

DREDGED MATERIAL RESEARCH PROGRAM



CONTRACT REPORT D-75-6

LABORATORY STUDY OF THE RELEASE OF PESTICIDE AND PCB MATERIALS TO THE WATER COLUMN DURING DREDGING AND DISPOSAL OPERATIONS

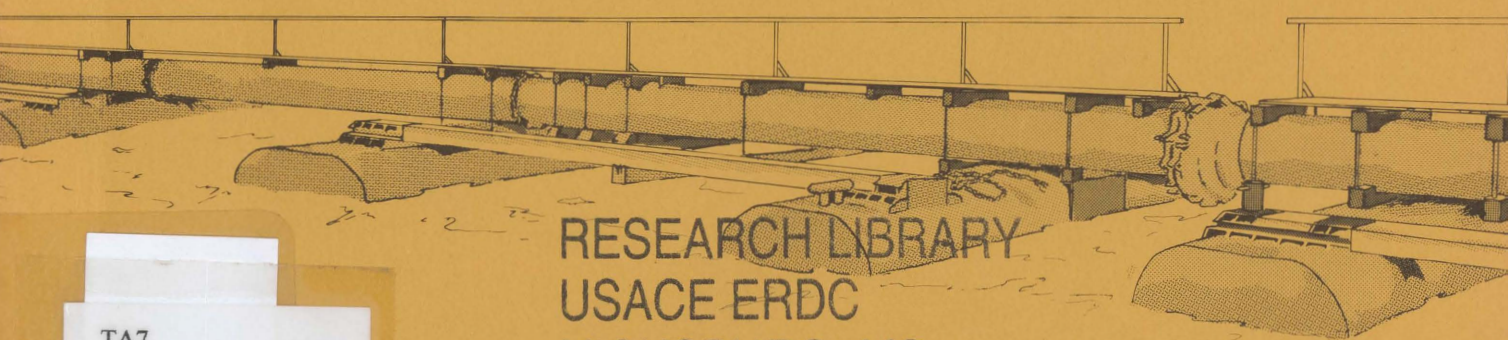
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Final Report

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1. The Contract Report transmitted herewith represents the results of one of several research efforts completed as part of Task 1C (Effects of Dredging and Disposal on Water Quality) of the Corps of Engineers' Dredged Material Research Program (DMRP). Task 1C is included as part of the Environmental Impact and Criteria Development Project of the DMRP, which among other considerations includes determining on a regional basis the short- and long-term effects on water quality due to dredging and discharging bottom sediment containing pollutants.
2. This research was conducted as Work Unit 1C04 to survey the release of pesticides and PCB's into the water column during dredging and open-water discharge of dredged material. Specific objectives were to characterize thoroughly the predominant pesticides or degradation products and PCB's that may be found in sediments and to quantify the possible migration of various pesticides into the water column during dredging and aquatic discharge of dredged material. To complete these objectives, sediments subject to maintenance dredging at selected marine and freshwater locations were sampled and fractionated as to pesticide and PCB location and form. The samples were then surveyed thoroughly both qualitatively and quantitatively as to the predominant pesticide, PCB, or degradation product present. The same procedure was conducted on the interfacial water immediately above the sampled sediment. The evaluation was conducted on selected fresh and saltwater areas and included sediments of various grain-size distributions.
3. This report includes both qualitative and quantitative descriptions of selected pesticides and PCB's in sediment, water-column water, and interfacial water samples from Chicago, Illinois; Green Bay, Wisconsin; Fall River, Massachusetts; Houston, Texas; and Memphis, Tennessee. Various interrelated physicochemical sediment and water-quality parameters at the various locations were investigated. Equilibrium and sorption-desorption tests were performed on representative samples from each dredged area to determine the transfer of pesticide materials from

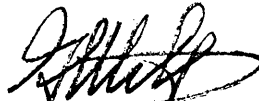
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a resuspended sediment to the water column. PCB materials were detected in most of the samples; of the pesticides, DDT and dieldrin compounds were the most common. No relationship was noted between sediment and interstitial water PCB concentrations and the various sediment-water physicochemical parameters. Transfer of PCB and pesticide material to the water column was found to be negligible, and chlorinated hydrocarbons associated with the suspended solids reached background or near background after settling periods of 5 to 24 hr.

4. The results of this study are particularly important in evaluating the water-quality impacts of aquatic disposal of chlorinated hydrocarbon contaminated sediments. To assess these effects, regional information on the quality of dredged material, methods of disposal, and the nature of the aquatic media in which they are disposed is needed. In addition, fundamental information is needed on contaminant-to-sediment attachment mechanisms. Finally, methods need to be developed to predict, prior to dredging and disposal operations, the nature and significance of the effects of the operations on water quality.



G. H. HILT

Colonel, Corps of Engineers
Director

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20. ABSTRACT (Continued)

dieldrin and DDT compounds were the most common. Aldrin and 2,4-D esters were present in a few samples. No correlation was found between the amount of TOC, oil and grease, and silt and clay fraction, and the sediment PCB content or the interstitial water PCB content. As a result of desorption tests and settling tests using several sediment to water ratios, the transfer of soluble pesticide material to the water was found to be negligible at sediment to water ratios of 1:10 or less. Chlorinated hydrocarbon materials associated with the resuspended solids reached concentrations at or near background water column levels after settling for periods ranging from 5 to 24 hr.

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Executive Summary

Chlorinated hydrocarbon pesticide materials tend to accumulate in the bottom sediments of waterways. During dredging operations, the possibility exists that some of this material may be transferred to the water column, through resuspension of sediment solids, desorption from the sediment solids, or dispersal of the soluble portion in the sediment interstitial water.

This laboratory study was initiated to determine the type and concentration of pesticide materials in sediments subject to dredging and to study the transfer of these materials to the water column during dredging or disposal operations. The work was performed on natural samples of sediments and water obtained from areas subject to dredging. Areas sampled were Calumet Harbor in Chicago, Green Bay near the mouth of the Fox River near Green Bay, Wisconsin; Mt. Hope Bay near Fall River, Massachusetts; Tabbs Bay near the Houston Ship Channel, Texas; and Tennessee Chute, the channel connecting the Mississippi River and Memphis Harbor at Memphis, Tennessee. All areas are routinely dredged except the Green Bay location, which is scheduled for dredging soon. The five areas sampled included fresh and saltwater sites, lakes, rivers, and bays, and represent a wide variety of sediment types. The Chicago samples came from a ship channel near a heavily industrialized area. Green Bay samples were from a previously undredged location and contained the highest fraction of sand. Samples from Fall River were from a seawater location subjected to tides. Samples from the Houston Ship Channel area were from a waterway containing a mixture of fresh and saltwater. The Memphis samples were from a river containing a large amount of suspended solids. At each location, five samples of sediment and interfacial water, and one sample of water column water were obtained. Sediment cores were divided into as many as four segments for analysis. Samples were analyzed for total organic carbon (TOC), solids concentration, oil and grease content, and the following pesticide materials: aldrin, dieldrin, endrin, lindane, 2,4-D esters, DDT and homologs, toxaphene, and polychlorinated biphenyls (PCBs). Although PCBs are not usually classed as pesticides, they were included in this study because of their prevalence and persistence. In this report, the term pesticide material includes PCBs.

