea, etc.).[8,9] If these anaerobic sediments become resuspended in an aerobic water column, each of these substances would react to some extent with dissolved molecular oxygen. The expeditious reaction of these materials with oxygen during dredging and dredged material disposal operations is of concern because of the rapid depletion of DO in the water column.

101. Three of the most commonly measured species which would be expected to exert an IOD are manganous manganese, ferrous iron, and sulfide. As a portion of another contract study for the DMRP, JBF Scientific Corporation conducted a review of Corps of Engineers data on the chemical characteristics of sediments prior to dredging.

Although the data were limited, the following values (Table 11) were found.

Table 11

Chemical Characteristics of Sediments Prior to Dredging

Chemical Species	No. of Samples	Average Values*	Maximum Value*
Sulfide	126	245	2,015
Total Iron	244	16,900	102,700
Total Manganese	35	415	880

*Values are mg/kg on a dry weight basis.

102. Breakdown was not given for values of Fe(II) and Mn(II) as compared to the total values. However, the presence of these metals and sulfide concentrations indicates that sufficient reduced chemicals are present to account for all the oxygen depletion observed near dredging operations. Other potentially oxidizable chemical species, especially the organics, have not been studied with as much emphasis. Therefore, it is more difficult to quantify their impact. The expected chemical oxidation behavior of each of these substances is briefly discussed below.

103. Occurrence and formation of free sulfides in areas which are likely to be dredged has been described in the literature.[10-14] The chemical oxidation reaction of free sulfide with oxygen in aqueous

solutions has been studied by many investigators. Half-lives of free sulfides ranging from 15 min to 70 hr have been reported. Several studies have described the oxidation of free sulfides as occurring by a second-order reaction mechanism.[5,12,15-21] However, such a description is a simplification of an extremely complex mechanism.[22] The oxidation of sulfides is catalyzed by the presence of metallic ions (e.g., nickel, manganese, iron, calcium, and magnesium) and is accelerated by some organic substances such as formaldehyde, phenols, and urea. This fact suggests that oxidation of free sulfides in the presence of dredged material may lie in the more rapid end of the time spectrum cited above because of the ubiquitous presence of these catalysts. Oxygenation of sulfide is also characterized by an induction period at all pH values. It can be concluded from the universal existence of this induction period and from the kinetic information that this catalytic oxidation proceeds through a chain mechanism.

104. Another study[23] found that there are two basic oxidation modes for free sulfide at neutral pH's: oxygenation, in which DO is the immediate oxidizing agent, and ferric iron oxidation, in which ferric ions are the oxidants. In the direct oxygenation mode, the rate is dependent only on the DO concentration in the aqueous phase. (It is the view of many soil scientists that this is the major mechanistic pathway.)[13] Ferric iron oxidation of sulfide is determined by the ferric/ferrous ratio and the metastable presence of free ferric ion (Fe^{+3}) concentration in solution. It is <u>not</u> affected by the DO. The ferric/ferrous ratio is often enhanced by non-equilibrium conditions

which can exist in regions of intense microbiological activity or in the open-water discharge of dredged material. While it is true that the oxidation of sulfide in dredged material is an important process, the immediate oxygen demand is only exerted by sulfide when direct oxidation of sulfide is occurring.

105. The sulfide ion S^{-2} is the most effective of the inorganic precipitants for heavy metals. As a result it is not commonly found in soluble form. It is a common constituent of anaerobic bottom sediments in the form of ferrous sulfide (FeS). The effectiveness of the sulfide ion as a binding agent for a particular metal ion is measured by the solubility product K_s of the sulfide of the metal.

106. Information on the solubility products of sulfides is summarized by Sillen and Martell.[24] The following list gives the values for some metals commonly found in bottom sediments:

Metal Ion	$\log_{10} K_s$ (at 25°C)
Hg^{2+}	-52.73
Cu^{2+}	-35.40
Pb^{2+}	-27.15
Cd^{2+}	-26.03
Zn^{2+}	-23.82
Ni^{2+}	-20.7
Fe^{2+}	-17.29
As^{3+}	(Hydrolyzes)

107. From the above list, it is evident that iron sulfide is the most soluble (largest solubility product) of the sulfides commonly found in bottom sediments. As long as FeS is present, the concentration of free sulfide in solution will be sufficient to precipitate the remaining metals almost completely. If too much excess sulfide is present, however, mercury and arsenic will form soluble complexes. The region of stability of the soluble mercury complex is discussed by Hem.[25] In addition to forming a sulfide complex, arsenic sulfide tends to hydrolyze to soluble compounds in the usual pH range of sediments. Sulfide ion is therefore not an effective precipitant for arsenic under natural conditions.

108. It has been demonstrated[19] that the chemically combined sulfide in the metal sulfides can also be oxidized in the presence of oxygen. Engler and Patrick[26] found that the degree of oxidation was directly related to the solubility of the sulfides.

109. Organic sulfur compounds do not respond to the analytical tests used to measure inorganic sulfide. The volatile organic sulfur compounds are very important odor components. They are principally of three types: thiols (also called mercaptans), thioethers, and disulfides. There are also nonvolatile sulfur compounds that cause none of the problems associated with the volatile compounds, but that may break down by biological action to yield inorganic sulfide. Naturally occurring compounds of this type are principally the albuminoid proteins. The effect of these compounds on the IOD is uncertain.

110. Iron occurs in two oxidation states: the divalent ferrous form, Fe(II), and the trivalent form, Fe(III). In dredged material and

the interstitial water, both soluble and insoluble species of hydrolyzed iron may be present. The hydrolysis products of ferric iron have very low solubilities in the pH range encountered in natural waters. Under oxidizing conditions most of the ferrous iron is precipitated as hydrous iron oxides. Anaerobic conditions brought about by the decomposition of organic matter by benthic bacteria result in the chemical reduction and subsequent dissolution of Fe(III) from the sediment substrate as the more soluble Fe(II) form. Many of the important reactions of the iron in dredged material have been discussed in the literature.[13,14] Another important aspect of the chemical behavior of iron is the formation of complex ions with inorganic as well as organic ligands.

111. The oxidation of ferrous iron has been extensively studied by various researchers.[27,28] It has been shown that the rate of ferrous iron oxygenation is first order with respect to the concentration of both Fe(II) and dissolved molecular oxygen and second order with respect to the hydroxide ion concentration. The buffer intensity of the water also has a definite influence on the oxygenation of ferrous iron.[29] Half-lives of ferrous iron ranging from 4 min to 300 days have been reported.[30] Many elements present in natural waters and dredged material have the capability of accelerating the oxidation of ferrous iron by catalysts.

112. On the other hand, organic materials may significantly retard the overall Fe(II) oxidation rate.[30-32] Localized high concentrations of organics can result from the leaching of dead vegetation. In the presence of this organic matter, the Fe(II) - Fe(III) redox couple, itself, acts as a catalyst for the oxidation of the organic matter

(i.e., ferric iron is a potent oxidant of organic material as well as sulfide). In this catalysis reaction, Fe(III) is chemically reduced to Fe(II). Some of the reduced iron is chelated by the organics, thereby retarding further oxidation. Because of this reaction sequence, a significantly high steady-state Fe(II) concentration may be maintained in natural waters containing organic matter even in the presence of DO or other oxidizing agents. Furthermore, this reaction sequence is complicated by hydrolysis reactions. When ferric iron hydrolyzes (pH greater than 3.0), Fe(III) is not as readily reduced by the organics. Only the metastable free ferric iron Fe^{+3}, not total Fe(III), is susceptible to reduction. Under equilibrium conditions, no appreciable quantities of Fe^{+3} can exist in solution above a pH of 6.3. However, it is improbable that equilibrium conditions exist in a water column subjected to the rapid influx of dredged material. In this environment, as ferrous iron is oxidized, there is a competition for the newly formed ferric iron between hydroxide and the organic material present. As a result, some degree of hydrolysis and reduction takes place, the relative proportions of which depend on pH and the concentration and specific type of organic matter. There is still some question as to the plausibility of this mechanism in dredged material disposal operations.[13]

113. In their investigation of the oxidation of iron pyrite (sulfide) over a broad range of pH's, Singer and Stumm[30] demonstrated that molecular oxygen may not serve as the specific, direct oxidant of this material. Oxygen is involved only indirectly, producing ferric iron which is, itself, the primary oxidant of FeS_2. The following catalysis reaction mechanism was verified:

$$FeS_2 + Fe(III) \longrightarrow Fe(II) + SO_4^{-2} \qquad (1)$$

$$Fe(II) + O_2 \longrightarrow Fe(III) \qquad (2)$$

The importance of this reaction sequence in the oxidation of dredged material disposed of in an aerobic water column or neutral pH values has not been adequately explored. It will be more fully discussed in the experimental sections to follow.

114. On the basis of thermodynamic data, manganous manganese is unstable with respect to oxidation by dissolved molecular oxygen over the entire pH range of natural water.[33] However, oxidation potentials do not provide practical information about either the rate or the nature of the manganese oxidation reactions. Morgan[33] conducted an extensive experimental study of manganese oxidation kinetics. He examined the effect of concentration, pH, oxygen, bicarbonate, sulfate, and temperature on this reaction in laboratory systems. He found that even in the presence of oxygen rates of oxidation could be extremely slow. No oxidation was observed at pH values less than 8.6 with an oxygen partial pressure of 1.0. Detectable (approximately 2 percent) oxidation was observable in 3 hr at pH 9.0 under these conditions. At pH 12, oxidation is apparently complete in less than 1 min. This rate is second order with respect to hydroxide ion concentration and first order with respect to the oxygen partial pressure. This complicated reaction in simple media is autocatalytic and heterogeneous in nature, resulting in nonstoichiometric solid oxidation products, showing various average degrees of oxidation ranging from approximately $MnO_{1.3}$ to $MnO_{1.9}$ (30-90 percent oxidation to MnO_2) under varying alkaline

conditions. These colloidal manganese oxide suspensions exhibit large sorption capacities for Mn^{+2} in slightly alkaline solutions. Therefore not all the Mn(II) removed from the solution is oxidized and some of this manganese is oxidized only after adsorption. Other solid surfaces, such as feldspathic sand, increased the oxidation rate of soluble Mn(II).[34] However, these reactions only become reasonably fast at pH values greater than 8.5. The chemistry of manganese under natural conditions and during dredging operations has also been studied.[13,14,35-37] It is clear from these studies that manganese oxidation would be secondary in importance to ferrous iron and sulfide oxidation in the systems under investigation in this study. Therefore it was not considered further in this laboratory study.

115. In view of the considerable variety of natural sources of organic material from both terrestrial and aquatic sources, a great diversity in the concentration of organic matter must be expected. Little specific information on the chemical composition of these materials as it relates to oxidation potential or the rate of oxidation is available. It is usually assumed that simpler compounds released in the surface waters are oxidized and utilized by aquatic organisms while the more resistant compounds sink to the bottom. The quantity of organic matter carried in natural waters is small compared to that in sediments. Many of these organics (i.e., humic residues) are persistent or slowly degraded even under the aerobic conditions.

116. Biochemical oxidation of organics is a relatively slow process and would not be expected to contribute to the IOD. Chemical oxidation

of the oxidizable functional groups by iron catalysts or by direct oxidation by molecular oxygen may be important in some cases; however, more study is needed to evaluate its impact in the case of open-water disposal of dredged material.

Measuring the Oxygen Demand of Sediments

117. Because of the common practice of using the oxygen demand as an aid in estimating industrial and municipal wastewater pollution loads, a number of tests have been developed to measure this property. Three of the more commonly used tests are the chemical oxygen demand (COD), total organic carbon (TOC), and the biochemical oxygen demand (BOD). Each of these standardized tests[8] yields results that are used to indicate the potential susceptibility of a given sediment to cause the consumption of oxygen in the aquatic environment. Generally, biochemical decomposition of the organic matter present in the sediment accounts for an overwhelming portion of the oxygen uptake measured. The applicability of these tests to dredging impact studies is briefly discussed below. This discussion is followed by a more detailed account of the evolution and recent refinement of the IOD test.

118. The COD determination provides an indirect measure of oxygen required to oxidize the sediment under specific test conditions using a strong chemical oxidant at a specified temperature for a given period of time. This parameter appeared in the original Federal Water Quality Administration criteria for open-water disposal of dredged material.[1] However, its usefulness for this application has recently been questioned.[38] Because the test nonselectively oxidizes substances which may not be oxidized under conditions encountered in natural water

systems, its use to predict what might happen in real situations is of doubtful value. One of the substances oxidized in this test but not in aquatic systems is chloride. Due to the extremely wide concentration ranges for this parameter in estuarine systems, the analyst must be careful to accurately account for these variations either in the test itself or by correcting for this interference in the calculations. On the other hand, the COD test is rapid and is routinely performed in most water pollution control laboratories. It has enjoyed wide application in dredged material disposal studies[39] prior to the development of more meaningful tests.

119. Whereas much of the ultimate oxygen demand exerted by the sediments is associated with the aerobic microbial degradation of the organic matter, the measurement of this sediment fraction provides a means of indirectly assessing the total potential oxygen-demanding load placed on the receiving water body. The TOC test involves the combustion of a sediment sample in the presence of oxygen to form carbon dioxide. A forerunner to this technique is the total volatile solids (TVS) determination, which is also a combustion technique. This latter parameter was also in the original FWQA criteria for open-water disposal of dredged material.[1] As with the COD test, there are some serious objections to the use of combustion techniques for the characterization of the oxygen-demanding properties of dredged material. Neither the TOC test nor the TVS test differentiates between the biochemically oxidizable organic matter fractions and the more refractory organic

species. Humic materials and other similarly ubiquitous high molecular weight chemical species are not readily oxidized in aquatic systems and hence should not be included in a measure of potential sediment oxidation. However, it is quite difficult to correct for this fraction in the calculations.

120. The BOD test is an empirical bioassay procedure which is most commonly used to measure the biodegradable fraction of organic matter in a sample. This standard method has been modified slightly for use in determining the sediment (or benthic) oxygen demand.[40] In this test, the analyst measures the oxygen consumed in the water above a static sediment in a closed glass system for a period of several days. Processes responsible for the occurrence of the BOD have been widely studied, both in situ[41-44] and in laboratory systems.[38,45-51] Studies in which sediments were resuspended during the BOD test showed an increased level of oxygen consumption.[9,52,53] Much of this increase in oxygen demand was noticed even after the microbiological population was intentionally destroyed. This suggests that the majority of the increased demand is chemical in nature, not biochemical.

121. When anaerobic sediments are discharged into open water, the increased oxygen demand due to the presence of chemical species results in a reduction in the concentration of DO in the water. This occurs rather quickly, and none of the previously discussed tests provides a reliable measure of the potential of a particular sediment to produce a sudden (but relatively short-term) demand for oxygen.

122. In recent investigations, the need for developing new analytical procedures to characterize this type of oxygen demand has been recognized.[38,54] Out of this has evolved the concept of an IOD which could be determined by suitable analytical procedures. Ideally, the IOD could be considered as a characteristic or property of the sediment and, when known, would provide a useful indication of that sediment's potential to deplete the DO in a disposal area.

123. The IOD concept is not a new one. In the standard methodology for the BOD test,[8] there is reference made to a property called the immediate dissolved oxygen demand (IDOD). To determine the IDOD, the DO of the sample (which in most cases is zero) and the DO of the dilution water are determined separately. An appropriate dilution of the sample and dilution water is prepared, and the DO is determined after 15 min. The calculated DO of the sample dilution minus the observed DO after 15 min is the IDOD (mg/ℓ) of the sample dilution. This value is normalized by dividing by the decimal fraction of sample used. This same test was used for bottom sediments in the Great Lakes sediment manual.[40] In this test it was suggested that 6 g of sediment be used for the 300-ml test volume. The calculation method provided an IDOD in milligrams of oxygen per kilogram of sediment on either a wet basis or a dry weight basis.

124. The test was refined in the EPA Region IX analytical manual.[55] In this method, 15 g of wet sediment are weighed out in triplicate and transferred to the BOD bottles which are filled with site water. The bottle is then stoppered and shaken for 1 min. After allowing the bottle to stand for 15 min, the stopper is removed and the DO measured

with a probe. The IOD is calculated in a manner identical to the sediment IDOD above.

125. While under contract to the U.S. Army Engineer District, San Francisco, JBF[56] refined certain techniques for conducting the IOD tests which considerably improved their repeatability. Exposure of the sample to air was prevented by using a disposable plastic syringe (10 or 20 cc) for handling the sediment and delivering it to the test container. When the sediment is reasonably compacted, the bottom of the syringe is cut off and the cylinder is used to bore a sample. If the sediment has a larger water content, a smaller hole can be bored through the bottom of the cylinder and the sediments drawn into the syringe. Even a diluted hydraulic dredge slurry can be accommodated in a properly prepared syringe. Once the sample is in the syringe, it can be weighed without undue exposure to the air, and the sample can be discharged directly into the test container. This is done below the water surface to avoid contact with air.

126. Another technique employed was continuous mixing with a magnetic stirrer throughout the test period. This ensures that the sediments remain suspended, that the mixture is nearly uniform, and that fresh sample water is continuously circulated to the DO probe.

127. There are other considerations of importance in establishing consistent and reliable procedures. These include specification of the dilution water, quantity of sediment, time of test, and consideration of the rate of oxygen depletion and the means of measuring it.

128. <u>Sample collection and handling</u>. In order to obtain meaningful IOD results, procedures must be developed to obtain representative

samples of the sediments that are scheduled for dredging. Because these sediments tend to be highly variable in composition, large numbers of samples may be needed in order to obtain representative samples of the area. It is beyond the scope of this report to discuss in detail the statistical procedures that should be used in the sampling program. The reader is referred to the EPA Region IX analytical manual[55] for guidance.

129. Once the sample is obtained, it should be carefully packaged, stored in ice, and promptly shipped to its destination. Further sample handling considerations which should be accounted for are listed in Reference 1.

130. If the sample is to be composited or homogenized in the laboratory prior to the IOD measurement, such procedures should be done in an inert atmosphere (e.g., using a glove bag purged with ultrapure nitrogen gas). In this manner the sediments will not be exposed to atmospheric oxygen prior to their use in the test. The aliquot of sediment that is used in the IOD test can then be extracted from the mixture with the syringe in the manner described above. When the sediment is extracted directly from the sample container, care must be exercised to avoid extracting the thin oxidized layer on either the sides, top, or bottom of the container.