Tests were performed on representative samples from each dredged area to determine the transfer of pesticide materials from a resuspended sediment to the water column. The role of desorption was studied by mixing sediment and water column water at several ratios ranging from 1:4 to 1:50 on a weight/weight basis. After 24 hr of mixing, the solids were removed by centrifugation and the soluble TOC and pesticide materials measured. The amount of pesticide materials adsorbed to solids

remaining suspended in the water column was tested by mixing sediment with water at one sediment-to-water ratio (usually 1:4 or 1:10) and allowing to settle for periods ranging from 0.5 to 24 hr. The supernatant samples from the various settling tests were analyzed for suspended solids, TOC, oil and grease, particle size, and pesticide material concentration. Interstitial water was separated from the sediment by centrifugation and analyzed for TOC and pesticide material.

PCB compounds were found in 59 of 64 sediment samples. The most prevalent form of PCB resembled Aroclor 1254. Dieldrin and DDT compounds were the next most common materials found. Aldrin and 2,4-D esters were present in only a few sediment samples. Toxaphene, lindane, and endrin were not detected.

Four of the five interstitial water samples contained PCBs. DDT compounds, dieldrin, and 2,4-D were also present in some interstitial water samples.

Water column samples contained PCBs and dieldrin. These materials were associated with the suspended solids. No soluble pesticide materials were found.

Interfacial water samples contained only PCB materials. Whether the PCBs were soluble or were associated with the suspended solids was not determined.

All parameters measured for a sediment varied widely between samples. High concentrations of the parameters appear to be distributed at various depths and various locations within the dredged areas sampled. This distribution appeared to be random for TOC and oil values in most cases. Some stratification of pesticide materials was apparent, however, for some dredged areas.

No significant correlation was found between sediment TOC, oil and grease, or silt and clay fraction and the concentration of PCB in the sediment or in the interstitial water. Similarly, no correlation was found between the amount of pesticide material in the sediment and the amount in the interstitial water. The only correlation that was statistically significant was an inverse relationship between interstitial water TOC and PCB concentration.

In the desorption tests, desorption occurred only at the highest ratios of sediment to water (1:4 or 1:5). No measurable desorption occurred at ratios of 1:10 or lower. The amount of soluble pesticide material added to a water column by dispersal of interstitial water was minor. In cases where measurable desorption occurred, the amount desorbed depended primarily on the concentration of the pesticide material in the sediment. The effects of sediment particle size and TOC were less important. The amount of PCB material desorbed was related to oil and grease content only at the highest sediment-to-water ratios.

The amount of PCB material remaining in the water column after various settling times was directly proportional to the amount of oil and grease remaining in suspension and the suspended solids content. The role of oil and grease was about 20 times more important than that of suspended solids in "describing" the concentration of pesticide material remaining in suspension. About 88% of the variation in suspended PCB concentration was associated with changes in oil and suspended solids concentrations. In all settling tests, the amount of PCB material remaining in suspension ranged from water column background level to 0.03 µg/l above background level after settling periods ranging from 5 to 24 hr.

Based on these tests, dredging operations and aquatic disposal of dredged material may affect the water column in the following ways:

- a. The amount of soluble pesticide material added to the water column by dispersal of the sediment interstitial water is negligible at sediment-to-water ratios of 1:10 or less.
- b. The amount of pesticide material desorbed from resuspended solids is negligible at sediment-to-water ratios of 1:10 or less.
- c. Pesticide materials are transferred to the water column by means of the resuspended solids. The concentration of the suspended pesticide material decreased with time to levels at or near background water column concentration.

Preface

This report describes work performed for the Environmental Effects Laboratory of the U. S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi, under Contract No. DACW39-74-C-0142 dated June 7, 1974, entitled "A Survey of the Release of Pesticides into the Water Column During Dredging and Disposal Operations". The work was performed as Work Unit 1C04, Task 1C of the Dredged Material Research Program.

The work described in this report was performed by Envirex Inc., (A Rexnord Company) Environmental Sciences Division, Milwaukee, Wisconsin.

Dr. Robert Agnew, Division Manager of the Environmental Sciences Division, was the Project Manager. Principal Investigator was Richard Wullschleger. Richard Fulk and Calvin Bruce, assisted by Eric Jahn, Roger Fehling, Ernest Bollinger and others of the laboratory staff, were responsible for the laboratory tests and analyses. Sampling and diving work was performed by David Gruber and Richard Race.

The Contract was monitored by Dr. Robert M. Engler, Chief, Environmental Impacts and Criteria Development Project, and Mr. James M. Brannon, Contract Manager. The Contracting Officer was Colonel G. H. Hilt, CE. Contracts with District Offices were coordinated at WES through Captain Robert M. Meccia, CE.

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Introduction

1. The sediments of waterways are repositories for contaminating materials which have an affinity for the suspended solids portion of the water column. Chlorinated hydrocarbon pesticides are an example of such material. The affinity of pesticides for suspended solids may be attributed to sorption on clay surfaces, suspended oily material, or natural organic solids. Within the sediment, the local concentration of pesticide material can be much greater than in the water column above. This increase in concentration may result in a shift in equilibria between the amounts associated with the solids and the amount dissolved in the interstitial water. Chlorinated hydrocarbon pesticides are very persistent and may remain in the sediment a long time. When the sediment is disturbed, such as during dredging operations or aquatic disposal of dredged material, the possibility exists that some of the pesticide materials may be transferred back to the water column, either through resuspension of the sediment solids, dispersal of the interstitial water, or desorption from the resuspended solids.

Review of the Literature

2. The association of pesticide materials with soils and sediments has been widely studied. The concentration of chlorinated hydrocarbon insecticides in the sediments of Lake Michigan was studied by Leland, Bruce, and Shimp¹. They found that the insecticide concentration was correlated with sediment organic carbon content. Johnson, Fuller, and Scarce² reported that chlorinated organic pesticides in the Fox River-Green Bay area of Wisconsin were found in highest concentrations in algae, in lower concentrations in suspended solids and sediments, and in lowest amounts in the water itself. Veith and Lee³ reported that PCB materials in the Milwaukee River were associated with the suspended solids in the water. The Aroclor 1254 content of biota, sediment, and water in Escambia Bay was measured by Duke, Lowe, and Wilson⁴.

3. Huang and Liao⁵ studied the adsorptive and desorptive properties of selected pesticides on several clay minerals. Adsorption of Aroclor 1254 by sand, clay, and soil samples was investigated by Hague, Schmedding, and Freed⁶. They found that surface area, type of surface (sand or clay), and organic content were important factors in adsorption. Khan⁷ studied the adsorption of 2,4-D by a fulvic acid-clay complex. King *et al.*⁸ found sorption by algae to be much greater than adsorption on clay; activated carbon and coal were even better adsorbents. Soils containing organics adsorbed 2,4-D better than soils low in organic content. Hartung and Klingler⁹ studied the sorption of DDT by mineral oil and by clay containing 0.25 percent mineral oil.

4. Reports of sorption and desorption tests involving material sediments are much less common. Lotse *et al.*¹⁰ used bottom sediments

from six lakes in a study of adsorption of lindane. They found that organic content of the sediment was more important than clay content in the adsorption of lindane. Samples of sediment and water from the same lake were used by Veith and Lee¹¹ in the study of desorption of toxaphene from the sediment. No desorption could be measured. Boucher and Lee¹² compared distilled water and natural lake water as the substrate in tests on the adsorption of lindane and dieldrin by natural and purified sands. It was found that naturally occurring dissolved organic matter in the natural waters reduced the adsorption of dieldrin but did not affect lindane adsorption.

5. Most of the published work deals with the sorption of pesticides by clays, soils, sands, and organic solids. Much less attention has been given to desorption. Some of the desorption work that has been reported, however, indicates that some pesticide materials are more easily adsorbed than desorbed^{5, 10, 11}.

Purpose and Approach

6. The purpose of the work reported here was to determine the type and concentration of pesticide materials in sediments subject to dredging and to study the transfer of these materials to the water column during dredging or disposal operations. The work was performed using natural sediments and waters from five locations including fresh and saltwater areas, lakes, rivers, and estuaries. All samples were taken from areas that are subject to dredging. Samples of water column, interfacial water, and sediment were obtained. At each location, sediment core samples were obtained at five sites to provide information as to the variation that might be expected at each location. In addition, each core sample was separated into two, three, or four segments so that variations due to depth might be studied. Samples were analyzed for total organic carbon (TOC), solids concentration, oil and grease content, and the following pesticide materials: Aldrin, dieldrin, endrin, lindane, 2,4-D, DDT (and its homologs), toxaphene, and polychlorinated biphenyls (PCBs). Although the PCBs are not usually classed as pesticides, they were included in this study because of their prevalence, persistence, and high concentration.

7. Representative samples of sediment from each location were used in migration tests designed to measure the pathway and degree of transfer of pesticide material from a resuspended sediment to the water column. All tests were performed using water obtained from the same waterway as the sediment being tested so that the laboratory test conditions would resemble natural conditions as much as possible. Laboratory tests were performed by mixing several ratios of sediment to water column water to determine the amount of pesticide material transferred to the water by dispersal of the interstitial water, desorption from the resuspended solids and to determine the amount of pesticide material associated with the solids remaining in suspension after various settling times.

8. Care was taken in planning this work to obtain data that would reflect natural conditions as much as possible. Only natural sediments were used, along with the pesticide materials that the sediments contained when sampled. Water used in the pesticide migration tests was obtained from the same area as the sediments tested. The water was used as sampled; it was not filtered prior to mixing with the sediment. In this manner, the effect of the natural suspended solids of the water column on the transfer of pesticide material in aquatic disposal could be included in the test results. This could be a factor in pesticide transfer during disposal of dredged material in waters containing algae (reported to be good sorbers of pesticides) or waters containing large amounts of silt. In cases where the water column water contained significant amounts of contaminants, determination of the total and soluble portions permitted the calculation of amounts sorbed or desorbed. Samples were obtained from a wide variety of locations so that an understanding of pesticide concentrations and migration in a broad range of situations might be acquired.

9. The chemical names of the pesticide materials studied in this work are listed in Appendix A. In this report, the term PCB is used to refer to the sum of all the polychlorinated biphenyl materials as determined by the procedure described in the Federal Register¹³. Individual PCB compounds are identified by the trade name of the commercial chemical they most closely resemble, such as Aroclor 1242 or Aroclor 1254, using the conventions described in the Federal Register. It is recognized that a similarity between sample chromatograms and chromatograms of specific commercial chemicals such as the Aroclors is not proof of the presence of these chemicals. The names Aroclor 1242 and Aroclor 1254 in this report are used only to indicate the presence of PCB compounds that produce chromatograms similar to these specific commercial chemicals. The term t-DDT refers to the sum of p,p'-DDT and o,p'-DDT and its homologs, p,p'-DDE, o,p'-DDE, p,p'-DDD, and o,p'-DDD. The term 2,4-D is used to refer to the sum of the acid form and the ester forms of the 2,4-D compounds. Total organic carbon is referred to as TOC.

10. Although PCBs are not used as pesticides, their general use has resulted in widespread contamination of the environment. Since the PCB chemicals act like chlorinated hydrocarbon pesticides in many ways, they have been included in this study and are included in the term pesticide materials as used in this report.

Description of Methods and Procedures

Choice of Sample Locations

11. Sites to be sampled were selected based on the dredging activity in the area and the sediment types expected to be encountered in the area. This information was obtained from the Corps of Engineers report, "Disposal of Dredge Spoil."¹⁴ The object was to obtain samples

of different sediment types under different environmental conditions. Five sites were selected for this study. The site names, locations, and descriptions are shown in the following tabulation.

| <u>Site Name</u> | <u>Location</u> | <u>Description (Selection Factors)</u> |
|------------------|---|---|
| Chicago | Calumet Harbor near Chicago, Illinois | Freshwater site: Industrial area Ongoing dredging program Sand, silt, and sludge sediment |
| Green Bay | Near Green Bay, Wisconsin east of mouth of the Fox River | Freshwater site: Not previously dredged but scheduled for near future Clay, sand, and silt sediment |
| Fall River | Mt. Hope Bay near Fall River, Massachusetts | Estuarine site (salt water): Ongoing dredging program Organic silt sediment |
| Houston | Tabbs Bay near Houston Ship Channel, Texas | Site has mixture of salt and fresh water: Industrial area (petrochemical) Ongoing dredging program Sand, silt, and clay sediment |
| Memphis | Tennessee Chute (connects Memphis Harbor and the Mississippi River) | Freshwater site: Low-energy zone Silt and sand sediment |

Sampling Methods

12. The sampling methods used in the major portion of this work were developed and tested in Milwaukee Harbor. These methods were used, with slight modifications, at all the sampling locations except Memphis, where it was necessary to obtain the sediment samples in a different manner. The specific methods used are described in the following paragraphs.

13. Water column water samples were taken using a Kemmerer sampler. One 4.2-liter sample was taken 0.5 meters below the surface, two samples at mid-depth and one sample 0.5 meters above the bottom. This was done at two sampling sites in each area. Samples were stored in specially cleaned glass bottles with Teflon-lined caps.

14. Interfacial water samples were taken manually using a specially made glass sampler. The sampler intake tube was positioned between 0.6 and 1.3 cm from the bottom during sampling. The intake tube flow was controlled to ensure that no sediment solids were picked up. The samples were sealed with caps protected by aluminum foil liners.