131. <u>Dilution medium for sediment</u>. Large variations in water quality are possible at potential dredging sites and disposal areas. Therefore, it seems appropriate to use one or two standard types of dilution water for the IOD test. It is not necessary to use nutrient-enriched media as outlined in the BOD methods because the oxygen-

demanding phenomena in the IOD test are largely nonbiogenic. The best choices for the dilution medium appear to be aerated distilled water or standard artificial seawater.[57] No matter what dilution water is used, it should be close to saturation with respect to air at the test temperature. It should also be free of oxygen-demanding substances.

132. In all the previous IOD tests, a single dilution was made with a recommended quantity of sediment. This practice ignores the fact that the concentration of DO can be measured more accurately at higher oxygen concentrations. A typical DO meter response is 90 percent in 10 sec at a constant (30°C) temperature. However, at low DO values the 90 percent reading takes 30 sec to reach. Because the accuracy of the DO reading may be ± 0.3 mg/ℓ,[58] a small oxygen depletion should be avoided. These problems can be avoided by conducting the laboratory IOD test on at least two, preferably three, different dilutions. The results from dilutions showing 40 to 70 percent depletion are the most reliable and should be the only results considered acceptable.

133. Time. Fifteen minutes has been arbitrarily selected as the IOD test time. This time can be maintained as the standard if the oxygen-depletion criteria stated above are adhered to by making the proper sediment dilutions. Using a longer time interval makes the test more cumbersome from an analytical viewpoint. Under some special circumstances it may be instructive to follow the DO concentration past the 15-min limit. However, this time interval is suitable for the purposes of a standardized IOD test.

134. Mixing. Mixing at the membrane surface of the DO probe is necessary to obtain an accurate reading. A BOD mixing accessory is available from many DO meter vendors which would induce a current in the vicinity of the probe membrane. This current would not, however, maintain the bulk of the sediments in suspension. A magnetic stirrer can be used for this purpose. However, it must be used with the proper precautions. Because magnetic stirrers tend to give off heat, they can raise the water temperature in the container within the 15-min testing period. Suitable insulation can be used to reduce this effect. Proper correction on the instrument for the temperature changes that do take place is necessary for accurate DO measurements. When using the magnetic stirrer to induce a current across the membrane surface, it must be remembered that the water in the center of the BOD bottle is swirling at a slower rate than at the perimeter. A sufficient stirring rate can be obtained by placing the probe in the dilution water and finding a stirrer setting that does not cause any appreciable change in the meter readings when the setting is increased or decreased slightly.

135. Calculation. The method of calculation presented in the Great Lakes manual[40] satisfied the purposes of the laboratory study. This calculation for a wet weight basis is as follows:

$$\text{IOD mg/kg} = \frac{(D_0 - D_1) \times 0.3}{\text{grams of sample in aliquot}} \times 1000 \qquad (3)$$

where D_0 is the initial DO reading (mg/ℓ) and D_1 is the DO reading (mg/ℓ) after 15 min. The 0.3 term is the volume (300 ml) of a standard BOD bottle.

136. For the IOD on a sediment dry weight basis, the calculation is as follows:

$$\text{IOD mg/kg} = \frac{\text{mg/kg IOD (wet basis)}}{\text{\% solids (decimal fraction)}} \qquad (4)$$

Description of Sediment Oxygen Uptake Rate

137. This section describes the experiments performed and the relevant observations made when anoxic dredged material was suspended in air-saturated water. Experiments of this nature were an attempt to simulate what processes are important during the open-water disposal of hydraulically dredged sediments. The modified IOD test described in the previous section was used to quantify these effects.

138. All the experiments described in this section were conducted on sediment samples obtained from the Gulf Intracoastal Waterway in Apalachicola Bay. Ten samples were obtained for JBF Scientific Corporation by a WES project team under the supervision of Mr. Thomas Moore on 24 July 1975 at a location in the center of the north-south channel adjacent to navigational aid Number 3 (Figure 56). The equipment used for sampling was a Petersen dredge of about 2-gal capacity, on 3/16-in. wire rope, handled with a manual winch and davit assembly. The sediment was discharged directly into 4-gal polyethylene sealable buckets to avoid unnecessary atmospheric exposure and metals contamination. Four of the samples were sealed with tape and packed in ice for shipment to the laboratory. They remained refrigerated in the lab until they were analyzed as a preservation precaution. The other six samples were also carefully sealed but otherwise remained unpreserved.

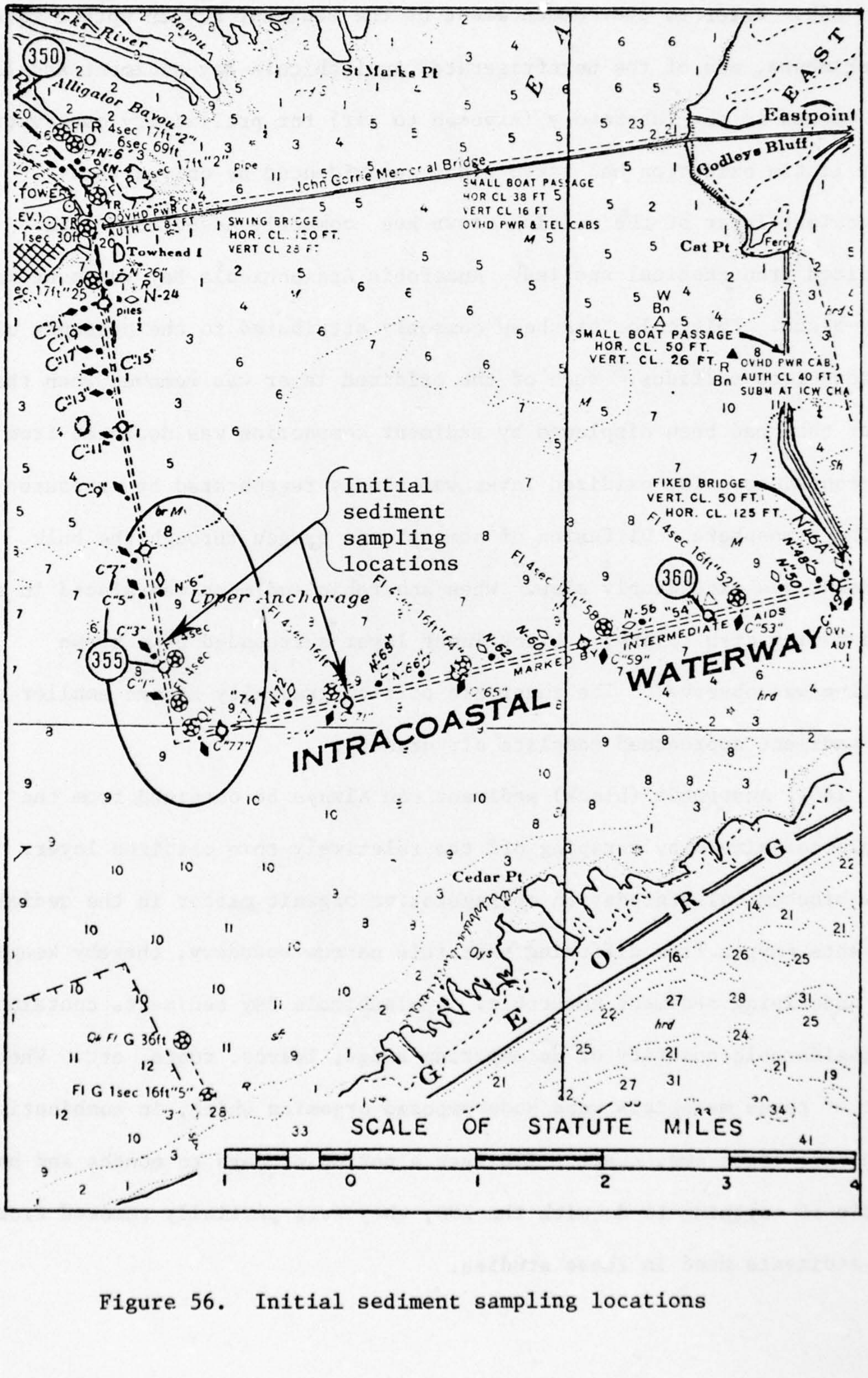


Figure 56. Initial sediment sampling locations

139. Prior to the commencement of the sediment oxygen uptake rate experiments, one of the unrefrigerated Apalachicola Bay sediment samples was opened in the laboratory (exposed to air) for preliminary observations. Very little oxidation had taken place as evidenced by only a thin flocculent layer of the reddish-brown hue commonly associated with oxidized iron chemical species. Anaerobic Apalachicola Bay sediment was gray-black. This color has been commonly attributed to the presence of ferrous iron sulfides. Much of the oxidized layer was removed when the water that had been displaced by sediment compaction was decanted from the container. The oxidized layer was slowly regenerated by exposure to the atmosphere. Diffusion of atmospheric oxygen through the bulk sediment was exceedingly slow. When anaerobic sediment was placed in an evaporating dish to dry, a black inner layer surrounded by a brown coating was observed. The anaerobic portion gradually became smaller as the sediment approached complete air dryness.

140. Anaerobic (black) sediment can always be obtained from the sample containers by scraping off the relatively thin oxidized layer. Slow biochemical degradation of vegetative organic matter in the sediment prevents oxygen from diffusing past this narrow boundary, thereby keeping the underlying sediment anaerobic. Apalachicola Bay sediments contained a considerable quantity of decomposing twigs, leaves, roots, etc. Whereas most of these materials were undecomposed organics which, in combination with microorganisms, exert a BOD over a period of days to months and have little if anything to do with the IOD, they were partially removed from the sediments used in these studies.

141. It is important that materials larger than sand size (> 1.0 mm) are carefully removed from the samples used for the IOD test. These materials cause a major problem in obtaining the weight used to normalize the IOD results. If a percentage of the weight of one small sample consists of an object which does not create an IOD, then it becomes quite difficult to get replicate samples to agree with one another. These objects can be removed by careful sieving in a nitrogen-filled glove bag.

142. There did not appear to be any need to homogenize the sediment samples in the glove bag. Replicate IOD analyses always agreed fairly well with one another as long as the test criteria described in the section above were carefully followed. The IOD expressed for a given sediment should be the average of at least two replicates at the optimum dilution. If one of the other IOD dilutions also falls in the 40 to 70 percent oxygen-depletion criterion, it can also be included in the calculated average.

143. The shapes of typical replicate oxygen-depletion curves which meet all the test criteria are shown in Figure 57. Notice the continual rate of oxygen depletion even after 1 hr of testing. For the purposes of discussion, the curves will be arbitrarily divided into three segments.

144. Section A of the curves represents the rapid consumption of dissolved molecular oxygen by sulfide and ferrous iron, which has been defined in the previous section as the IOD. It is this section

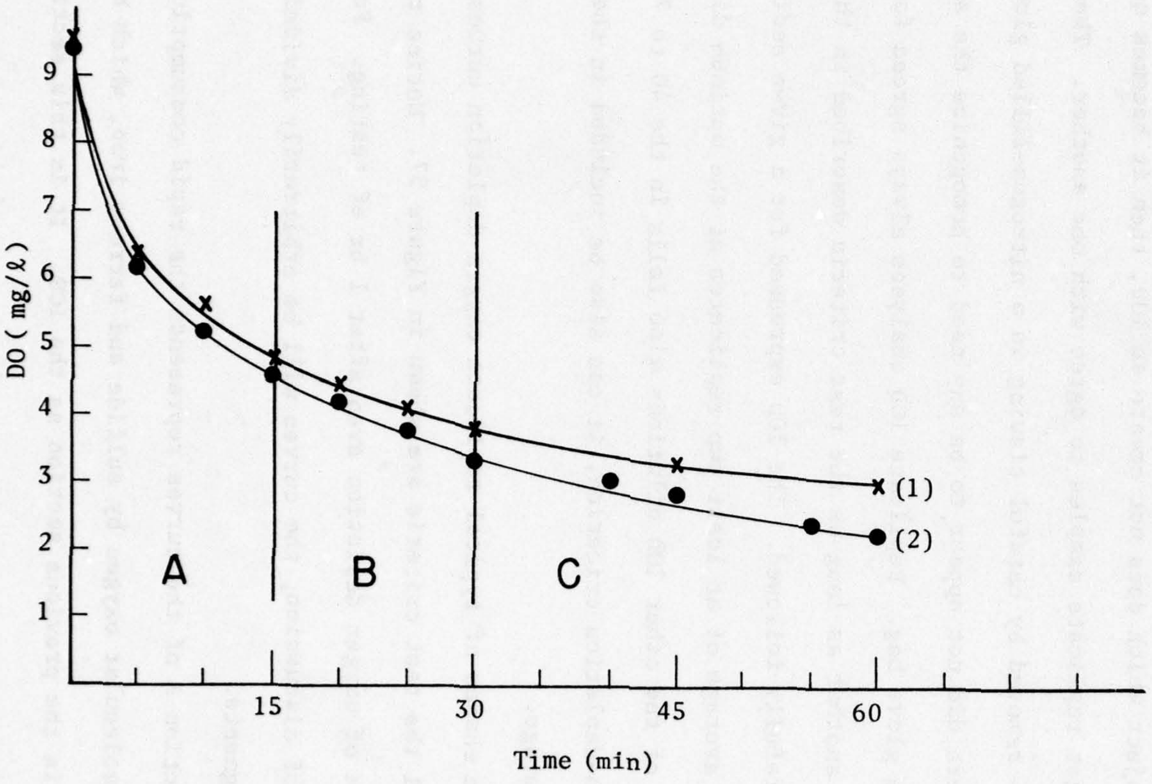


Figure 57. Typical oxygen-demand curves

of the curve that has the greatest potential for describing the effects of dredging and dredged material disposal on the DO levels in the receiving water column. Table 12 indicates that the rate of oxygen consumption is much greater within this segment of the curve. The 15-min period was arbitrarily selected. However, the rates in this segment of the curve are clearly more rapid than in the other segments.

Table 12

Rate of Oxygen Depletion in a Typical Oxygen-Demand Curve

Curve Segment	Elapsed Time min	Rate of Oxygen Depletion mg O_2/min	
		Curve 1	Curve 2
A	0-5	0.64	0.66
	5-10	0.14	0.18
	10-15	0.16	0.12
B	15-30	0.07	0.09
C	30-45	0.04	0.06
	45-60	0.02	0.03

145. In the second segment of the curve, Section B, the rate of oxygen consumption is considerably reduced. It is during this period that the secondary oxidation-reduction reactions are probably taking place. These reactions have not been studied in any detail for dredged material disposal. However, they are most likely similar to the reactions described above in which ferric iron catalytically oxidizes organic matter and sulfide iron. The ferrous iron formed in these reactions

slowly consumes the DO. In this manner, ferric iron is catalytically regenerated. In many shallow water disposal sites, most of the sediment will have settled from the water column before these reactions can exert any measurable impact on the DO.

146. At some point in time the slower biological reactions will have completed their incubation period and begin to exert a BOD. It is impossible to arbitrarily determine when this will take place. If experimental conditions are favorable and the sediment has an active microbiological component, it is not unlikely that these reactions could be measured within the time shown in Figure 57. Biological influences make the description of an ultimate IOD quite difficult because it is difficult to separate these effects without some degree of sediment manipulation to destroy the biological component. From the standpoint of describing actual dredged material disposal operations, such an ultimate IOD may have little practical significance.

147. A typical series of analyses run at various sediment dilutions are shown in Table 13. The only replicates which both meet the IOD criterion for the 40 to 70 percent oxygen depletion are the 3- and 4-ml samples. These IOD results are the most consistent obtained in the series. However, none of the values are drastically different because the amount of sediment used is accounted for in the calculations. The sediments used for this series were taken directly from the sample container without any preliminary sample manipulation (i.e., homogenization). This may account for some of the variability observed. As discussed in the section above, the error associated with the DO measurement at high and low oxygen depletions also contributes to the uncertainty of the measured IOD.

Table 13

IOD's Obtained in a Typical Dilution Series

Sediment Wet Volume ml	Calculated Sediment Dry Weight g	DO Depletion in 300 ml mg/ℓ	IOD_{15} mg O_2/g dry wt
1	0.36	1.1	0.92
2	0.69	2.2	0.96
2	0.75	2.8	1.12
3	1.07	4.1	1.15
3	0.95	3.9	1.23
4	1.43	5.6	1.17
4	1.43	5.8	1.22
5	1.84	6.0	0.98
5	1.80	7.0	1.17
6	2.13	8.1	1.14
8	2.81	8.6	0.92
10	3.53	depleted	

148. A number of different dilution media were examined to see if they had any effect on the IOD test. These media included distilled water, seawater from the Massachusetts coast (27 ^{o}/oo), artificial seawater, and sodium chloride solutions in distilled water. All the dilution media were free of oxygen-demanding substances as determined in blank sample runs. In none of these cases could the IOD results be distinguished as being different from one another. No pH variations outside ±0.1 pH unit were evident within the 15-min test period.

149. The IOD tends to increase gradually with time in an unpreserved sediment sample. A stepwise increase in IOD from 0.82 to 1.31 mg/kg sediment dry weight was measured during a 5-month period. Much of this increase is attributable to the reduction of ferric iron and sulfate to form the oxidizable species ferrous iron and sulfide. However, as stated

above, the organic matter fraction of the sediment is also being biochemically decomposed. This process may release oxidizable inorganic species such as ferrous iron and sulfide which may have been tightly bound in the organic matter when the sample was obtained. Iron and sulfur are commonly incorporated in porphyrin and protein molecules. In addition, many of the organic metabolites which are by-products of the BOD process may also contribute to this increased IOD. Care must be taken to inhibit these processes to the maximum extent possible without drastic modification to the sample. Refrigeration will slow down the biological activity. However, even with this method of preservation, the IOD test should be conducted with as little delay as possible. If the quantity of organic matter is low and the time between sampling and testing is less than 2 weeks, the increase in IOD in a refrigerated sample is not a very important source of error.

150. This simple experiment indicated that the IOD of the sediments was possibly a function of the level of reducing activity (i.e., Eh) in the sediment. This was briefly examined in greater detail by spiking IOD test containers with quantities of ferrous iron, manganous manganese, and sulfide (i.e., reducible components). As expected, both ferrous iron and sulfide increased the measured IOD. Manganous manganese had no effect on the IOD under the test conditions.

151. No oxygen depletion was noted when excess quantities of either ferrous iron (as $FeCl_2 \cdot 4H_2O$; pH=5.0) or sulfide (as $Na_2S \cdot 9H_2O$; pH=6.0) were added to a BOD bottle with air-saturated distilled water. If the water was made alkaline with sodium hydroxide prior to the addition

or if seawater (higher alkalinity) was used, all the oxygen in the BOD bottle was depleted in the case of ferrous iron. This was expected because of the known dependence of ferrous oxidation on the hydroxide ion concentration. Sulfide oxidation did not take place within the 15-min test period under similar conditions. However, this reaction could be catalytically initiated by adding ferric iron (as $FeCl_3 \cdot 6H_2O$) to the BOD bottle. The addition of freshly precipitated ferrous sulfide to the BOD bottle also caused oxygen consumption.

152. Addition of ferric iron directly to the IOD test inhibited the amount of oxygen consumption observed. The ferric iron additions were expressed as grams $FeCl_3$ added per liter of a dredged material slurry which was 20 percent solids by weight. Figure 58 illustrates the phenomenon observed. Engler and Patrick[59] performed a similar experiment using ferric phosphate as an oxidant. Their results suggest that oxidant increased the redox potential to the point where the sulfide ion was oxidized. As the redox potential decreased, when the ferric iron was spent, sulfide production replenished the oxidized sulfide. Another possible explanation for this phenomenon is that a dramatic increase in the ferric/ferrous ratio would provide the chemical driving force for the oxidation-reduction reaction between sulfide and ferric iron. Free sulfide concentrations in the slurry decreased in these tests from about 1.6 mg/ℓ to less than 0.2 mg/ℓ. At the same time an excess of ferric iron inhibits the oxidation of ferrous iron by forcing the reaction towards the reactants. The ferric chloride doses required to produce a 50 percent reduction of IOD on a hydraulic dredge operating at 10,000 gpm would be on the order of 800 lb $FeCl_3$/min. It is evident that this

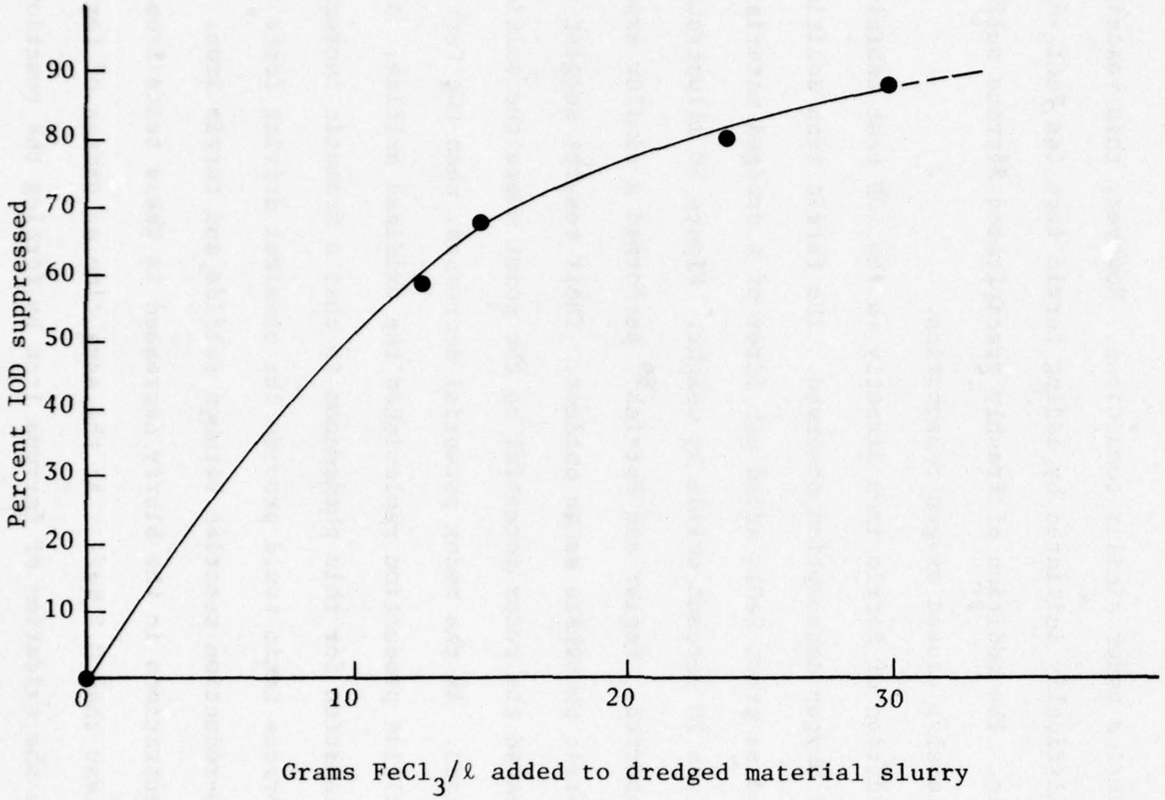


Figure 58. IOD suppression observed after ferric chloride addition

application does not offer any practical potential for use as a dredged material treatment technique. However, it could provide future researchers with a tool for investigating the relative importance of sulfide and ferrous iron oxidation-reduction reactions in accounting for the IOD.

153. No attempt was made to investigate the effects of selected organic chemicals on the IOD test. Many chelating organics have been shown to be capable of creating conditions whereby the oxidation of ferrous iron in well-oxygenated environments is inhibited.[31] A plot of the rate of oxidation of ferrous iron in the presence of organics extracted from natural water systems (see Figure 59) shows a remarkable resemblance to the IOD phenomenon illustrated in Figure 57. More research should be conducted on the relationship of the organic matter chelation and oxidation-reduction reactions to the observed IOD phenomena in dredging operations.

Laboratory Oxygenation Experiments

154. In order to interpret the field demonstration results and to test the applicability of the theoretical information, a series of laboratory oxygenation experiments were conducted. In this manner it would be possible to observe the oxidation of dredged material under a number of different but manageable circumstances. Three types of experiments are described in this section. They include oxygenation in open containers, oxygenation in closed containers, and oxygenation in a closed loop. The effects of oxygenation on the sediment particle size were investigated in the first case.

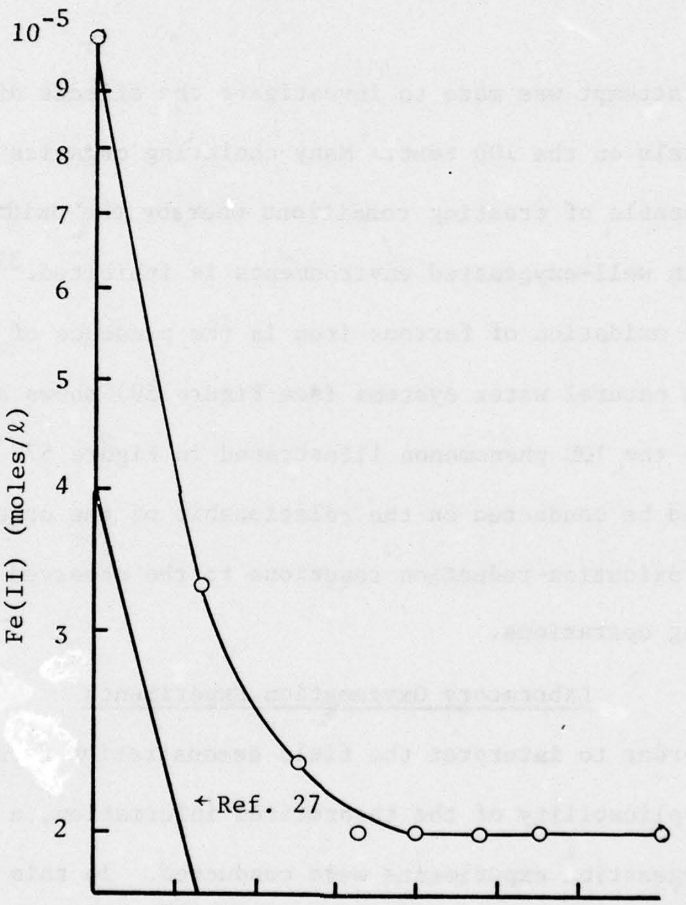


Figure 59. Rate of oxidation of ferrous iron in the presence of humic acids extracted from natural waters[31]

155. Oxygenation in open containers. A series of experiments were designed in which 100 g wet sediment was added to standard graduated cylinders and diluted with artificial seawater to the 1-ℓ mark. These conditions are identical to the nondispersed particle-size determinations. Oxygenation of the sediment was conducted by introducing oxygen gas into the column through a fine porosity fritted glass diffuser. (Arrangements similar to these are used on a plant scale in industrial and municipal wastewater applications.) The problem of oxygenation in this manner is that the efficiency of oxygen transfer between gas and liquid phases depends on the type and porosity of the diffuser, the size of the bubbles produced, the depth of submersion, and a variety of other factors. In general, this efficiency has been reported to vary from 5 to 15 percent, with 8 percent probable from porous tube diffusers.[60]

156. Using a flow rate of 8-10 cu ft/hr it took nearly 1 hr of oxygenation to satisfy the IOD of the sediment as evidenced by the color change and the lack of oxygen depletion in the column when the oxygen source was removed. Even though the process is relatively inefficient, the sediments were oxidized. If these sediments were allowed to settle and sit for about a week, they became anaerobic again. In this case, slow biochemical processes deplete the oxygen in the sediment and cause the anaerobic conditions and hence the IOD to return once again. Oxygenation, therefore, is only temporary.

157. This oxygenation method was used to suspend sediments in a nondispersed particle-size distribution analysis (see Appendix A).

Working under slightly different conditions and with a different sediment Moore and Newbry[54] noted that oxygenation took greater than 2 hr. The nondispersed test was used to simulate open-water disposal conditions. Nitrogenated sediment particle-size distribution was determined as a control to account for any possible physical effects the gas stream may exert in the column. Two separate trials were run. In both cases oxygenation appeared to increase the relative percentage of fines. The results of these trials are graphed in Figures 60 and 61. Visual observations made at the time of the test indicated that the oxygenated sediments not only settled more slowly but also occupied a greater volume at the bottom of the cylinder (i.e., less compaction).

158. A standard dispersed particle-size distribution test was run with both oxygenated and nitrogenated (i.e., anaerobic) sediments. As in the nondispersed tests described above, the oxygenated sediments had a greater percentage of fines (Figure 62). The cause of this phenomenon is not certain. One possibility may be the in situ generation of colloidal hydrous ferric oxide and elemental sulfur species. Generation of these colloidal species would skew the particle-size distribution toward larger percentages of finer materials. It must be kept in mind that these sediments were exhaustively oxygenated over a long time interval in a manner that does not simulate conditions found in a hydraulic dredging operation. The generation of materials which are finer and settle more slowly may serve to negate many of the beneficial effects of the in-pipe oxygenation of hydraulic dredging slurries. More study of

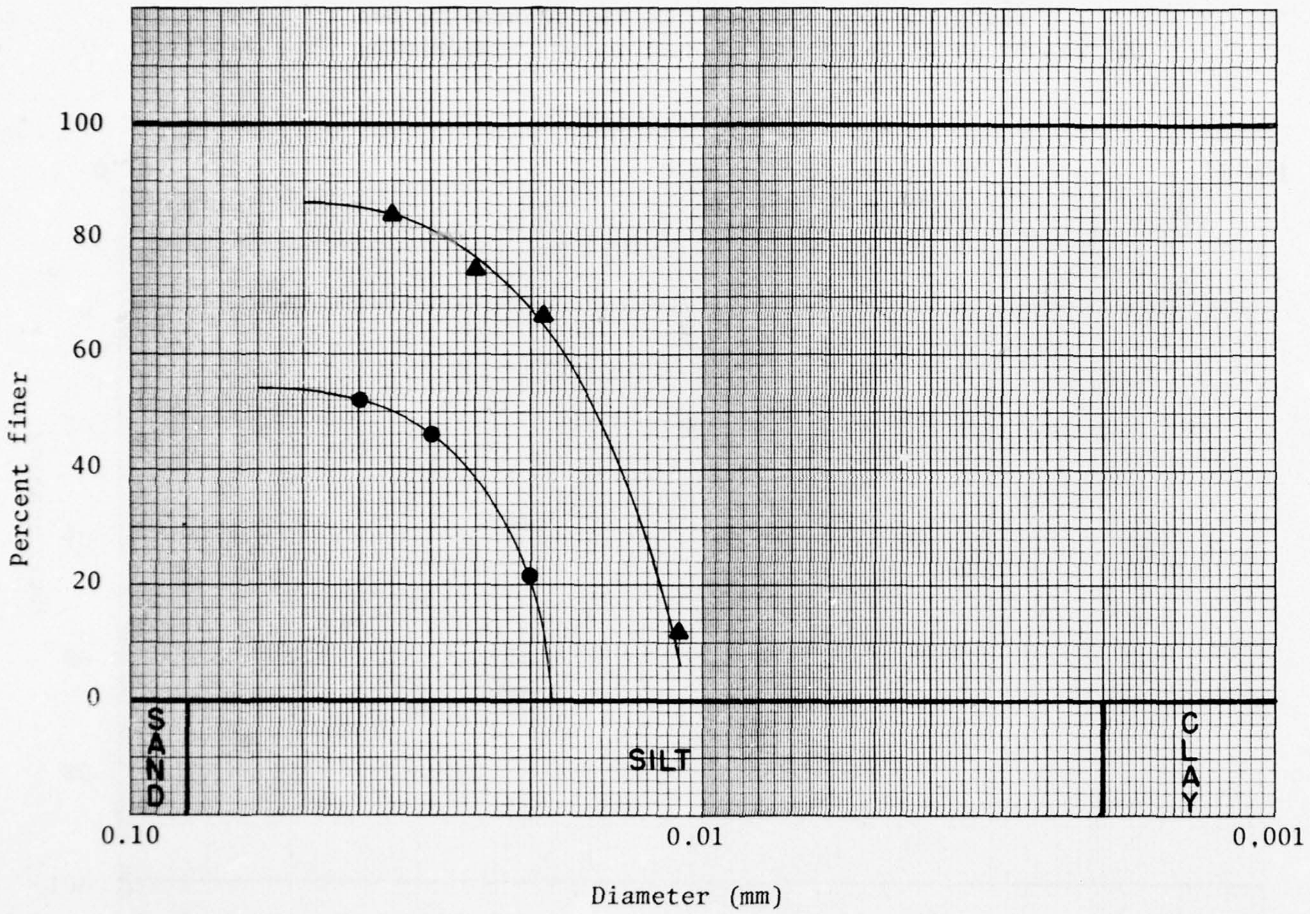


Figure 60. Preliminary nondispersed particle-size distribution of anoxic (●) and oxygenated (▲) Apalachicola Bay sediments

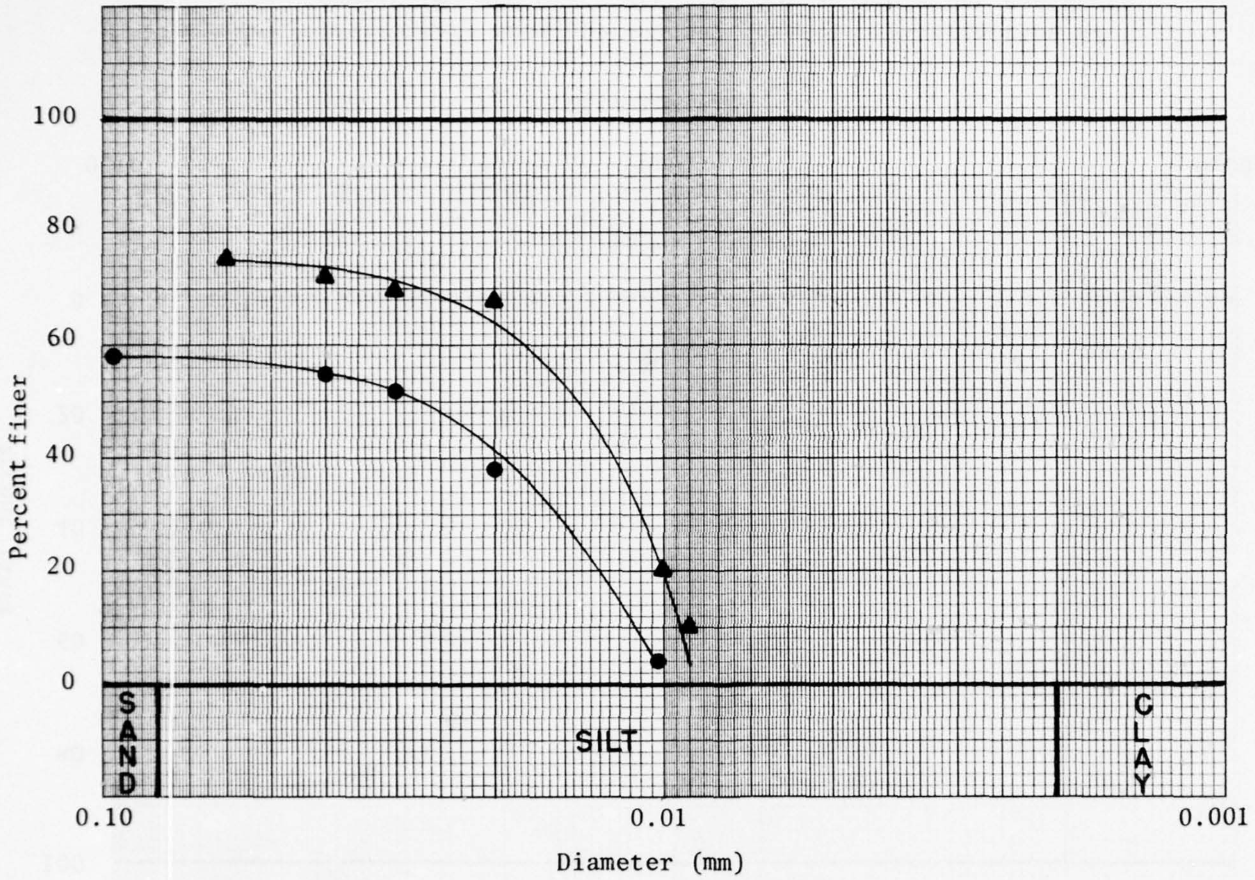


Figure 61. Nondispersed particle-size distribution of anoxic (●) and oxygenated (▲) Apalachicola Bay sediments