15. Sediment samples were obtained by forcing acrylic plastic tubes (6.3 cm diameter and 2.13 m long) into the bottom sediment as far as possible. The top of the tube was capped with a rubber stopper; the tube pulled out of the sediment; and the bottom of the tube capped with a second rubber stopper. In deep water, this work was done by divers. In shallow areas, such as Green Bay, this work was done from the sampling boat. The tube was then taken to the surface for removal of the sediment core and sectioning. The water in the tube was removed and the sediment core transferred to a sheet of aluminum foil and cut into segments. Each segment was placed in a glass freezer jar for transportation and storage. Aluminum foil liners were used on the jar caps to prevent contact of the sample with the caps. The depth of penetration of the tube and length of the sediment core obtained were measured and recorded. Three core samples were taken at each of the five sampling sites in each of the waterways tested.

16. Conditions at Memphis Harbor required that a different method of obtaining sediment samples be used. A Wildes K.B. core sampler operated from the sampling boat was used. No measure of sampler penetration into the sediment was possible. The sediment cores were measured and handled in the same manner as in the other sampling tests.

Sample Preservation, Handling, and Storage

17. Samples were iced soon after sampling and remained iced during transportation to the Envirex laboratory in Milwaukee. Samples from Chicago and Green Bay were received by the laboratory the same day as sampled. Samples from Fall River, Houston, and Memphis were shipped by air freight and arrived the following day. After arrival at the laboratory, a representative portion of each sediment sample was frozen and stored at -19°C until analyzed. The remaining sediment was placed in a 27-liter pyrex container and thoroughly mixed to prepare a composite sediment sample. Approximately 4 liters of the mixed sediment were placed in 2-liter glass jars, capped with aluminum foil, and stored in the refrigerator at 4°C until used for the equilibrium and settling tests.

Interstitial Water Preparation

18. The major portion of the solids were removed from the mixed sediment samples by a large-capacity centrifuge operated at 1000 times gravity. The solids remaining in suspension were then removed by centrifuging in a Sorvall high-speed centrifuge. Aluminum cups were used in the first centrifuge and Teflon tubes in the high-speed centrifuge.

Migration Test Methods

19. Equilibrium test - Appropriate aliquots of the refrigerated mixed sediment were combined with samples of the water column water on a weight-to-weight ratio basis and the mixture placed in clean, round 4-liter glass jars. The final volume of the mixture was about 3 liters. Great care was taken to ensure the complete dispersion of the sediment in the water. The sediment-water mix was placed on a six-station Phipps-Bird stirrer and agitated for 24-hr at 100 rpm using broad-blade metal stirrers. The 100 rpm agitation was sufficient to maintain all particulates in suspension except the coarse sand and grit; however, even these particulates were subjected to scouring during the 24-hr stirring event. The metal stirrers were placed off-center in the 4-liter containers to avoid forming a vortex and to avoid concentrating the heavier particulates along the wall of the glass jar. The dissolved oxygen content of the suspensions were not measured or controlled during the mixing period.

20. After 24-hr agitation, the samples were centrifuged at 1000 times gravity in 250-ml aluminum cups on an International Model V centrifuge to remove the larger particulates, and finally centrifuged on a Sorvall high speed unit at 10,000 times gravity using Tefzel centrifuge tubes to remove the remaining particulates. The clarified sample was stored in 4-liter, foil covered glass jars at 4°C until analyzed.

21. Settling Test - Aliquots from the refrigerated mixed sediments were mixed on a weight-to-weight basis with water column water and placed in a 4-liter glass jar; final volume was about 3.5 liters. The mixture was agitated for 2 min. to disperse the solids and then allowed to settle.

22. The settling times used were based on the settling rate of the solids as determined by a preliminary settling test. The ratio of sediment to water was chosen so that, after settling, at least 2.5 liters of supernatant fluid could be obtained. Sandy sediments, such as the samples from Green Bay, formed a very compact settled solids layer allowing the use of a high sediment-to-water ratio (1:4). The silt and clay sediments from Chicago, however, compacted poorly and a much lower sediment-to-water ratio (1:15) was necessary.

23. A sample of the supernatant fluid was withdrawn from the test container at the end of the settling period by a glass siphon tube. The inlet end of the siphon was bent in a U-tube fashion to reduce the possibility of including settled solids in the sample. The inlet end of the siphon was positioned 2 cm above the interface between the settled solids and the supernatant fluid. This sample was split into two aliquots. One portion was stored in a foil-covered glass jar at 4°C until it could be extracted for chlorinated hydrocarbons. The remainder was used for oil and grease, organic carbon, suspended solids, turbidity, and particle-sizing analysis.

24. Those settling test samples which were very high in suspended solids could not be analyzed for chlorinated hydrocarbons by simple liquid-liquid extraction due to emulsion formation. For these samples the solids were allowed to settle and the supernatant fluid decanted and extracted by liquid-liquid extraction. The solids were dried with anhydrous sodium sulfate and extracted using a Soxhlet apparatus using the same procedure used for the analysis of sediment samples.

Analytical Methods

25. Analytical methods described in the EPA Manual for Chemical Analysis of Water and Wastes, 1971¹⁵ or in Standard Methods for the Examination of Water and Wastewater, 13th Edition¹⁶ were used for pH, solids, oil and grease, chloride, turbidity, and TOC analysis. The specific procedures used are identified in Appendix B. Some special analytical procedures were also used and are briefly described in the following paragraphs.

26. Dissolved oxygen and temperature readings were taken at various depths at each sampling point using a Weston and Stack Model 330 dissolved oxygen meter.

27. Pesticides and PCB analyses were performed according to the general procedure prescribed for National Pollutant Discharge Elimination System (NPDES) analytical work.¹⁰ Some modifications and additions to the procedure were made to accommodate the interferences and special conditions peculiar to the samples tested. Water samples were extracted with 15 percent methylene chloride in hexane using a separatory funnel. Sediment samples were dried with anhydrous sodium sulfate and extracted with a 1:1 hexane-acetone mixture for 24-hours using a Soxhlet apparatus. After concentration of the extracts using a Kuderna-Danish concentrator, the extracts were subjected to Florisil and silicic acid column separation. Sulfur was removed by reaction with elemental copper. Micro-alkali dehydrochlorination was used as a chemical derivation - confirming and clean-up technique. Separation and measurement was performed using a Barber-Colman gas chromatograph equipped with a Ni⁶³ electron capture detector. Details of the procedure used are included in Appendix B.

28. Oxidation-reduction potential (Eh) was measured with a Beckman SS-2 pH meter equipped with a platinum and a calomel electrode. At the time of sampling, sampling containers were filled completely with a sample of sediment and sealed. This was done under water to minimize contact with air. One sample for Eh was obtained from each of the dredged areas sampled. On arrival in the laboratory, the electrodes were inserted in the sediment sample several centimeters and allowed to equilibrate until a steady reading was obtained.

29. Sediment bulk density was determined by adding a representative portion of sediment to a graduated centrifuge tube and measuring the amount added by weight. The water added to wash down the sides of the tube was also measured. The tube was then centrifuged to remove entrapped air and the total volume measured. Subtraction of the amount of the wash water added resulted in the original volume of sediment added and allowed calculation of the density.