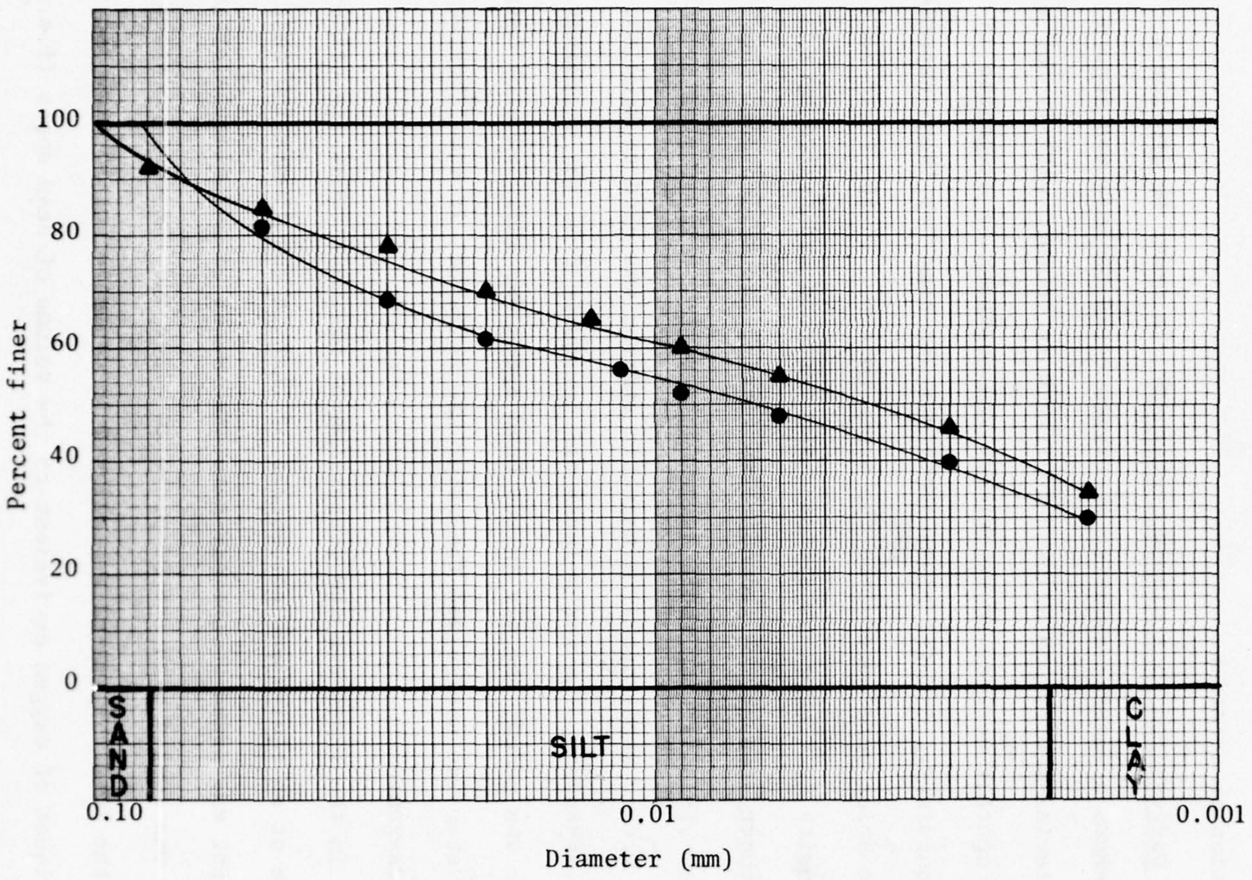


Figure 62. Dispersed particle-size distribution of anoxic (●) and oxygenated (▲) Apalachicola Bay sediments

these phenomena is needed before the relative trade-offs between these effects can be assessed, but it should be noted that the field tests discussed earlier showed no increases in plume suspended solids as a result of oxygenation or aeration.

159. Oxygenation in a closed container. In order to provide a situation where a metered quantity of oxygen could be injected into a dredged material slurry and allowed to remain in contact with it for a measurable contact period, an experiment was designed to oxygenate in a closed container. A 1-gal glass container was used for these experiments. Two holes were bored into the screw-on cap. In the first hole a fine porosity fritted glass diffuser was inserted and sealed by a one-hole rubber stopper. A ground glass fitting was sealed into the second hole. This fitting would accommodate either a glass stopper or a DO probe with a water seal. A magnetic stirrer was used to keep the sediments suspended. The water level did not quite fill the container. When oxygen was added, the air in the head space was enriched with oxygen. Once the system was sealed and the water was agitated, it equilibrated with this oxygen.

160. In the first run the proportion of sediment added was calculated to be at an equivalent percentage of that in the 15-min IOD test. This sediment was added to the air-saturated water with a plastic syringe. The system was sealed with the DO probe in place and the concentration of oxygen in the reaction vessel was allowed to decrease for 15 min. At this time an aliquot of oxygen equivalent to the volume of head space (i.e., approximately 5 cu in.) was added to the system. The DO concentration in

the slurry increased back to the saturation level and did not exhibit the slow decrease with time noticed in the IOD tests described in the previous section. The oxygen exchange between the head space and the circulating slurry is sufficient to satisfy this low level demand and keep the water saturated with respect to DO.

161. This laboratory oxygenation system could not be used effectively with larger quantities of dredged material because of the inefficient nature of contacting the slurry with the oxygen in the head space. Therefore, a closed-loop system was designed to study the oxygenation phenomena in more detail.

162. Oxygenation in a closed loop. A laboratory-scale closed-loop circulating system was set up to simulate the uptake of oxygen by a sediment slurry in a hydraulic pipeline. This system consisted of approximately 28 ft of 0.5-in. ID Tygon tubing attached to a self-priming pump. T-connectors provided access to the system for oxygen injection, sediment addition, DO measurement, and equalization to allow for volume expansion following the oxygen addition. The volumes of the various system components were as follows: main circulation loop, 63.62 cu in. (1.043 ℓ); equalizer branch, 18.85 cu in. (0.309 ℓ); and input branch and pump, 3.54 cu in. (0.058 ℓ) (Figure 63).

163. Gas injection was made into the system through a fine porosity fritted glass diffuser positioned vertically just below the main flow channel in an inverted T-connector. A manifold was designed so that either nitrogen or oxygen gas could be metered into the system under controlled conditions. Dissolved oxygen concentration was monitored by means

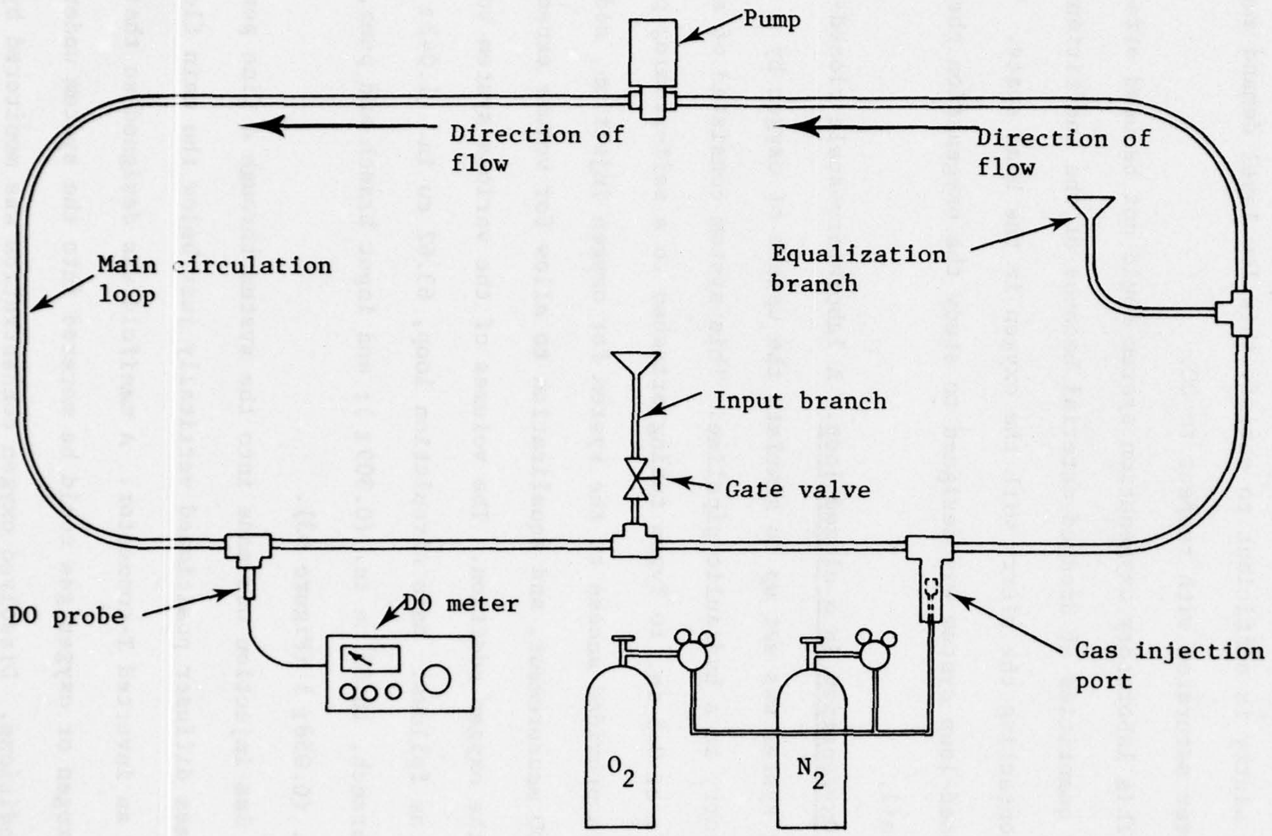


Figure 63. Schematic of closed-loop system to simulate oxygenation

of a DO probe threaded into a T-connector perpendicular to the flow but in the same plane as the main flow channel. The tip of the membrane was in the flow channel in order to provde the level of agitation across its surface necessary for proper DO measurement. A large funnel on the sediment addition arm facilitated the expeditious addition of the slurry. A gate valve prevented the slurry from backing into this arm once the pump was turned on.

164. The first sample run with the closed-loop system was conducted with distilled water that had been purged of oxygen by bubbling nitrogen through it. First, the empty loop was purged with nitrogen gas. With the gas turned off, the water was then rapidly fed into the loop through the slurry addition arm. A stream of nitrogen gas was fed over the top to the funnel to minimize solution of atmospheric oxygen. The bubbles that were present in the main loop were forced into the equalizing arm by manipulating the level of the various system's components. When the system was free of bubbles, the pump was turned on and the water allowed to circulate. The DO meter indicated zero DO in the solution. No significant permeation of oxygen into the system through the Tygon tubing was observed. Approximately 12 cu in. of oxygen were metered into the system in 8.5 sec at a rate of 3 cu ft of oxygen/hr. The oxygen was added as fine bubbles, that had a tendency to coalesce in the main circulating loop to form large bubbles that circulated around the top of the system. During the injection, water was forced into the equalizing arm to relieve the pressure. Surprisingly, the gas did not appear to escape during the short test period. With the time it took to add the

oxygen, the DO meter registered a fully saturated DO level. An aliquot of the water was removed from the system by pumping through the input arm into a BOD bottle. The bubbles were forced to the top of the bottle on a magnetic stirrer. A DO probe was inserted and the DO was measured. This reading confirmed the readings taken in the loop.

165. A potential problem with the loop was the water temperature increases brought about by the friction of the pump impeller. Temperature changes of 10°C in 15 min were not uncommon. However, residence times of dredged material in a hydraulic dredge pipeline are usually only on the order of a few minutes. Therefore, temperature increases in this extended simulation were not a significant factor if only fast reactions were examined. In any event, proper temperature correction of all DO measurements was always made.

166. The second test run was made with a dredged material slurry. In order to generate a slurry with a solids content which is representative of that present in a hydraulic dredge, 282 g of Apalachicola sediments (dry weight basis) were suspended in a total volume of 1.410 ℓ of distilled water. This provided a slurry solids content which was 20 percent by weight. Nitrogen gas was vigorously added to this mixture to prevent sediment oxidation. The DO concentration of the slurry before nitrogen addition was zero. In a manner similar to that in the first test run, the slurry was fed into the nitrogen-purged test loop; the bubbles were removed; and the pump was turned on. The quantity of oxygen gas required to satisfy the 100 percent of the IOD of the sediment was calculated from

the measured IOD and the quantity of sediment. At a flow rate of 2 cu ft/hr, it would take 12.5 sec to meter the oxygen into the system. The same quantity of oxygen was used in this run as in one first run. The DO level in the slurry increased to saturation in the time it took to meter the oxygen into the system. This saturation level was maintained in the loop throughout the test period. After 10 min an aliquot was removed from the system into a BOD bottle and the bubbles were allowed to rise and escape. The oxygen was rapidly depleted from this sample as measured with a DO probe. It is obvious that the IOD was not satisfied within the circulating system.

167. A third test run was conducted under similar conditions, except that the oxygen was metered into the loop at 4 cu ft/hr for 6.3 sec. Once again the slurry DO in the loop remained saturated for the entire period. However, the DO in the slurry was rapidly depleted by the sediment when the nonsoluble gaseous oxygen was allowed to escape.

168. It would appear from this bench-scale demonstration that simple in-pipe oxygenation of dredged material would not be an effective means of completely satisfying the IOD of the sediment. However, by oxygenating the water in the slurry and by creating increased upwelling in the receiving waters with escaping oxygen gas, the observed oxygen depletion in the vicinity of the hydraulic pipeline outflow should be reduced.

Comparative Investigation of the Effects of Dredged Material Oxygenation

169. In this phase of the laboratory study, several sediments with variable chemical and physical characteristics were investigated relative to one another to determine their potential for exerting an IOD when dispersed in an aerobic water column and to determine what would happen to the sediment and solution characteristics if the materials were dredged with or without oxygenation. Of particular interest in this section was the concern over whether the process of oxygenation would promote the elutriation of heavy metals to the water column leading to the potential degradation of the receiving water quality.

170. For the sediment comparisons two sediments provided by the U.S. Army Engineer District, New England, were used. These sediment samples, which were from New London, Connecticut, and Fall River, Massachusetts, were taken in conjunction with proposed maintenance dredging operations at these sites. The other two sediments were obtained from Apalachicola Bay in the Gulf Intracoastal Waterway. One of these samples was obtained during the time of the field demonstration and the other was the preliminary sample used in the laboratory studies previously described.

171. Each of these four samples was characterized by the following tests: percent solids, volatile solids, dispersed particle size, total carbon, ferrous iron, free sulfide, COD, and IOD. Nitric acid sediment digestions were performed to determine the total concentration of each of the following metals: iron, manganese, copper, cadmium, nickel, zinc,

arsenic, and mercury. The results of these tests are summarized in Table 14. All the sediment characterization techniques are described in Appendix A.

172. One important aspect of the comparative laboratory study was to examine the relationship between the particle-size distribution and its oxygen-demand characteristics. Such a relationship would be quite useful for estimating IOD levels throughout a potential maintenance dredging location. The Illinois State Water Survey[41] found a significant difference between the sediment BOD rates for sand- and gravel-size sediments and sediments consisting predominantly of silt- and clay-size particles. Other investigators have shown that oxygen-demanding substances are generally adsorbed to clay-size particles in natural waters. These particles become flocculated in an estuary and tend to settle out within a particular region governed by variable estuarine sedimentation patterns. While it is logical that a relationship should exist between particle size and oxygen demand, it may only be a casual relationship because of a source of relatively uncontaminated silts or clays which may dilute or otherwise alter this relationship in selected reaches of the estuary. Because the modified IOD test is a simple one to conduct, there is really little need to rely completely on other sediment properties to indicate what the oxygen-demanding properties of the dredged material may be.

173. In this comparative laboratory study, the sediments with the largest silt-clay composition (Apalachicola Bay) had the largest IOD, COD,

total carbon, percent volatile solids, and ferrous iron concentration. The results for each of these parameters were the lowest for the sediment sample with the lowest silt-clay composition (New London) and intermediate for the sediment with the intermediate silt-clay composition (Fall River). These results are presented in Table 14. The free sulfide analyses, although considered to be an important immediate oxygen-demanding parameter, did not follow this same trend. The sample with the lowest sulfide had the greatest IOD value. This set of samples, which were selected randomly, was very small, however. A larger sample size is needed to determine whether or not the trends established are statistically valid.

174. Another important aspect of the comparative laboratory study was to determine whether oxygenation would enhance the release of chemical substances in quantities that would violate water-quality criteria. The National Academy of Sciences[62] lists the following receiving water concentrations (in mg/ℓ) as posing a hazard to marine organisms when exceeded: arsenic, 0.05; cadmium, 0.01; copper, 0.05; iron, 0.30; manganese, 0.10; mercury, 0.0001; nickel, 0.10; sulfide, 0.01; and zinc, 0.10. To evaluate the effect of oxygenation on the concentration of selected parameters in the dredged material slurry prior to discharge, each of the three sediments described above was subjected to elutriate tests under both oxidizing and reducing conditions. The elutriate test was similar to the revised method used for the evaluation of dredge and fill operations;[63] i.e., vigorous gassing of the slurries with oxygen or nitrogen (10 to 12 cfh) was substituted for the 30-min shaking step. Elutriate tests were conducted in seawater obtained from the Atlantic Ocean at Marblehead,

Table 14

Comparative Study Analytical Results

Parameter	Apalachicola Preliminary	Fall River	New London	Field Demonstration Apalachicola
Percent solids	33.6	40.7	48.3	40.5
Volatile solids, percent	15.5	11.1	6.1	-
Particle size, percent				
Sand	6	33	63	36
Silt	59	50	26	44
Clay	35	17	11	20
Total carbon, percent	4.6	3.8	3.4	-
Free sulfide, mg/kg dry weight	417	1,434	575	-
Ferrous iron, mg/kg dry weight	10,060	7,686	5,556	-
Chemical oxygen demand, mg/kg dry weight	87,460	70,070	65,820	-
IOD, mg/kg dry weight	0.934	0.487	0.174	-
Iron, mg/kg dry weight	39,535	25,620	19,385	33,995
Manganese, mg/kg dry weight	215	28.9	23.9	152
Copper, mg/kg dry weight	27.9	124	75.9	25.9
Cadmium, mg/kg dry weight	<0.58	<0.41	<0.41	<0.45
Nickel, mg/kg dry weight	<1.16	26.4	20.6	<0.90
Zinc, mg/kg dry weight	127.9	413.2	239.2	98.4
Arsenic, mg/kg dry weight	<4.65	<3.31	<3.30	<3.58
Mercury, mg/kg dry weight	*	<0.66	<0.66	<0.72

* Erroneously high readings probably caused by an incomplete digestion allowing interfering vapors of sulfur and nitrogen oxides to be absorbed at 2537Å[61]

Massachusetts. This water (27 °/oo salinity) was diluted with deionized water to a salinity of 5 °/oo to simulate actual concentrations encountered in Apalachicola Bay and other estuaries where dredging operations may be expected.

175. Oxygenation elutriate tests were conducted in open 1-gal jugs in a manner similar to the laboratory oxygenation studies discussed above. Oxygenated sediments in the elutriate tests were slower to settle. No precautions were taken to avoid exposure to oxygen during the decanting and filtering operations. Nitrogenation was conducted in the closed jugs described in the laboratory oxygenation experiments. Nitrogen was allowed to escape during the agitation period. However, the surface of the water was maintained under a continuous stream of nitrogen during the settling period. Elutriate water was drawn from the test container in a syringe and transferred to the filter mechanism, which was maintained under a stream of nitrogen gas. In each case, the jugs were swirled occasionally during the 30-min gas contact period to ensure contact of the sediment with the gas stream and water. The filtered (0.45μ) elutriate samples were analyzed for ferrous iron, free sulfide, total iron, manganese, copper, cadmium, nickel, arsenic, zinc, and mercury. Metals analyses of the elutriates were performed using conventional atomic absorption spectrophotometry. Special preconcentration and extractive techniques were only used to confirm the lack of metals in the diluted seawater. The detection limits are quite adequate to observe metals release in the dredged material elutriation slurry prior to its disposal in the receiving water with its relatively large dilution factor. Results are shown in Table 15.

Table 15

Elutriate Test Results*

Parameters	Apalachicola GIWW Sample N_2	Apalachicola GIWW Sample O_2	Fall River Sample N_2	Fall River Sample O_2	New London Sample N_2	New London Sample O_2
Iron	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Manganese	1.75	1.90	<0.01	<0.01	0.12	<0.01
Copper	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cadmium	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Nickel	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Zinc	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Arsenic	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Mercury	**	<0.008	<0.008	<0.008	<0.008	<0.008
Sulfide	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ferrous Iron	0.02	<0.005	0.009	<0.005	0.01	<0.005

*All concentrations expressed as mg/ℓ.

**Erroneously high reading (see note in Table 14).

176. Elutriation of the Fall River and New London sediments did not release significant quantities of chemical constituents in either the nitrogen or oxygen mode with the single exception of the manganese found in the New London nitrogen elutriate. Similar results were obtained with the preliminary Apalachicola sediments. In this case, larger quantities of manganese were released in both oxygen and nitrogen modes. Very small levels of ferrous iron were found in each of the nitrogenated elutriates.

177. Acid digests of the sediments confirmed the presence of iron, manganese, copper, and zinc in all the samples tested. Nickel was found

in the New London and Fall River sediments. No cadmium or arsenic was detected in the sediments examined. Comparing these results to the elutriate results above, it is obvious that no large-scale release of chemical constituents occurred in any of the above cases. It is interesting to note that the Apalachicola elutriate results agree with previously published[64] results.

178. A number of recent studies have contributed to the understanding of metals and nutrient release from anaerobic and aerobic sediments. Chen et al.[65,66] examined the release of chemical species upon disposal of dredged material by subjecting various sediment-water samples to different redox conditions. In every case (with the exception of iron) metal release, if it occurred at all, was generally limited to less than 1 μg/ℓ over background seawater levels. This same group[65,66] noted that nitrogen and phosphorus (nutrient) compounds were released in less than 1 mg/ ℓ levels over the background concentrations. Most of the concentrations in the soluble phase are well below the allowable concentration levels of marine water criteria. Lee et al.[63] reported that manganese may also be released in larger quantities because of its kinetic resistance to oxidation in the aerobic water column. This group[63] noted that substantial quantities of ammonia-nitrogen were released. Phosphate release was retarded because of the strong sorption tendencies of this anion.

179. Oxygenated and unoxygenated slurries obtained from the field demonstration were sent back to the laboratory for a comparison with the elutriates. However, these samples had a greater solids/liquid contact time than the elutriate tests. The supernate was decanted from the

sample containers and filtered through 0.45-μm membrane filters. Each filtrate contained approximately 31 mg/ℓ iron and 1.3 mg/ℓ manganese. None of the other heavy metals were detected.

180. Both filtrates had a perceptible yellow color due to the presence of soluble humic (fulvic acids) complexing materials. It has been estimated[67] that about 3,400 tons per month of these naturally occurring organics are discharged into Apalachicola Bay by the Apalachicola River. The same report claims there may be as much as 1 million tons of humic material located in discontinuous beds over an area of 300-500 sq miles along the Florida panhandle. These organic substances have been shown to chelate manganese and iron species and maintain them in solution.[36] The concentration of fulvic acids in the Apalachicola River water and other riverine systems varies seasonally. Use of this site water for elutriate tests when the fulvic acids concentration is high could lead to different mobilization phenomena. None of the elutriate tests in this study had the characteristic yellow color associated with these organic substances.

181. The sample size used in this brief comparative elutriation study was necessarily quite small. Sediments from more polluted locations should be tested to confirm the results presented above. However, based on these findings it does not seem likely that in-pipe oxygenation of hydraulically dredged material would increase the likelihood of the elutriation of significantly greater quantities of hazardous metals and nutrients into the receiving water column.

Use of Hydrogen Peroxide as Alternate Oxidant

182. Because hydrogen peroxide has been used as an oxygen source in biological wastewater treatment plants,[68] its use for satisfying the IOD of sediments was briefly investigated in the laboratory.

183. A number of experiments were conducted by suspending 100 g wet dredged material in 1 ℓ of distilled water in an open beaker. Suspension of the sediments was maintained throughout the test by means of a magnetic stirrer. These mixtures were titrated stepwise with a 10 percent hydrogen peroxide solution. The DO concentration was measured with a DO probe following each hydrogen peroxide addition.

184. In every case no change was noted in the DO after adding increments of hydrogen peroxide totaling 0.5 ml. The DO readings at this stage in all the experiments were less than 2.0 mg/ℓ. As the 1.0-ml mark was approached, the DO began to rise. The increase in DO was always delayed by a few seconds from the peroxide addition. This was probably due to the meter response. The addition of 1.5 ml of peroxide saturated the water with respect to DO and 2.0 ml raised the DO to values above 15 mg/ℓ. In the latter case, small bubbles were noted forming on the inside of the beaker walls. The dredged material started turning a brownish hue after 1.0 ml was added, signifying a visible amount of oxidation in the sediment. The sediments were allowed to settle and an IOD test was run in each case to make sure that the IOD had been satisfied.

185. By converting the 1.5-ml value to a 100 percent hydrogen peroxide basis, it would take approximately 0.007 lb H_2O_2 to satisfy the

IOD of each pound of sediment on a dry weight basis. This calculation includes saturating the water after the sediment IOD has been satisfied. The IOD of the sediment used was approximately 0.90 mg oxygen/g sediment dry weight.

186. Assuming that hydrogen peroxide is catalytically converted to oxygen in the following manner:[69]

$$2\ H_2O_2 = 2\ H_2O + O_2 \quad \text{(Reference 69)} \quad (5)$$

the theoretical amount of this oxidant needed to satisfy the IOD of this dredged material is calculated to require 0.002 lb H_2O_2 per pound sediment on a dry weight basis.

187. A comparison of these calculations indicates that the hydrogen peroxide by no means selectively satisfies the IOD. The experimental hydrogen peroxide demand must include *a fraction of the* more slowly oxidized sediment fractions (i.e., organics). However, if the hydrogen peroxide treated sediments are allowed to settle in the beaker and remain for about 1 month, an anoxic layer develops once again as witnessed by the IOD exerted when resuspended in the water. This phenomenon indicates that the addition of the peroxide neither completely oxidized the sediment organics (BOD fraction) nor created toxic intermediates at the concentration and addition rates used in the experiments. Smaller amounts of peroxide could be used to satisfy only a portion of the IOD. The use of liquid hydrogen peroxide solutions also eliminates some kinetic problems associated with getting gaseous oxygen to dissolve in water and react with the substances creating the IOD. This is an important consideration for the application of in-pipe oxygenation of hydraulic dredging slurries, because the oxidant contact period is often quite short.

188. The considerations of cost and technology for using hydrogen peroxide are discussed elsewhere in this report. Therefore, they will not be considered further in this section.

Column Studies

189. Column tests were conducted during which laboratory prepared sediment slurries were released into a large column and the concentrations of several parameters were measured as a function of time. These tests provided an additional procedure for evaluating the nature of the sediment oxygen demands. The IOD and elutriate tests were not considered to be fully representative of field conditions, and the field demonstration did not offer an opportunity to closely observe sediment/water interactions. Column testing was conceived to bridge this gap.

Equipment and procedures

190. The column used in these tests was 7.5 ft high by 1.0 ft in diameter and was constructed of cast acrylic (Plexiglas). For simplicity of construction and ease of cleaning, it was constructed in two sections. Sample ports were provided at 1-ft intervals along the front, and a drain was provided to empty the column at the completion of a test. A wooden frame supported the column.

191. The sediments used in the tests were from Apalachicola, Florida, and Fall River, Massachusetts. Both were maintained in an anoxic state until used in these tests. The physical and chemical characteristics of these sediments are described in Table 14. Sediment slurries were prepared with tap water in a pail and homogenized with a mixer blade driven by an electric hand drill. These test mixtures were poured into

a plastic sheet at the top of the column. In each case the volume of slurry was 4 ℓ. A knife was used to rapidly slit the plastic and dump the sediment/water mixture. An essentially instantaneous release was accomplished in each case.

192. Four parameters were measured in the column prior to release and then at various time intervals. These parameters were suspended solids, ferrous iron, free sulfide, and DO.

Test results

193. The first test was conducted with Apalachicola Bay sediment having a water content of 75.0 percent. When the plastic was cut, the sediment fell in large clumps rather than well dispersed as planned. At this low water content, cohesiveness of the sediment-water mixture (due to the high proportion of silt and clay) prevented extensive mixing as it settled even though it had been thoroughly mixed immediately prior to the drop. Water samples and DO readings were taken at distances of 1 and 4 ft from the bottom of the column. The concentration of each of the parameters versus time and depth is shown in Figures 64 through 67.

194. The DO level at the 1-ft level (as shown in Figure 64) fell within a few minutes from the initial value of 10.3 mg/ℓ to a level of 7.0 mg/ℓ. At the 4-ft elevation, the DO fell to 9.2 mg/ℓ within 1 min. Once these levels were established, little variation was noted. Suspended solids concentrations at both elevations were greatest immediately after the drop (Figure 65). Settling was slow and approximately 30 min was required before fairly constant readings were observed. It is interesting

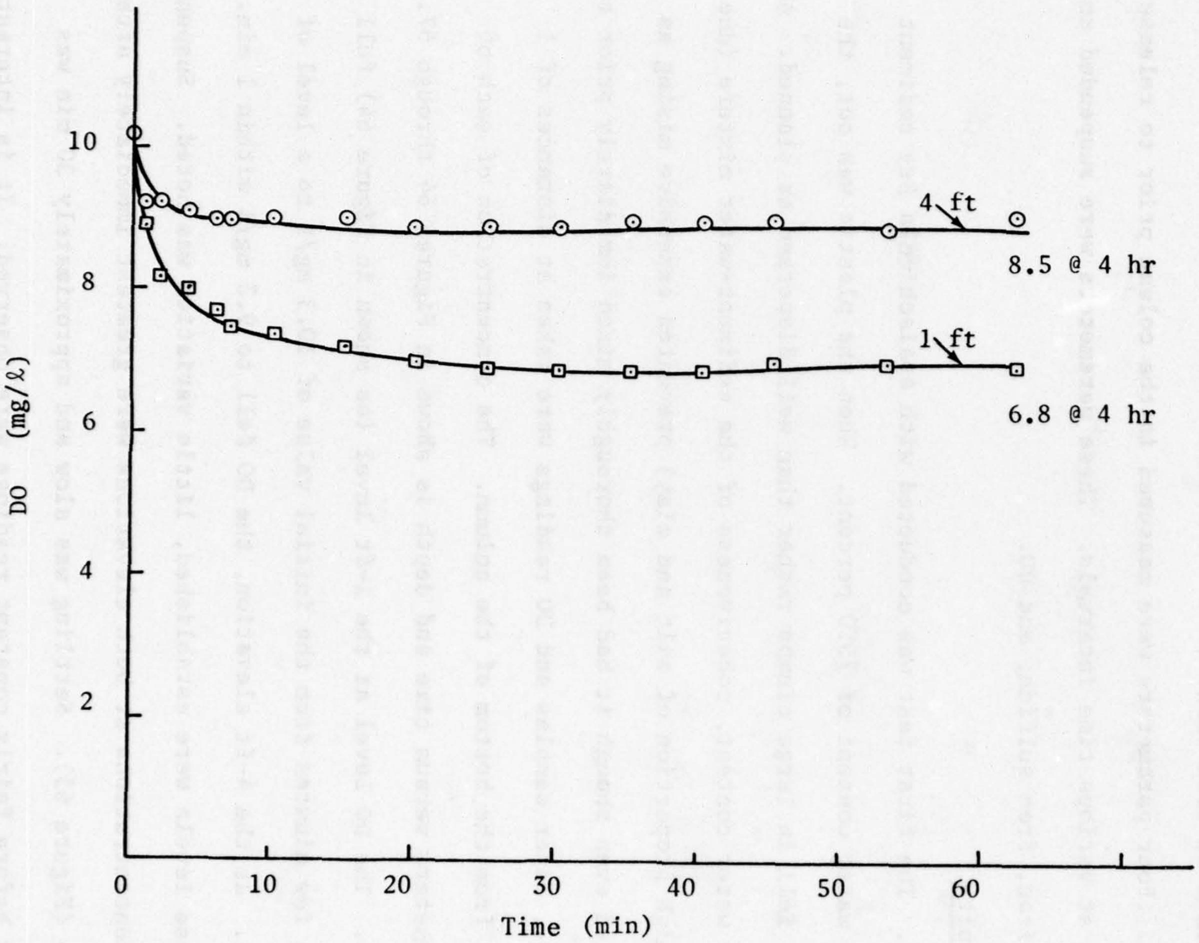


Figure 64. DO variation in Apalachicola sediments (column test no. 1)

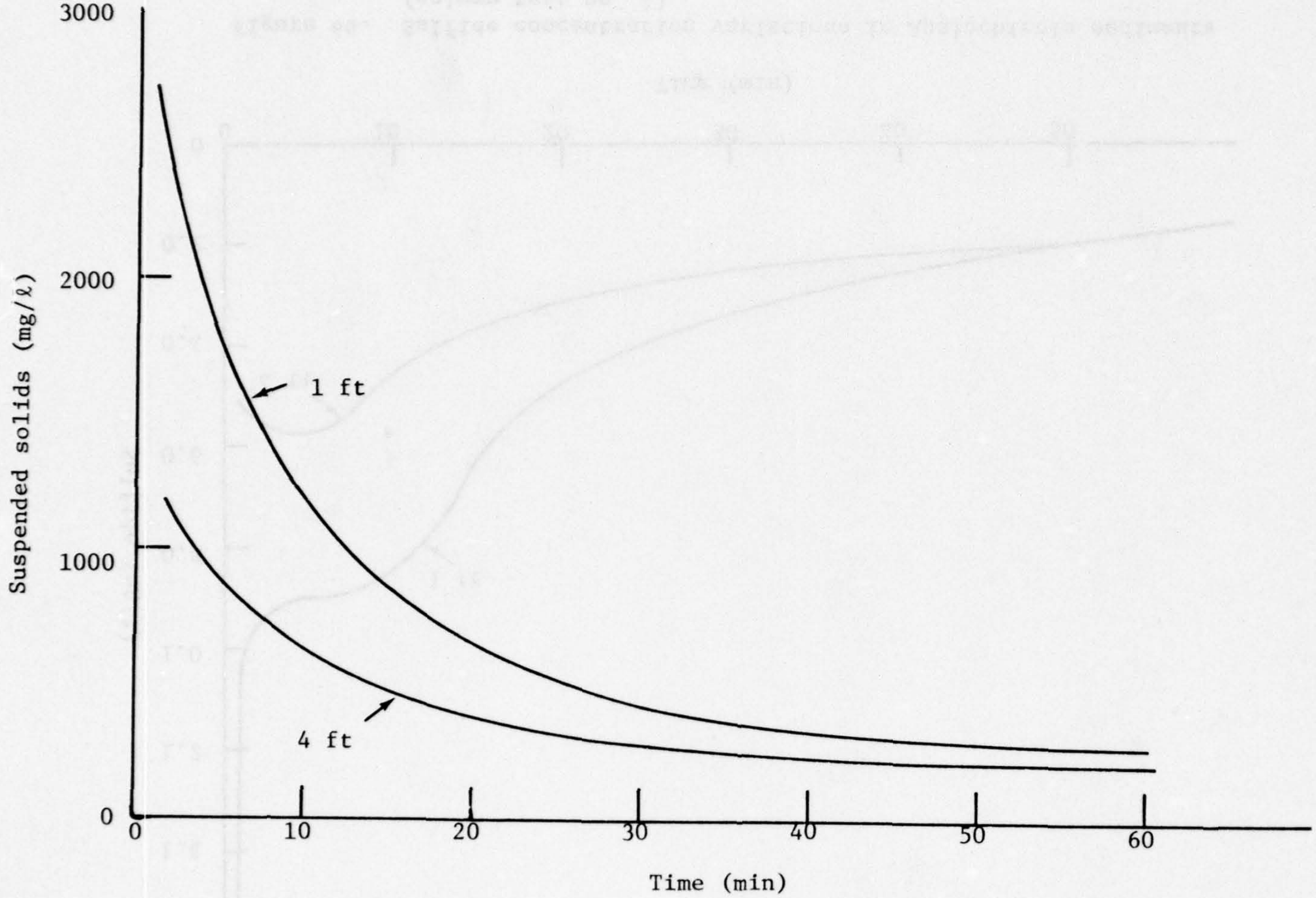


Figure 65. Suspended solids variations in Apalachicola sediments (column test no. 1)