30. Sediment particle size was determined by dry sieving. Samples of sediment were air dried at room temperature. The dried sediment was partially crushed by means of a rolling pin and an appropriate size sample (about 20 g) separated using a sample splitter. This sample was then carefully crushed, using the rolling-pin technique, and sieved through a series of eight-inch screens ranging from U.S. No. 8 to U.S. No. 325 by shaking fifteen minutes on a Ro-Tap sieve shaker. Samples of sediments used in the migration tests were dried and crushed in a similar manner but were sieved using three-inch screens in an Allen-Bradley Sonic Sifter. Screen sizes used included 20, 10, and 5 micron screens in addition to the range of sizes used in the eight-inch sieving tests. Particles retained by a U.S. No. 10 screen were designated as gravel, particles passing a U.S. No. 10 screen and retained by a U.S. No. 230 screen were designated as sand, and particles passing the U.S. No. 230 screen were designated as silt and clay.

31. Particle size of solids remaining in suspension during the settling test portion of the migration tests was determined using an ElectroZone System particle-size analyzer made by Particle Data, Inc.

Description of Work Performed and Results

32. Testing of the sampling methods and equipment was performed in Milwaukee Harbor. Samples obtained were used to determine the proper analytical and migration test procedures. As a result of this work, original plans for obtaining sediment samples, separating interstitial water, and performing migration tests were modified. The modified procedures were used in subsequent work and are the procedures described in this report. The results obtained from this work are presented in Appendix C. The highest levels of TOC (36,700 mg/kg), oil and grease (9,550 mg/kg), and PCB (6,420 µg/kg) measured in this work were found in the one sediment sample from Milwaukee Harbor.

33. It was originally intended to analyze water samples for pesticide materials at minimum levels of µg/l for PCB, toxaphene, and 2,4-D and at 0.1 µg/l for DDT and its analogs, endrin, dieldrin, lindane, and aldrin. It was later determined, however, that greater sensitivity was needed. The detection limits were lowered to 0.02 µg/l and 0.002 µg/l respectively, by increasing the volume of sample extracted to 2000 ml and concentrating the extract to smaller volumes. Original

plans also called for freezing the sediment samples as soon as possible to minimize changes in pesticide concentration between sampling and analysis. This was done on the samples from Chicago, Green Bay, and Fall River. The possibility of freezing affecting the nature of the interstitial water and altering the behavior of the sediment used in the migration tests became apparent at about the same time as the need for lower detection limits. Unfortunately, all the sediment obtained to that time had been frozen and insufficient volumes of water samples remained for re-analysis at the low detection limits.

34. Return trips were made to Chicago, Green Bay, and Fall River for the purpose of obtaining additional sediment samples for preparation of interstitial water and for use in the migration tests. Sampling procedures were modified for the sampling trips to Houston and Memphis so that sufficient volumes of samples were obtained for analysis at the desired detection limits.

Chicago Samples

35. Sampling - Calumet Harbor in Chicago, Illinois, was sampled on August 8, 1974, and January 7, 1975. Samples were taken from a heavily used shipping channel connecting Lake Michigan with the Port of Chicago in Lake Calumet. The harbor is adjacent to a heavily industrialized area of Chicago. The positions sampled are shown in Figure 1. The water depth at sites 1 and 2 was 9.45 m and at sites 3, 4, and 5 was 9.14 m. On August 8, 1974, water temperatures varied from 22°C at the surface to 16°C near the bottom. The same day, dissolved oxygen values varied from 8.7 mg/l at the surface to about 6.9 mg/l near the bottom for sites 1, 2, and 4. At sites 3 and 5, the bottom dissolved oxygen concentrations were 0.8 and 5.2 mg/l, respectively. A listing of all the temperatures and dissolved oxygen measurements taken on August 8, 1974, can be found in Table D1 of Appendix D. On the second sampling trip, additional samples of water column water, interfacial water, and sediment were obtained between sites 2 and 3.

36. Analysis of water samples - The results of the analyses performed on the Chicago water samples are listed in Table 1. No detectable amounts of pesticide materials were found in the water column water. Interfacial water samples varied in suspended solids content. The highest value, 12,000 mg/l at site 5, was from a sample taken immediately after passage of a ship through the channel and illustrates the effect of ship movement on sediments. The sample of interfacial water taken on January 7, 1975, contained 0.08 µg Aroclor 1254/l, the only chlorinated hydrocarbon found at the detection limits used. The suspended solids and TOC concentrations of this sample were similar to that of three of the five samples obtained in August.

37. Analysis of sediment samples - The physical characteristics of the sediment samples are listed in Table 2. Because of the thin layer

of sediment at site 1, this core sample was not divided into segments. Samples from the other four sites, however, were divided into four segments for analysis. The sediment core samples ranged from about 40 to about 90 percent silt and clay. Site 4 contained the most sand and some gravel; site 3 contained the most silt and clay material. There was no apparent pattern between silt and clay content and thickness of the sediment layer.

38. The results of the chemical analyses of the sediment core segments are presented in Table 3. Only those pesticide materials occurring in a measurable amount in one of the core segments are listed in the table. No detectable amounts of aldrin, lindane, endrin, 2,4-D, or toxaphene were found. PCB concentrations were higher in the upper portions of the sediment. This was most pronounced at sites 2, 3, and 4, which were near the edge of the shipping channel. No other parameter showed any pattern with depth.

Green Bay Samples

39. Sampling - Samples were obtained from a previously undredged area which is scheduled to be dredged in the future to provide access to a proposed marina. The location of the sampling sites is shown in Figure 2. The area immediately adjacent to the sampling sites contains light industry, homes, and, a short distance to the east, a wildlife sanctuary. Sites 1 and 2 are near the mouth of the Fox River, which drains an area containing much industry, particularly paper mills. The water in the area sampled is very shallow, ranging from 1.2 to 1.8 meters in depth. Little or no compaction of the sediment occurred during sampling.

40. On the first day of sampling, September 9, 1974, the water temperature ranged from 22°C at the surface to 18°C at the bottom. Dissolved oxygen levels ranged from 6.2 mg/l at the surface to 4.5 mg/l at the bottom at sites 1, 2, and 3. Sites 4 and 5, which were nearer the shore, had dissolved oxygen concentrations ranging from 9.0 mg/l (surface) to 6.2 mg/l (bottom). All the temperature and dissolved oxygen measurements obtained at Green Bay are listed in Table D-2 of Appendix D. On the second sampling trip on January 18, 1975, additional samples of sediment, interfacial water, and water column water were obtained between sites 4 and 5. These samples were taken through holes drilled in the ice. Sediment samples were taken from 10 holes located in a line between sites 4 and 5. The water samples were obtained near site 4. At the time of sampling, ice thickness was about 0.45 m at site 5. Due to loss of the interfacial water sample, another sample was obtained on April 8, 1975. This sample was obtained from the edge of the ice shelf near site 5.

41. Analysis of water samples - The results of the analysis of the water samples obtained from Green Bay are listed in Table 4. The

TOC and suspended solids content of all the samples were similar in spite of the difference in sampling times. The soluble TOC values of the samples taken through the ice were slightly lower than that of the samples taken in September, but were still higher than those found at the other four dredging locations. An oil and grease analysis was performed on the water column sample to determine the amount of hexane extractable material. The result was 25 mg/l. There was no odor or visual evidence of oil in the samples, but the samples did contain algae. Perhaps the presence of algae may be the reason for the high TOC and hexane extractable values.

42. Green Bay was the only location tested that contained PCBs similar to both Aroclor 1242 and 1254. The PCBs found in the water column were apparently associated with the suspended solids, since no detectable soluble amount was found. Although the chromatograms indicated that equal amounts of 1242 and 1254 were present in the water column water obtained in January, almost all the PCB in the interfacial water obtained in April was similar to Aroclor 1254. The total amount of PCB was similar for both samples, however. The small amount of dieldrin (0.004 µg/l) found in the water column was not found in the interfacial water sample. No measurable amount of dieldrin was found in the water column water after removal of the suspended solids.

43. Analysis of sediment samples - The physical characteristics of the samples obtained from Green Bay are listed in Table 5. Samples from sites 1 and 2 were black and appeared to be a mixture of muck and sand. The bottom segment from site 1 contained some plant roots. The bottom segment from site 2 and all the samples from sites 3, 4, and 5 were primarily sand. The migration test sample appeared to be representative of the samples from sites 4 and 5 in particle-size characteristics.

44. The chemical characteristics of the Green Bay Sediments are presented in Table 6. Site 5, farthest from the mouth of the Fox, had the highest PCB and oil levels. Nearby, site 4 had the lowest levels of each parameter (except total solids). The sediment from site 1 did not appear to be unusually contaminated with oil or PCB materials in spite of its nearness to the mouth of the Fox River. The high TOC value for the bottom segment from site 1 is probably due to vegetative material.

45. The concentrations of Aroclor 1242 were much greater in the upper segment for all sites. TOC values were slightly higher and total solids values were slightly lower in the upper portions of the sediment at sites 2, 3, 4, and 5. Oil and Aroclor 1242 concentration showed no pattern with depth of sediment. Whereas equal amounts of Aroclor 1242 and 1254 were found in the water column and Aroclor 1254 predominated in the interfacial water, the predominant form in the sediment was Aroclor 1242. No measurable amount of dieldrin was found in the sediment.

Fall River Samples

46. Sampling - Samples were taken from a shipping channel connecting Fall River, Massachusetts, with Rhode Island Sound through a passage between the island of Rhode Island and the mainland to the east. The area sampled was in the southern end of Mt. Hope Bay several miles south of the city of Fall River, Massachusetts. The sites sampled are shown in Figure 3. Water depths ranged from 6.7 m at sites 2 and 3 to 11.0 m at site 4. These sites are near sites previously sampled by the Corps of Engineers in 1951. Site 5 was a short distance south of a sewage plant outfall. Water temperatures on October 7, 1974 ranged from 16°C at the surface to 14°C near the bottom. Dissolved oxygen levels ranged from 6.5 mg/l at the surface to 7.6 mg/l near the bottom. Except for site 3, the dissolved oxygen concentration generally increased with depth. A list of all temperature and dissolved oxygen measurements made on October 7 are in Table D-3 of Appendix D. The additional samples were obtained on January 9, 1975, near sampling sites 4 and 5.

47. Analysis of water samples - The results of the analysis of the water samples from Mt. Hope Bay are presented in Table 7. The pH, TOC, and soluble TOC concentrations were similar in all water samples. Only suspended solids values varied. The closeness between the TOC and soluble TOC values indicates that these suspended solids were primarily inorganic. No measurable amount of pesticide material was found in any of the water samples from Mt. Hope Bay.

48. Analysis of sediment samples - The physical characteristics of the sediment samples are presented in Table 8. The depths of sediment at sites 4 and 5 near the mainland were deeper than at sites 1, 2, and 3. No compaction of the sediment occurred during sampling except at site 5. The amount of silt and clay, sand, and gravel in the sediments varied widely from site to site and at different depths.

49. The results of the chemical analyses are listed in Table 9. PCB concentrations were less than those measured at Chicago or Green Bay, but more dieldrin, aldrin, and DDT were found, particularly at site 4. At most of the sites, but not all, the concentration of pesticide material decreased with depth. No such trend was observed for TOC, oil, or suspended solids.

Houston Samples

50. Sampling - Ship traffic in the Houston Ship Channel was too great to permit sampling directly in the channel. Samples were taken in Tabbs Bay from locations near dredged channels connecting industries southeast of Baytown, Texas, with the Houston Ship Channel (See Figure 4). The area sampled is a likely repository of sediment entering Galveston Bay from the Houston area by means of the ship channel. Water depths at the sampling sites ranged from 1.2 to 1.8 meters. On January 30, 1975, the day of sampling, water temperatures ranged from 18 to 20°C and

dissolved oxygen concentrations ranged from 10.6 to 11.2 mg/l. As at Fall River, oxygen concentration increased slightly with depth. A complete listing of measured temperature and dissolved oxygen values are included in Table D-4 of Appendix D.

51. Analysis of water samples - The results of the water sample analyses are listed in Table 10. The water column water was similar to the least turbid of the interfacial water samples in TOC, soluble TOC, and suspended solids concentrations. No measurable amount of pesticide material was found in the water column sample. Small amounts of Aroclor 1254 were found in two of the five interfacial water samples.

52. Analysis of sediment samples - The sediment depth was greater at sites 1, 2, and 3 and the sediments compacted more during sampling than the sediments from sites 4 and 5 (Table 11). The silt and clay portion of the samples ranged from 31 to 49 percent.

53. The chemical characteristics of the sediment samples are listed in Table 12. At all sites, the oil concentration was highest in the lower segment. In most cases, however, the concentrations of Aroclor 1254, DDT, and dieldrin were greater in the upper portion of the sediment. Relatively high concentrations of 2,4-D, DDT, and dieldrin were found at sites 4 and 5. No measurable quantities of these pesticides were found at sites 1, 2, and 3.

Memphis Samples

54. Sampling - Sampling by diving in the lower Mississippi River was considered impractical and unsafe because of the high turbidity, possibility of snags, and unknown currents. A portion of Tennessee Chute connecting Memphis Harbor to the Mississippi River was chosen for sampling because it was expected that sediments in this area would include silt deposited from the Mississippi River and contaminants from the industrial portion of Memphis Harbor and because the charts showed that the area was shallow enough that samples could be obtained from the sampling boat in a manner similar to that used to get samples through the ice at Green Bay. On the day of the sampling, January 27, 1975, however, the river was much higher than normal and this method could not be used. A second trip was made on February 11, 1975, and samples of sediment were obtained using a gravity core sampler. Although the river was still high, this method of sampling allowed the taking of samples at the entrance to Memphis Harbor (see Figure 5).