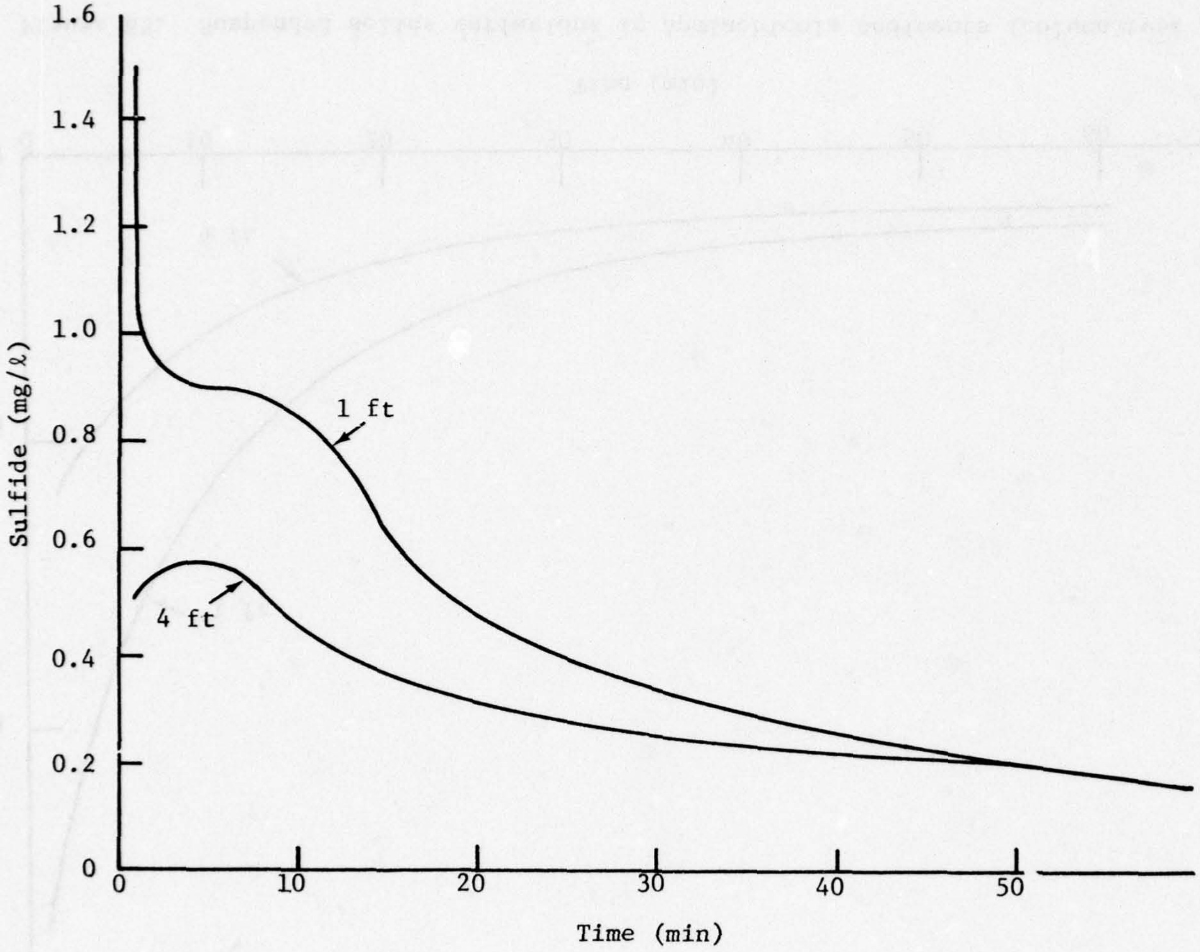


Figure 66. Sulfide concentration variations in Apalachicola sediments (column test no. 1)

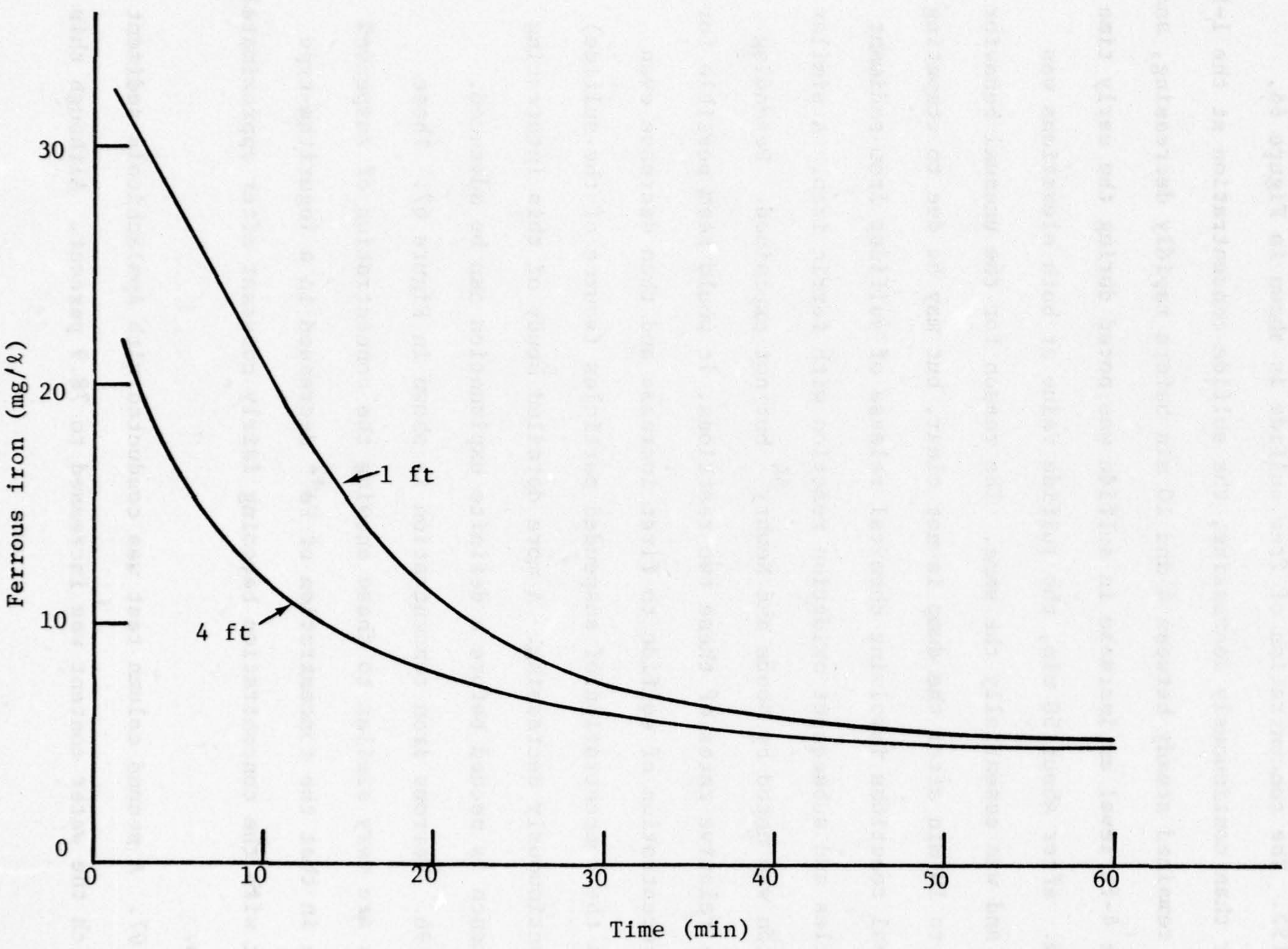


Figure 67. Ferrous iron variations in Apalachicola sediment (column test no. 1)

to note that suspended solids levels in this test decreased more slowly than DO levels.

195. The concentration of free sulfide is shown in Figure 66. Rather than continuously decreasing, the sulfide concentration at the 1-ft level remained steady between 4 and 10 min before rapidly decreasing, and at the 4-ft level an increase in sulfide was noted during the early time period. After about 50 min, the sulfide value at both elevations was noted and was essentially the same. The reason for the unusual behavior prior to 10 min after the dump is not clear, but may be due to competing chemical reactions involving chemical release of sulfides from sediment particles and subsequent oxidation reaction with ferric iron. A similar reaction was noted by Moore and Newbry[54] but not explained. Depending on the relative rates of these two reactions, it would seem possible for the concentration of sulfide to first increase and then decrease even though the concentration of suspended particles (source of the sulfide) was continuously decreasing. A more detailed study of this interesting phenomenon is needed before a definite explanation can be advanced.

196. Ferrous iron concentration is shown in Figure 67. These curves are very similar to those showing the concentration of suspended solids in that the concentration of Fe^{+2} decreased in a logarithm-type manner with the concentration becoming fairly constant after approximately 30 min.

197. A second column test was conducted with Apalachicola sediment in which the water content was increased to 78.9 percent. Although this

change was not great, the effect was to significantly increase dispersion of the sediment/water mixture as it settled through the water. This in turn increased the concentration of suspended solids, sulfide, and ferrous iron and produced a greater drop in DO.

198. Figure 68 shows the DO concentration in the column as a result of the second drop of Apalachicola sediment. Figure 69 depicts the suspended solids concentration versus time, Figure 70 the sulfide concentration and Figure 71 the ferrous iron concentration. These curves are very similar to those for the previous drop, but the greater water content produced greater dispersion and a larger effect on the column water.

199. A third test was conducted with sediment from Fall River, Massachusetts. The result is shown in Figure 72. For this test water samples were taken only at an elevation of 1 ft from the bottom.

Test discussion

200. Significant differences are apparent between the behavior of Fall River sediment and that from Apalachicola. A summary of these results is shown in Table 16. The Fall River sediment caused a maximum suspended solids concentration over twice as great as the maximum for Apalachicola although the water content was less and would have a tendency to reduce fluidity and therefore dispersion. The reason for the increased dispersion is considered to be the large difference between the two sediments in terms of its particle-size distribution. The Fall River sediment contained a considerably greater proportion of sand and only half as much clay. The tendency to larger size particles considerably lowered the cohesiveness of the sediment even after mixing with water prior to the

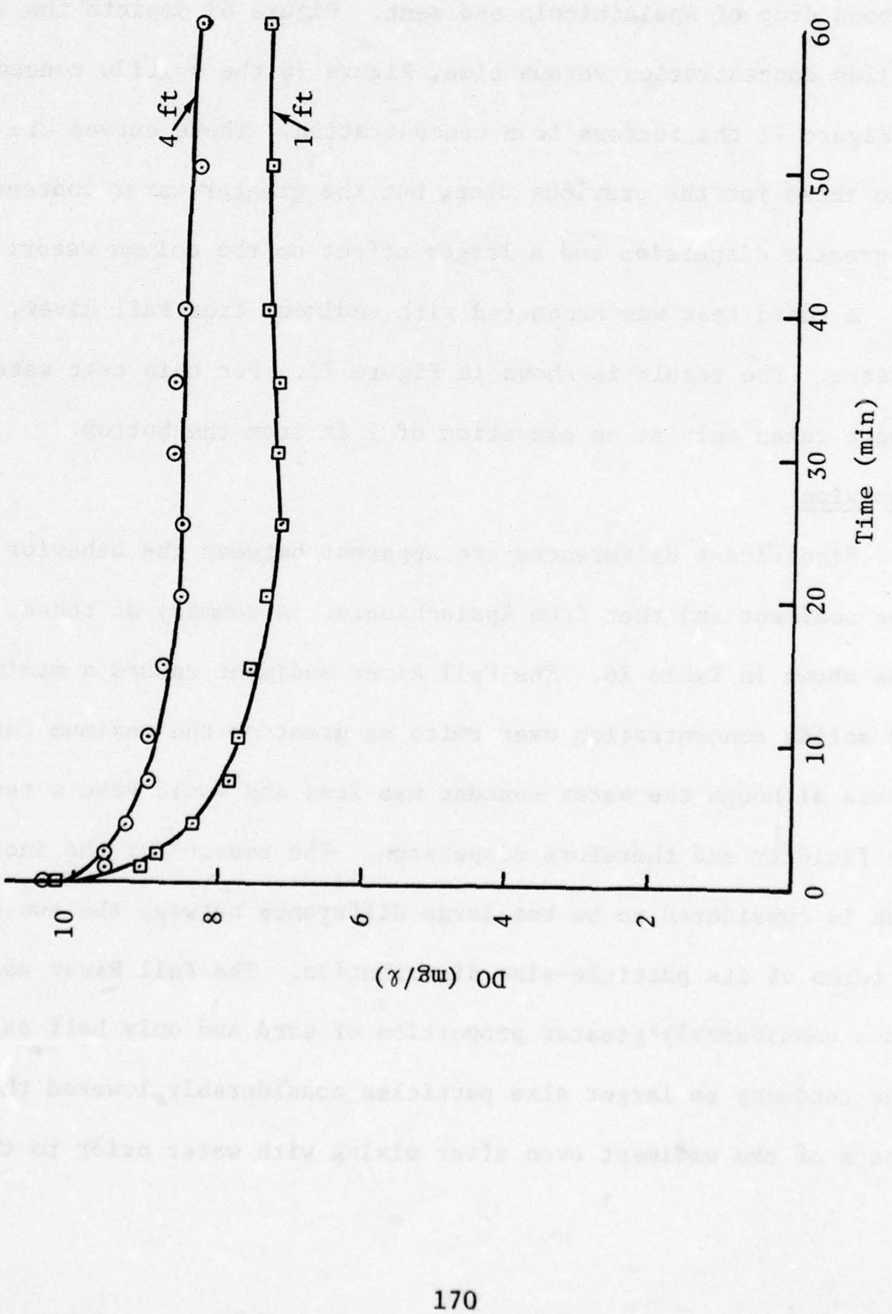


Figure 68. DO variation in Apalachicola sediments (column test no. 2)

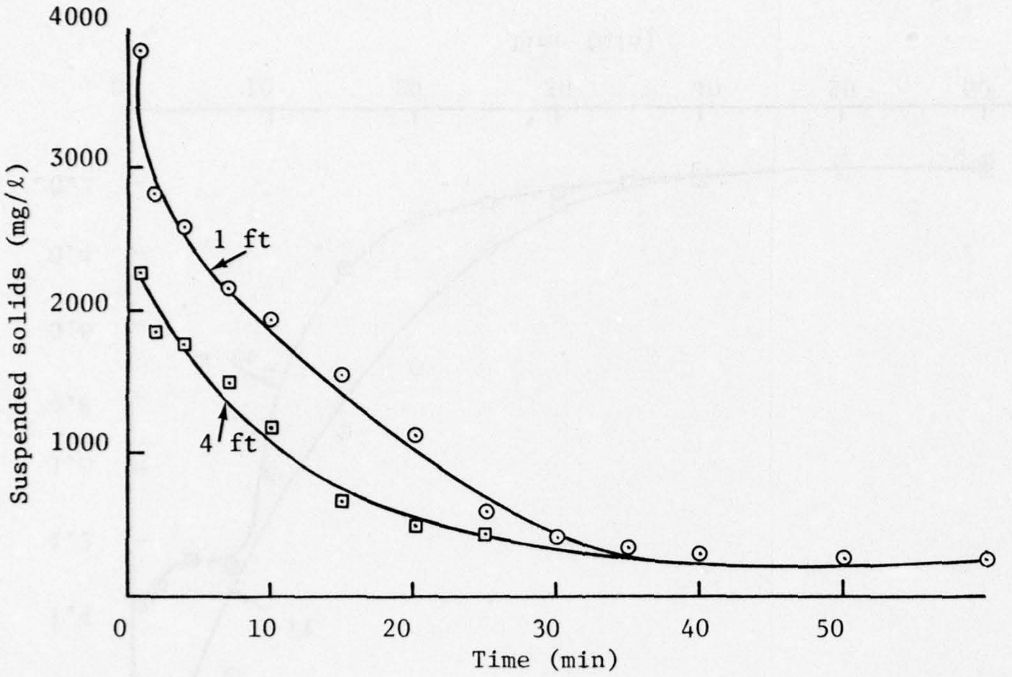


Figure 69. Suspended solids variations in Apalachicola sediments (column test no. 2)

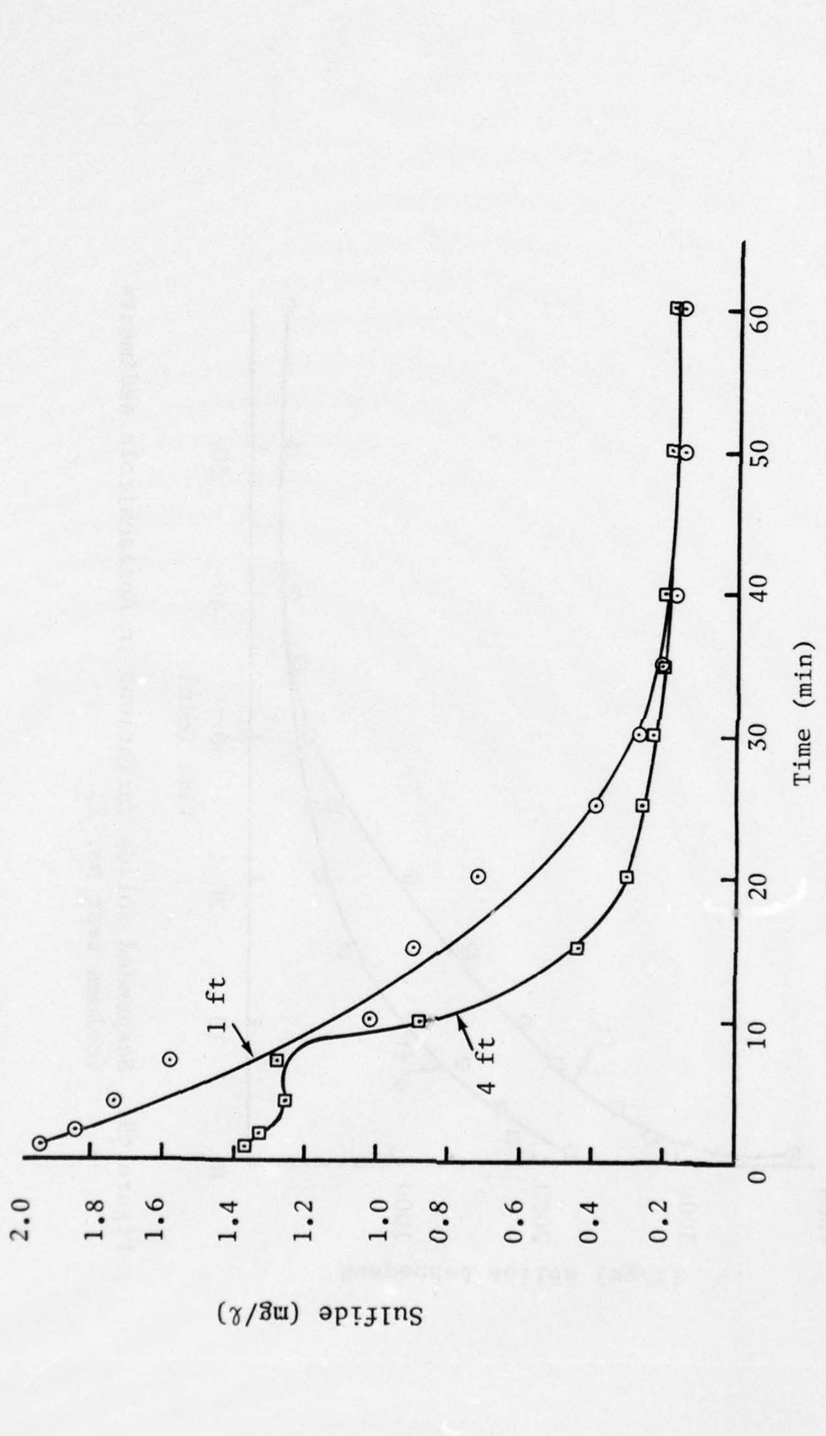


Figure 70. Sulfide concentration variations in Apalachicola sediments (column test no. 2)