55. On the day of sampling, water temperatures ranged from 4 to 7.5°C, with the warmer temperatures at the surface near the Mississippi River. Dissolved oxygen readings ranged from 8.2 to 11.6 mg/l with the lower readings associated with the warmer water. (See Table D-5, Appendix D for all measurements).

56. Analysis of water samples - The water column sample (Table 13) contained 0.02 μg Aroclor 1254/l and 0.002 μg dieldrin/l. Removal of the suspended solids by centrifugation and re-analysis showed that these materials were associated with the suspended matter. Two of the five interfacial water samples (sites 2 and 3) contained Aroclor 1254. Measurable amounts of other pesticide materials were not found.

57. Analysis of sediment samples - The results of the physical measurements on the sediment samples are presented in Table 14. The amount of compaction could not be measured at Memphis because of the method sampling. It was estimated by the sampling personnel, however, that the depth of sediment sampled was at least twice as great as the length of the core sample obtained. The core segments ranged from 27 to 72 percent silt and clay. Sites 1 and 3 contained more silt and clay than sites 2, 4, and 5. There was no apparent pattern between sediment depth and particle size.

58. The chemical characteristics of the sediments are presented in Table 15. Measurable quantities of Aroclor 1254, DDT, and dieldrin were found at all sites. At four of the five sites, dieldrin concentrations decreased with depth. No other parameter measured showed any pattern with depth.

Migration Test Sediments and Interstitial Water Analyses

59. Some parameters of the samples used for the migration test studies have been included in the tables listing the physical and chemical characteristics of the sediment samples. These values were included to show that the migration test samples were representative of the samples obtained from that area. A more complete analysis of each migration test sample is listed in Table 16, along with the analysis of the interstitial water obtained from each sample. In general, the parameters measured show that the sediments from the different locations were very different.

60. The variation in particle size is best illustrated by a graph of cumulative percent distribution with particle size (Figure 6). The Green Bay sediment had the narrowest particle-size range and contained the most sand. The Fall River sediment contained the widest range of particle sizes. Chicago sediment contained the most silt and clay; Memphis ranked next.

61. The relative amounts of silt and clay, TOC, oil and grease, and PCB in the migration test sediments are shown by bar graphs in Figure 7. Green Bay and Chicago sediments contained the most PCB, although they were at opposite ends of the scale as far as TOC, oil and silt and clay contents were concerned. The two saltwater sediments contained by far the least PCB, but were about average in TOC, oil, and silt and clay concentration. The five migration test samples also varied in the identity of other pesticides present (Table 16). Green

Bay and Fall River sediments contained no measurable quantity of pesticide material other than PCB; the Chicago sample contained DDT; the Houston sample contained 2,4-D and dieldrin; and the Memphis sample contained DDT and dieldrin. Aldrin, found in two of the five sites at Fall River, was not found in the migration test sample.

62. The TOC and PCB concentrations of the interstitial water samples did not follow the same pattern as those of the sediment samples (Figure 8). It appears, however, that high interstitial TOC values may be inversely related to interstitial PCB concentrations. Although PCB, DDT, and dieldrin were found in Memphis sediment, only dieldrin could be found in the interstitial water. For the Chicago sediment, PCB and DDT were found in both the sediment and the interstitial water.

Salinity of Saltwater Samples

63. Chloride analyses were performed on the saltwater samples to determine the relative salinity. A sample of interfacial water from Fall River: Mt. Hope Bay area contained 17,000 mg chloride/l and the interstitial water contained 15,000 mg chloride/liter. Since the literature¹⁷ indicates that ocean water contains 18,990 mg chloride/l, it appears that the Mt. Hope Bay water sampled was only partially diluted by fresh water. The Houston water column water and the interfacial water contained 2800 mg chloride/liter. The Houston interstitial water contained 7400 mg chloride/liter. Apparently the area sampled is diluted considerably by fresh water.

Chicago Migration Tests

64. Equilibrium test results - Of the sediments from the five dredged areas sampled, the sediment used for the Chicago batch desorption tests was highest in oils (hexane extractable), silt and clay fraction, t-DDT, and PCBs. The data in Table 17 demonstrate that only PCB (as Aroclor 1254) and t-DDT were detected in the well-mixed sediment. That these were associated substantially with the particulates is evidenced by the low concentrations found solubilized in the interstitial water. The interstitial water concentrations accounted for 0.05 percent of the PCB and 2.1 percent of the t-DDT's present in the wet sediment. The water column water used was the lowest of all sites in suspended solids, and all chlorinated hydrocarbons of interest were below the detection limits of this study.

65. Measurable desorption occurred at the 1:5 sediment ratio only, and only PCBs were desorbed after 24-hr contact. The data in Table 18 represent the contributions of the various system constituents to the measured desorption values. The PCBs desorbed at the 1:5 mixing ratio represented 0.8 percent of the total initial concentration of the system while the t-DDT's not only did not show desorption but apparently adsorbed the 0.014 µg/l of soluble t-DDT contributed by the interstitial

water. The soluble TOC concentrations increased 2.0 percent for the 1:5 ratio and 3.4 percent for the 1:15 ratio, while decreasing 1.4 percent at the 1:50 ratio. However, no apparent correlation existed between the desorption of all organic carbon and the chlorinated hydrocarbons PCB and t-DDT.

66. Settling test results - The TOC values, oils, and PCBs decreased with decreasing concentrations of suspended solids (Table 19). The desorption tests showed no significant solubilization of PCBs. Measurable levels of PCBs were present for all settling tests, however, indicating the PCBs still in the supernatant were associated with the suspended particulates. The percent organic fraction of the suspended particulates increased with settling time: at 30 min, the suspended particulates were 2.3 percent organic and after 5 hr, they were 5.6 percent organic. (Calculated from the TOC, soluble TOC, and suspended solids values). The trend suggests that the particulates associated with organics tend to settle more slowly, perhaps due to slightly decreased density, and tend to remain suspended in the water column somewhat longer. The dissolved organic concentration increased slightly with time, but, as in the desorption tests, no relationship between the increase and the migration of PCBs was apparent.

Green Bay Migration Tests

67. Equilibrium test results - The Green Bay sediment was unique in that it represented an undredged site and it was the highest of all sites in sand fraction (90 percent). The Green Bay water column was highest in hexane extractables although, by observation, the residue from the oil and grease analysis did not have the oil consistency noted in the Chicago water column water sample but seemed somewhat waxy. This observation also held for the oils (hexane solubles) extracted from the sediment used in the equilibrium test. Concentration of dieldrin (0.004 $\mu\text{g}/\ell$) and total PCBs (0.08 $\mu\text{g}/\ell$) reported in Table 20 represent the highest values of these species of all the overlying water columns tested; however, after centrifugation all values dropped below the limits of detection. Green Bay was also unique in that it was the only site which contained PCB Aroclor 1242 and Aroclor 1254. The ratio of 1242/1254 differed widely depending on the medium investigated. In the sediment, for example, the ratio was 25.3:1; while in the interstitial water and water column water, the ratios were 0.63:1 and 1:1, respectively.