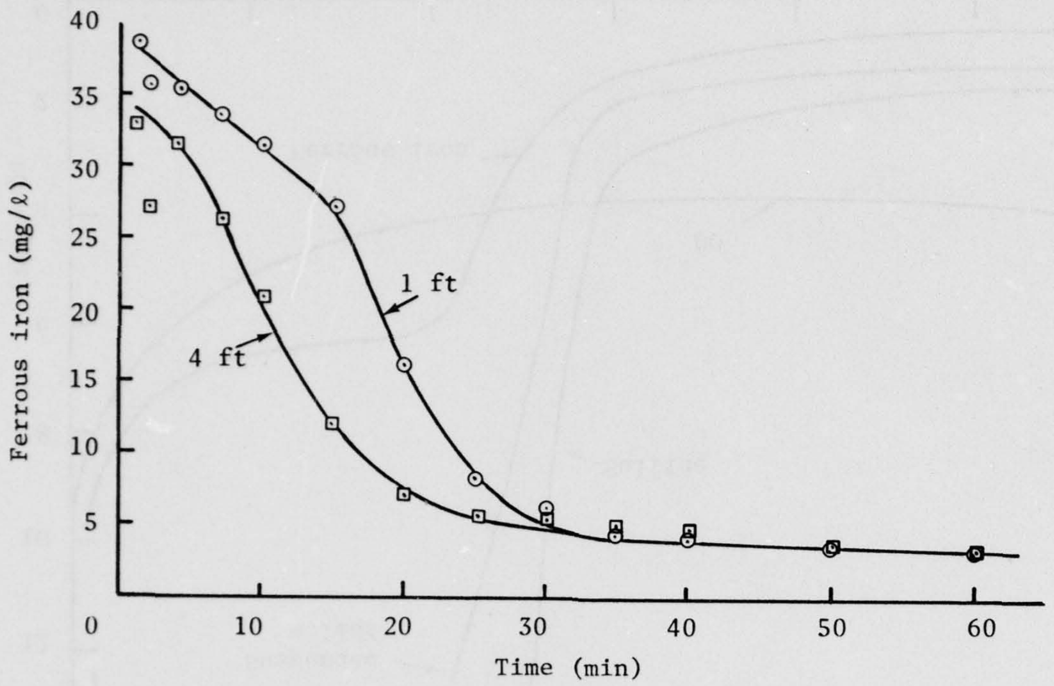


Figure 71. Ferrous iron concentration variations in Apalachicola sediments (column test no. 2)

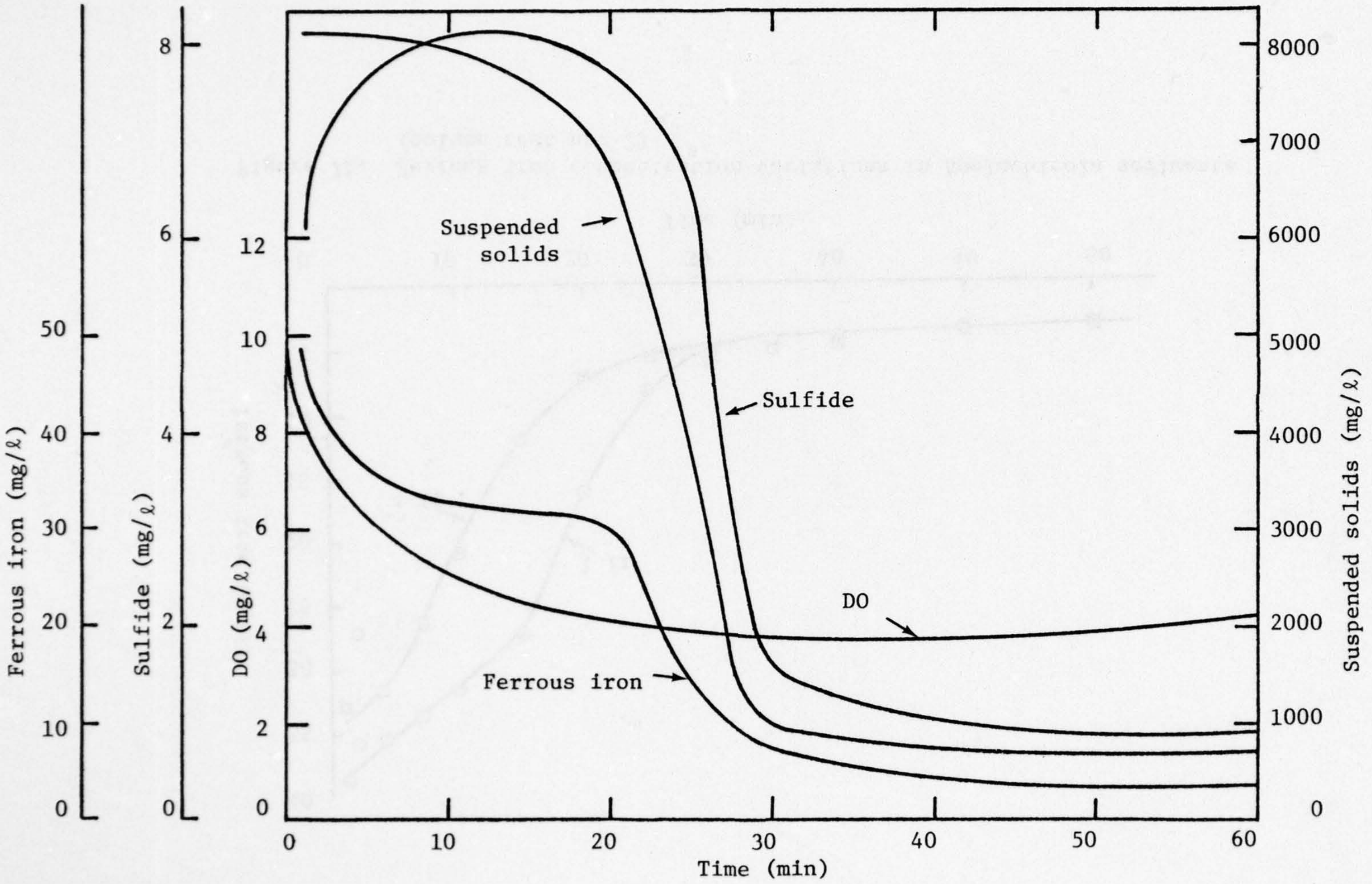


Figure 72. Parameter variations in Fall River sediments (column test no. 3)

drop, and although larger particles will expose less surface area per grain of solids, increased chemical release occurred. If this hypothesis is correct, the dispersion into the water column is more important to chemical release than bulk chemical analysis, and dispersion is controlled by particle-size distribution and water content. Particularly for sediments with a high clay content, limiting the water content during dredging, even to a small extent, may have a significant effect on water quality in the disposal area.

Table 16

Column Test Summary

	Apalachicola No. 1	Apalachicola No. 2	Fall River
Maximum DO Drop, mg/ℓ			
4 ft	1.3	2.2	---
1 ft	3.4	3.0	5.6
Maximum Susp. Solids, mg/ℓ			
4 ft	1,150	2,250	---
1 ft	2,700	3,800	8,200
Maximum Sulfide, mg/ℓ			
4 ft	0.58	1.4	---
1 ft	1.5	1.9	8.1
Maximum Fe^{2+}, mg/ℓ			
4 ft	22	33	---
1 ft	32	38	50

201. A rough mass balance can be performed on oxygen and ferrous iron in the column. Assuming that the theoretical reaction scheme is followed and the sulfide is oxidized by ferric iron, the reaction can be expressed as

$$4\ Fe^{2+} + O_2 + 8OH^- + 2H_2O = 4Fe(OH)_3 \qquad (6)$$

Thus, four moles of iron will react with each mole of oxygen. In the first Apalachicola drop it can be calculated that approximately 2.8 g of ferrous iron was consumed. The amount of oxygen theoretically required for this reaction would be 0.40 g. Based on the DO readings in the column, only 0.18 g of oxygen was reacted.

202. A similar calculation for the second Apalachicola drop shows that 4.5 g of ferrous iron reacted. This would have required 0.65 g of oxygen. However, only 0.32 g was consumed. Thus, for both Apalachicola drops the amount of oxygen depletion in the column was only about half of what it should have been based on the amount of ferrous iron reacted.

203. For the Fall River sediment, 3.8 g of ferrous iron reacted, which would require 0.54 g of oxygen. The amount of oxygen actually reacted was 0.53 g.

204. No reactions were found in the literature search that would realistically account for the oxidation of ferrous iron in dredged material without the consumption of dissolved molecular oxygen. Ferrous iron reactivity differs from that of sulfide ion which is potentially oxidized by ferric iron with a greatly reduced consumption of molecular oxygen. Humic substances can stabilize ferrous iron through the formation of iron (II) - organic complexes which resist oxidation or reduction

reactions. Upon acidification of the sample for preservation purposes, humic acids precipitate removing ferrous iron from solution. The sample is then filtered before the color development step in the spectrophotometric determination of ferrous iron. In this manner it would appear that the ferrous iron is being oxidized when it is simply being removed from the detection reaction. Sample acidification is necessary to quench other ferrous-ferric oxidation reactions. However, this step may create problems in the presence of relatively large quantities of humic acids. As stated above, all the rivers in the Florida panhandle have appreciable concentrations of humic acids. Similar concentrations would not be expected in Fall River. In the absence of humic materials interference, the amount of DO consumed in the IOD should be roughly equivalent to the amount of ferrous iron oxidized. A more detailed study of these analytical problems is needed before it is possible to clarify these important reactions which take place during the open-water disposal of dredged material.

CHAPTER IV: SYSTEM DESIGN CRITERIA

Purpose and Scope

205. In this study, the only oxidants which were considered were those which would not result in introducing potentially harmful materials into the environment. For this reason, compounds such as potassium permanganate, chlorine , and nitrates were eliminated from further consideration. The use of potassium permanganate would introduce other compounds of manganese and possibly color, depending upon the dilution. Some forms of manganese were also not acceptable since they are important micronutrients in the eutrophication process.[36] If chlorine were used, it would react with organic matter to form persistent chlorinated organic compounds[70,71] which have received considerable attention in the literature because of their possible ecological effects, both in the short and long term.[72]

206. Nitrate has been used for sulfide control in the past for both agricultural applications[59] and in sanitary sewage systems.[73] However, the use of nitrate in dredging operations is restricted because it is a critical macronutrient for phytoplankton in aquatic systems.[13] Also, the high cost of nitrate, due to its heavy demand as an agricultural fertilizer, would make its use economically prohibitive. The EPA[73] estimates that the amount of nitrate required to oxidize a pound of sulfide is about 10 lb of $NaNO_3$ when sulfide concentrations are high. The amount of nitrate may increase to 20 or 30 lb when the sulfide concentrations are lower.

207. Most of the effort in the laboratory study was devoted to the use of gasecus oxygen as the oxidant. However, some laboratory tests were conducted with hydrogen peroxide. Costs have been estimated for both oxygen and hydrogen peroxide systems.

208. Another oxidant that was considered in this study is ozone, which is more reactive than oxygen and would introduce no polluting substances into the environment. Commercial ozone generating equipment is available that operates with a feed stream of air or of pure oxygen. In either case, only a relatively small fraction of the oxygen is converted to ozone.

209. Typical generating equipment operating on pure oxygen can deliver a stream that contains from 1 to about 6 percent ozone because power is utilized most efficiently at this setting.

210. Even though equipment is not available that produces pure ozone, it was felt that ozone's much greater reactivity might justify the cost for adding the equipment to a conventional oxygen system. Technical and cost data were therefore obtained to evaluate this alternative.

211. While it was found that the incremental costs for ozonation were not prohibitive (i.e., system costs increased 20 to 30 percent), an overriding technical difficulty was uncovered. Ozone generators produce a product stream that is limited to pressures no greater than about 30 psig. This is a serious limitation. The system pressure should be at least 100 psig or greater in order to be able to inject at a point far upstream of the dredge discharge. This is an inherent limitation because ozone is not stable at elevated pressures or temperatures and would only

decompose to oxygen if a booster compressor were added to the system. For this reason, ozone augmentation was considered no further.

212. Costs have been estimated for two types of systems and for a range of parameters of interest. The system costs were then compared to dredging costs in a variety of locations. In the case of an oxygen feed, calculations have been made for two levels of pipe diameter (12 and 27 in.), of IOD (0.2 and 1.3 mg/g), and of slurry solids concentration (14 and 20 percent). Comparative costs have been calculated under a few of these conditions for hydrogen peroxide systems. Costs for air systems were not developed because the field demonstration did not yield enough information to establish air requirements.

213. The pipe diameter range is representative of most of the dredges used in this country. The IOD range includes typical values of materials which have been examined by JBF Scientific Corporation. These values were determined on samples from Apalachicola (Florida), Fall River (Massachusetts), and New London (Connecticut), as well as from other locations involved in previous company studies. The range of solids content was observed in samples taken during the field demonstration. The oxidant sources to be considered are on-site generation of gaseous oxygen and purchased hydrogen peroxide. It must be realized that more of the IOD of the dredged material will be satisfied at the discharge of the pipe when hydrogen peroxide is used. Because this is a more reactive form of oxygen, the transfer kinetics between gas and solution states is much faster. It will then have to be determined whether the increased cost

of a more active form of oxygen is justified in terms of maintaining suitable DO concentration levels in the discharge area.

214. The amounts of oxygen which must be supplied, assuming continuous operation during the day, are given in Table 17. A sample calculation to show how these amounts were determined is given in Appendix B.

Table 17

Oxygen Requirements (tons/day) of Dredged Material*

Solids Content percent (weight)	IOD mg/g	Diameter of Pipeline 12 in.	27 in.
14	0.2	3.0	14.9
	1.3	9.8	49.2
20	0.2	3.5	17.8
	1.3	13.7	69.0

* The IOD of the slurry has been satisfied and the water has been saturated. An average velocity of 19 fps has been assumed.

215. In the discussion to follow, the treatment costs have been calculated as a percentage of the cost of excavating a cubic yard of material. Some available costs for removing sediments with a hydraulic dredge are given in Table 18. More facts pertinent to each project are given in Appendix C. It must be emphasized that there is a great variation in dredging costs due to such factors as magnitude of the job, nature of the disposal site, time of year, and availability of contractors. For this reason, the costs in Table 18 should only be considered as some information which was available for a given area, not the basis of an average cost of dredging in that area. The costs of systems for injecting oxygen

and hydrogen peroxide are presented and compared in the following sections. The assumption was made when calculating costs that the dredge would be operating 95 percent of the time for 10 days out of 14. The 5 percent downtime is attributable to equipment failures and to plugging of the cutter head or the pipeline. On this basis the fractional utilization of the dredge is 0.68.

Table 18

Dredging Costs

Site	Cost $/cu. yd
New England	
Clinton Harbor, Connecticut	2.73
Connecticut River, Connecticut	2.34
Menemsha Creek, Martha's Vineyard, Massachusetts	3.90
Scarboro River, Maine	3.13
Southeast Coast	
Pompano Beach, Florida[74]	2.23
Charleston, South Carolina[75]	0.82
Great Lakes	
Average of 35 projects[76]	1.15
West Coast	
Redondo Beach, California[74]	1.98

Note: All costs are adjusted to 1976 assuming an 8 percent price increase annually. Conditions of each dredging operation are given in Appendix C.

216. It has been assumed in the calculations of system costs that enough oxygen is supplied to both satisfy the IOD of the solids and to saturate the water.

Oxygen System

Concept

217. A self-contained oxygen plant will be placed on a barge at the point of oxygen injection along the pipeline. Electricity to operate the plant will be supplied by a diesel-electric generator which, with a month's supply of fuel, will be located on a second barge a safe distance from the oxygen plant. The power cable connecting the two units will be mounted on the pipeline.

Basis of design

218. Costs were calculated for the equipment to supply the amounts of oxygen listed in Table 17. There were three choices available for the oxygen supply: liquid oxygen delivered in tank trucks, an on-site plant in which the nitrogen in air is removed by adsorption onto molecular sieves, and a low temperature process in which liquefaction of air is followed by fractional distillation to separate it into its components (mainly nitrogen and oxygen). The latter two processes are known as Pressure Swing Adsorption (PSA) and the cryogenic process, respectively. Although liquid oxygen stored in vacuum insulated dewars was used in the field demonstration, its operational use was ruled out since the projected demands (Table 17) are all above 2 tons/day, the production rate at which on-site generation becomes economically feasible.

219. Below 100 tons/day, the costs of the PSA and cryogenic plants are essentially equivalent. However, the PSA has been chosen for the current application because of its versatility in operating at other than 100 percent of capacity, and because it is inherently safer. A cryogenic plant is not suitable for automatic response to fluctuations in demand. Almost all such plants are run at steady state, and this is usually 100 percent, regardless of demand. Safety is inherently incorporated into the basic PSA process design because any hydrocarbon contaminants are adsorbed and do not pass through the system with the oxygen product.

220. The PSA system requires less maintenace. The adsorption system and control valves are reported to operate for years without maintenance of any kind. The control valves are readily replaced in minutes without significantly disrupting the operating cycle. The entire system can be started up and shut down in only a few minutes and operates completely automatically with only routine inspection being required.

Costs

221. Values of capital cost, annual operating cost, and cost per cubic yard of material dredged are given in Table 19. As an example, the cost per cubic yard for the case of the 12-in. pipe, the 20 percent slurry, and 1.3-mg/g IOD is calculated in Appendix D. The cost is $0.044/cu yd. When this number is calculated as a percentage of the dredging costs from Table 18, the range of values is from 1.1 to 3.8 percent. As previously mentioned, the costs for oxygenation given above are calculated using amounts of oxygen to satisfy all the IOD of the sediment and to saturate the water.

Table 19

Cost ($) of Injecting Oxygen into Dredged Material

Solids Content (wt %)	IOD mg/g		Diameter of Pipeline	
			12 in.	27 in.
14	0.2	Capital Cost	$690,000	1,700,000
		Annual Operating Cost	61,000	190,000
		Cost/cu yd	0.016	0.011
	1.3	Capital Cost	1,400,000	3,400,000
		Annual Operating Cost	200,000	640,000
		Cost/cu yd	0.053	0.035
20	0.2	Capital Cost	710,000	1,700,000
		Annual Operating Cost	65,000	210,000
		Cost/cu yd	0.011	0.0075
	1.3	Capital Cost	1,600,000	3,900,000
		Annual Operating Cost	250,000	830,000
		Cost/cu yd	0.044	0.029

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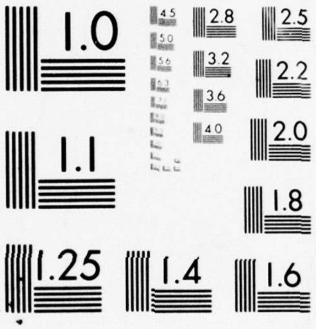

MICROCOPY RESOLUTION TEST CHART
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Hydrogen Peroxide System

Concept

222. Two barges will be fitted with aluminum storage tanks and pumping facilities for hydrogen peroxide. While hydrogen peroxide is being pumped into the pipeline from one of these barges, the other will be at dockside being loaded from 4000-gal tank trucks of 70 percent hydrogen peroxide. This material will be diluted to 50 percent at that time. The loaded barge will then replace the one at the pipeline.

223. Electric power to operate the pumps will be supplied by a diesel-electric generator which with a month's supply of fuel will be located on a barge a safe distance from the hydrogen peroxide tanks. The power cable connecting the two units will be mounted on the pipeline.

Basis of design

224. Although 70 percent hydrogen peroxide can be delivered in 8000-gal quantities by railroad tank car, system cost estimates have been based upon deliveries from 4000-gal tank trucks, which can be brought to most dock loading sites.

225. Hydrogen peroxide solutions may become highly unstable if contacted by certain contaminants. Small amounts of materials containing catalysts (silver, lead, copper, chromium, mercury, and iron oxide rust) can cause immediate decomposition and explosive rupture of the containing vessel if it is not properly vented. The absence of these metallic impurities is ensured by handling the hydrogen peroxide in aluminum alloy piping and tanks which have been cleaned and passivated with 42° Bé nitric acid. Such precautions are reflected in the equipment costs.

Costs

226. Values of capital cost, annual operating cost, and cost per cubic yard of material dredged are given in Table 20. As an example the cost per cubic yard for the case of the 12-in. pipeline,the 20 percent slurry, and 1.3-mg/g IOD was applied to the dredging costs in Table 18. The resulting percentages for treating with hydrogen peroxide ranged from 26 to 89. These high costs are due to the price of hydrogen peroxide, $0.28 per pound for the 70 percent material. The capital cost is only 58 percent of that for an oxygen system.

Table 20

Cost ($) of Injecting Hydrogen Peroxide into Dredged Material

Solids Content (wt. %)	IOD (mg/g)		Diameter of Pipeline 12 in.	Diameter of Pipeline 27 in.
		Capital Cost	920,000	2,500,000
20	1.3	Annual Operating Cost	5,800,000	29,000,000
		Cost/cu yd	1.02	1.00

227. One problem which must be investigated as to its influence on the cost of using hydrogen peroxide is that of its injection into the pipeline. Organic material and iron oxides, previously mentioned as causing violent reactions with hydrogen peroxide, are in abundance within the pipeline. Therefore there must be a safe method of control for preventing injection when the dredge flow is suddenly reduced or interrupted. Solving these problems may add to the system cost figures; however, it is likely

that the cost of the material itself would remain the overriding cost of treatment.

Comparison of Systems

228. The cost data for the two systems examined are summarized in Table 21. For a variety of locations, it appears that the cost of oxygen injection would increase the total cost of dredging by a modest amount, ranging from 1 to 4 percent. On the other hand, hydrogen peroxide injection would increase the dredging costs by 26 to 89 percent.

Table 21

Summary of Dredging Treatment Costs*

Location	Excavation Cost $/cu yd	Percent Cost Increase to Add Oxygen: Gaseous Oxygen	Percent Cost Increase to Add Oxygen: Hydrogen Peroxide
New England	2.34-3.90	1.9-1.1	44-26
Great Lakes	1.15	3.8	89
Southeast	2.23	2.0	46
West Coast	1.98	2.2	52

* All costs adjusted to an April 1976 basis.
Enough oxygen added to saturate water and satisfy IOD.

229. These costs should not be evaluated by direct comparison, however. In both cases, the quantity of oxidant has been determined by providing sufficient amounts to react with the sediment IOD and to saturate the water. In the case of oxygen, both the laboratory and field work demonstrated that for residence times of 1 or 2 min in the pipeline, very little of the IOD was reacted. Nevertheless, sufficient oxygen went into

solution so that the level of DO in the discharge area was appreciably increased. It may well be that less oxygen could have been injected, while still achieving a similar result. Future work, particularly in a field demonstration, should be directed toward determining the relationship between DO levels and oxidant flow over a much wider range of flow rates.

230. In the case of hydrogen peroxide, it is significantly more reactive than the oxygen. Hence, for a given residence time, hydrogen peroxide would react to satisfy more of the IOD than would a comparable fraction of oxygen. This suggests that less hydrogen peroxide could be used to achieve a given effect. However, it is not clear that reacting to satisfy the IOD would necessarily result in higher DO levels in the discharge area. Sufficient oxygen must still be available to replace any DO reacted, and it is not known how hydrogen peroxide might perform in this respect.

231. The use of hydrogen peroxide should not be dismissed, however, for two reasons. First, because of its reactivity, it may still be effective enough at lower injection rates to reduce its unit cost considerably. Second, the high reaction rates may also be an advantage in dredging situations where sediment IOD's are high and the discharge line is relatively short.

CHAPTER V: CONCLUSIONS AND RECOMMENDATIONS

Conclusions

232. Measurements made during the oxygenation field demonstration showed conclusively that the direct injection of oxygen will significantly reduce the depletion of DO in the disposal area. The DO levels were seriously depressed near the bottom of the water column when oxygen injection was not occurring. During injection, the DO levels rose to approximately those observed at the 3-ft depth. Oxygenation at a position providing longer oxidant residence time in the discharge pipe produced increased DO enhancement in the receiving water. The IOD values for oxygenated sediment slurries were statistically lower than those of non-oxygenated samples. However, variability introduced by rapidly changing conditions in the pipeline and by conducting the IOD test under field conditions made this test somewhat uncertain.

233. It is uncertain whether the aeration field demonstration was as effective. Inferences drawn from this demonstration were hindered by frequent discharges of material with little or no anaerobic sediment from the pipeline. Furthermore, the amount of air injected in this demonstration was not designed to satisfy the IOD fully, but was well in excess of that required to saturate the water. This combination of factors may have influenced the observation of little apparent benefit from aeration.

234. For a variety of locations, it appears that the cost of oxygen injection would increase the total cost of dredging by a modest amount,

ranging from less than 1 to about 3 percent. Both the laboratory and field work demonstrated that for residence times of 1 or 2 minutes in the pipeline, very little of the IOD was reacted. The results of the aeration demonstration were not sufficiently definite to allow conceptual designs and cost estimates.

235. A system based on hydrogen peroxide would be many times more expensive than oxygen if the same amount of available oxygen were delivered. However, for a given residence time, hydrogen peroxide, which is much more reactive, would satisfy more of the IOD than would a comparable fraction of oxygen. This suggests that less hydrogen peroxide could be used to achieve a given effect. However, it is not clear that reacting to satisfy the IOD would necessarily result in higher DO levels in the discharge area. Sufficient oxygen must still be available to replace any DO reacted, and it is not known how hydrogen peroxide might perform in this respect.

236. Other oxidants considered included ozone, potassium permanganate, chlorine, and nitrate. For these four substances, one or more undesirable characteristics eliminated them from further consideration.

237. The IOD of a sediment can be satisfied by extensive oxygenation. However, the IOD is slowly regenerated in the settled sediment by the microbiological decomposition of organic matter, which causes the sediment to become anaerobic again. Oxygenation in a closed-loop dredge pipeline simulation did not completely satisfy the IOD of the sediment after a 15-minute contact period with the theoretical quantity of oxygen gas. The DO

content of the water, however, did approach air saturation within the loop. Batch dumping of sediments in a column demonstrated that the degree of dispersion of sediment particles in the water had a greater effect on oxygen demand than indicated by bulk analysis of the sediments.

238. Particle-size distribution of exhaustively oxygenated sediments was skewed to smaller particle sizes that settled more slowly than the corresponding anoxic (nitrogenated) sediments. Oxygenation did not appear to alter the process of elutriation of heavy metals and nutrients from the sediments.

Recommendations

239. Since the cost of providing oxidant is likely to be significant, it is desirable to provide the capability for continuously sensing the pumping rate and solids fraction. Using this information, it would be possible to modulate the rate at which the oxidant is injected. More work is needed in this area.

240. It may well be that less oxidant could have been injected, while still achieving a similar result. Future work, particularly in a field demonstration, should be directed toward determining the relationship between DO levels and oxygen flow over a much wider range of flow rates.

241. The potential use of hydrogen peroxide should be investigated further for two reasons. First, because of its reactivity, it may still be effective enough at lower injection rates to reduce its unit cost considerably. Second, the high reaction rates may also be an advantage

in dredging situations where sediment IOD's are high and the discharge line is relatively short.

242. A means of predicting oxygen depletion prior to dredging needs to be developed. This capability would probably be based upon ferrous iron, sulfide, and IOD analytical tests. Problems in conducting these tests and interpreting the results must be resolved.

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APPENDIX A: ANALYTICAL METHODS

Solids - Percent and Volatile

Great Lakes Region sediment manual,[A1] pp 85-86

Solids, Suspended

Standard Methods,[A2] Method 148B

Particle-Size Distribution

ASTM Method D-421, modified. Dispersed wet sediment was contacted with 125 ml of 10 percent celite (sodium metasilicate) solution in a stream of nitrogen gas for 15 min. Nondispersed wet sediment was contacted with seawater for 30 min in a stream of nitrogen gas. Hydrometer readings were corrected for the density differences in the supporting media.

Total Carbon

Leco Combustion Technique - Arnold Green Testing Laboratory (subcontractor)

Sulfide, (Total) Free

Sediment slurries were preserved with an equal volume of an antioxidant buffer solution.[A3] This solution prevented further oxidation of sulfide and fixed the free sulfide as essentially (total) free sulfide ions. Sulfide content was obtained by measuring concentration on an ion specific meter equipped with a silver/sulfide membrane electrode. The concentration scale was calibrated with standard sulfide solutions.

Ferrous Iron

Standard Methods,[A2] Method 124

Chemical Oxygen Demand

EPA Method,[A4] p 25

Immediate Oxygen Demand

JBF Scientific Corporation Method, Chapter III of this report.

Total Metals

EPA Digestion Technique,[A4] pp 82, 83. Analyses for iron, manganese, copper, cadmium, nickel, and zinc were on a Jarrell Ash Model 82-810 atomic absorption spectrophotometer. Arsenic analyses were performed with a graphite tube furnace. Mercury analyses were performed with the mercury kit. Both arsenic and mercury were performed on the same instrument.

Dissolved Oxygen

Yellow Springs Instruments DO probe and meter.

Salinity

Yellow Springs Instruments conductivity-salinity probe and meter.

pH

Fisher Scientific Company combination pH electrode and Orion Model 407A meter and Fisher Accument Model 150 meter.

Turbidity

HACH Model 2100A Turbidimeter

Ammonia-nitrogen

EPA[A4], p 159

Total Phosphorus

EPA[A4], p 249

Analytical References

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APPENDIX B: SAMPLE CALCULATION METHOD OF DERIVATION OF NUMBERS IN TABLE 17, OXYGEN REQUIREMENTS (TONS/DAY) OF DREDGED MATERIAL

Operating condition in Table 17 -

Diameter of pipeline (in.)	12
Solids content (wt. %)	20
IOD (mg/g)	1.3
Velocity in pipeline (fps)	19

Data -

Specific gravity of 20% slurry	1.15
Oxygen needed to saturate water (mg/ℓ)	45.5
Seawater density (g/cc)	1.01

Calculations -

Pound flow per day

$$19 \frac{\text{ft}}{\text{sec}} \times 3600 \times 24 \frac{\text{sec}}{\text{day}} \times 0.79 \text{ ft}^2 \times 62.4 \frac{\text{lb}}{\text{cu ft}} \times 1.15 = 92 \times 10^6$$

Solids per day

$$92 \times 10^6 \frac{\text{lb}}{\text{day}} \times 0.20 = 18.4 \times 10^6$$

Oxygen demand of solids (ton/day)

$$18.4 \times 10^6 \frac{\text{lb solid}}{\text{day}} \times 0.0013 \frac{\text{lb oxygen}}{\text{lb solid}} \times \frac{\text{ton}}{2000 \text{ lb}} = 12.0$$

Oxygen demand of water (ton/day)

$$92 \times 10^6 \frac{\text{lb}}{\text{day}} \times 0.80 \times \frac{28.32 \frac{\ell}{\text{cu ft}}}{1.01 \times 62.4 \frac{\text{lb}}{\text{cu ft}}} \times \frac{0.0455 \text{ g}}{\ell}$$

$$\times \frac{\text{lb}}{454 \text{ g}} \times \frac{\text{ton}}{2000 \text{ lb}} = \underline{1.7}$$

$$\text{oxygen requirement} = \underline{\underline{13.7}} \text{ ton/day}$$

APPENDIX C: DESCRIPTION OF DREDGING PROJECTS LISTED IN TABLE 18

Clinton Harbor, Connecticut

31,000 cu yd was moved to land disposal during 1973. The unit cost was $2.16/cu yd.

Connecticut River, Connecticut

140,500 cu yd was moved in a 12-in. pipeline 5,000 ft to land disposal during 1973. The unit cost was $1.86/cu yd.

Menemsha Creek, Martha's Vineyard, Massachusetts

16,000 cu yd was moved to land disposal during 1973. The unit cost was $3.09/cu yd.

Scarboro River, Maine

150,000 cu yd was moved during 1974. The unit cost was $2.68/cu yd.

Pompano Beach, Florida

Material was moved from 40 - 70 ft of water through 6000 ft of 24-in. pipe to the beach. The unit cost was $1.40/cu yd in 1970.

Charleston, South Carolina

The cost in Table 18 is derived from a study conducted to determine the best long-term dredging and disposal methods for the Cooper River area. The annual volume of dredgings was estimated to be 6,400,000 cu yd. The cost includes pipeline dredging to a diked rehandling basin. Costs associated with the dike and subsequent rehandling are not included. It is assumed that prices were as of 1970.

Great Lakes

Costs were estimated for 35 projects in a pilot study. The total material of 8,573,000 cu yd was to be dredged and deposited in open lake disposal areas. Costs have been assumed on a 1973 basis.

Redondo Beach, California

The contractor awarded this project modified a 16-in. hydraulic dredge with a 90-ft ladder and in lieu of a cutter head utilized high-powered water jets. A total of 1.4 million cu yd was placed on the beach in 1968 at a cost of $1.5 million.

APPENDIX D: COST ESTIMATE OF 13.7-TON/DAY OXYGEN PLANT

Diesel-electric generator and fuel tanks	$ 46,000
Compressor to raise pressure from PSA plant	32,000
Electric cable	3,000
Protective enclosures on barges	15,000
Partial equipment cost	96,000
Equipment installation	76,000
Partial physical plant cost	172,000
Engineering and construction	51,000
Linde PSA plant	980,000
Barges	156,000
Direct plant cost	1,359,000
Contractors fee and contingency	231,000
Fixed capital	$1,590,000
Annual operating cost -	
Amortization of capital (in 10 yr)	$ 159,000
Oxygen plant operating cost @ $10.30/ton/day	35,000
Fuel cost	55,000
	$ 249,000

Cost per cu yd excavated -

$$\frac{\text{cu yd excavated}}{\text{year}} \text{ (see Appendix E)} = 5.7 \times 10^6$$

$$\frac{\$249{,}000}{5.7 \times 10^6 \text{ cu yd/year}} = \underline{\underline{0.044}}$$

APPENDIX E: SAMPLE CALCULATION OF CONVERSION OF PIPELINE SLURRY FLOW TO CUBIC YARDS EXCAVATED

Operating condition in Table 17 -

Diameter of pipeline (in.)	12
Solids content (wt. %)	20
Velocity in pipeline (fps)	19

Data -

Solids content of channel sediments (wt. %)	37
Specific gravity of dry solids	2.5
Fractional utilization	0.68

Calculation -

Pound flow per day

$$19 \frac{\text{ft}}{\text{sec}} \times 3600 \times 24 \frac{\text{sec}}{\text{day}} \times 0.79\ \text{ft}^2 \times 62.4 \frac{\text{lb}}{\text{cu ft}} \times 1.15 = 92 \times 10^6$$

Solids per day

$$92 \times 10^6 \frac{\text{lb}}{\text{day}} \times 0.20 = 18.4 \times 10^6$$

Let X = weight of an excavated cu yd

$$X = 0.37X + \left(27 \frac{\text{cu ft}}{\text{cu yd}} - \frac{0.37\ X}{62.4 \times 2.5}\right) 62.4 \frac{\text{lb}}{\text{cu ft}}$$

$$X = 2160 \frac{\text{lb}}{\text{cu yd}}$$

$$\text{Dry solids/excavated cu yd} = 0.37 \times 2160 \frac{\text{lb}}{\text{cu yd}} = 800$$

$$\frac{\text{excavated cu yd}}{\text{day}} = \frac{18.4 \times 10^6}{800} = 23{,}000$$

$$\frac{\text{excavated cu yd}}{\text{year}} = \left(365 \frac{\text{day}}{\text{year}}\right) (0.68) \left(23{,}000 \frac{\text{cu yd}}{\text{day}}\right) = \underline{\underline{5.7 \times 10^6 \frac{\text{cu yd}}{\text{year}}}}$$

In accordance with letter from DAEN-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.

Neal, R W
Oxygenation of dredged material by direct injection of oxygen and air during open-water pipeline disposal / by R. W. Neal, R. B. Pojasek, and J. C. Johnson, JBF Scientific Corporation, Wilmington, Massachusetts. Vicksburg, Miss. : U. S. Waterways Experiment Station ; Springfield, Va. : available from National Technical Information Service, 1977.
199, [8] p. : ill. ; 27 cm. (Technical report - U. S. Army Engineer Waterways Experiment Station ; D-77-15)
Prepared for Office, Chief of Engineers, U. S. Army, Washington, D. C., under Contract No. DACW39-75-C-0105 (DMRP Work Unit No. 6B06)
Literature cited: p. 194-199.

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