68. The desorption evaluations in Table 21 show that the initial soluble total PCB concentration contributed little to the total amount of soluble PCB percent after 24-hr mixing at the 1:4 ratio. Aroclor 1254 demonstrated greater desorption than 1242, illustrated by a 1242/1254 ratio of 0.14:1, the lowest ratio of all media tested at Green Bay. No pesticides of interest were found at soluble concentrations above the detection limits of this study for all mixing ratios.

69. Soluble TOC increased substantially during all three batch desorption tests at the 1:30 sediment-to-water ratio, a 45.9 percent increase in soluble TOC was measured. At the 1:4 and 1:10 ratios the increases in soluble TOC were substantially less, 14.2 and 9.0 percent, respectively. The Green Bay desorption tests results showed no apparent relationship between the desorption of TOC and the desorption of the nonpolar chlorinated hydrocarbons.

70. Settling test results - Oils, PCBs and TOC reported in Table 22 decreased in concentration with a decrease in suspended solids. In the sediment-to-water ratio (1:4) used for the Green Bay settling tests, desorption of PCBs occurred in the equilibrium tests, and it is possible that the PCB concentrations reported for the various settling times may include soluble PCB. However, it is reasonable to assume that, if desorption did take place, it occurred at a reduced rate from that observed during the equilibrium tests due to the fact that the sediment-to-water contact time during a settling test was much less than during the 24-hr of agitation for desorption tests. The final total PCB concentration in the settling tests was lower than the total PCBs desorbed after 24-hr for the 1:4 desorption tests.

71. The role that the suspended particulates, with associated PCBs, play in increasing the supernatant total PCB concentration can be dramatically demonstrated by using the water column total PCB concentration as a reference total PCB level and comparing the decrease with time. After 30-min settling, the total PCB concentration in the settling test water column was increased 13.4 times over the initial concentration; after 1 hour the increase was 8.8 times; after 3 hours 2.8 times; and after 24 hours the level of total PCB had returned to the initial water column concentration of 0.08 µg/l.

72. The ratio of Aroclor 1242 to Aroclor 1254 remained reasonably consistent throughout the settling test, averaging 0.61:1.

73. The organic fraction of the suspended solids increased with settling time ranging from 8 percent after 30 min to 25.4 percent after 24 hr. The soluble TOC values were not significantly different for the samples from the four settling tests.

74. An analysis of the oil and grease values from Table 22 points out an incongruity between the initial oil concentration and those subsequently measured during the settling tests. The 30-min and 1-hr oil concentrations are not possible given the initial oil concentration. Efforts to resolve the inconsistency were fruitless, and it is suggested that the cause may have been due to the nonhomogeneity of the sandy sample, which contained roots and decaying vegetative matter.

Fall River Migration Tests

75. Equilibrium test result - The Fall River sediment used for migration testing was similar to the Houston sediment in that both were

saline (Fall River = 1.7 percent chloride, Houston = 0.3 percent chloride); both were low in PCB content; and both contained about 27 percent silt and clay. The major difference between the sites was the concentration of oils, with Fall River much lower at 344 mg/kg dry solids. The Fall River water column contained no detectable chlorinated hydrocarbons of interest for this study. The data and subsequent evaluation of the Fall River equilibrium tests are summarized in Tables 23 and 24.

76. No measurable desorption of the chlorinated hydrocarbons of interest occurred at either the 1:4 or 1:10 mixing ratio, despite the fact that the Fall River sediment used for these tests had an interstitial water PCB concentration of 0.15 $\mu\text{g}/\ell$ or 0.85 percent of the total PCB concentration of the wet sediment, the highest soluble fraction of all sites. While the contribution of the soluble PCBs in the interstitial water alone could not contribute a detectable amount of PCB to the equilibrium system, it should provide some clue as to the sediment's potential for desorption. However, no measurable desorption occurred. There was also a very slight reduction in the soluble TOC values for both mix ratios, all of which indicates a system more disposed to adsorption than desorption for both the total and nonpolar organic species.

77. Settling test results - The results of the settling tests, recorded in Table 25, show measurable concentrations of both oils and PCBs after 30-min settling time only. There was, however, a decrease in TOC with suspended solid through the 24-hr settling period. As with the Chicago and Green Bay tests, the organic fraction of the suspended solids increased with settling time from 2.3 percent after 30 min to 20 percent after 24-hr. Given the data from Fall River equilibrium tests, it would be highly improbable that any of the measured PCBs present after 30-min settling would be in the soluble form.

Houston Migration Tests

78. Equilibrium test results - The similarities which exist between the Houston and Fall River sites have already been mentioned; however the major difference is the oil content of the Houston sediment, which was 4.5 times higher than Fall River (Table 26). The mixed sediment used in the migration testing contained 13 μg PCBs/kg, 0.2 μg dieldrin/kg, and 1.3 μg 2,4-D butyl ester/kg. Of these, only PCBs and 2,4-D butyl ester were detected in the soluble form in the interstitial water at concentrations of 0.08 and 0.02 $\mu\text{g}/\ell$, respectively. The overlying water column contained no measurable amounts of any of the chlorinated hydrocarbons of interest. The desorption data, summarized in Table 27, reveals measurable concentrations of PCBs at the 1:4 mix ratio only; neither dieldrin nor 2,4-D butyl ester were detected. The theoretical contribution of the interstitial water was about half of the final soluble concentration reported at the 1:4 ratio, and the

apparent amount desorbed may have been approximately one-half the 0.02 µg/ℓ detected. The dissolved organic carbon concentration was approximately 10 times higher for the 1:4 mix ratio than the 1:10 ratio.

79. Settling test results - The settling test data summarized in Table 28 lack the dramatic decrease in PCB concentration with suspended solids that was observed in Chicago and Green Bay settling tests but rather seem to follow a combination of suspended solids and oil and grease concentrations. It is difficult to draw definite relationships from the data due to the fact that the oil values are very close to detection limits and subject to large variations (See Appendix B). The data from the desorption tests at the 1:10 mix ratio show no significant contribution of the soluble PCB fraction to the total concentrations reported in the Houston settling test. The Houston suspended solids did not exhibit the increase in organic carbon fraction with settling time as was reported for Chicago, Green Bay, and Fall River.

Memphis Migration Tests

80. Equilibrium test results - The Memphis sediment used for migration tests was second highest in silt and clay fraction; second lowest in oils and grease; and contained 78 µg PCB/kg, 5.1 µg t-DDT/kg, and 3.9 µg dieldrin/kg. The Mississippi River water column contained 0.02 µg PCB/ℓ and 0.002 µg dieldrin/ℓ, neither of which was found to be in the soluble form. The results of the batch desorption tests summarized in Tables 29 and 30 indicate, as with all sites tested, that no measurable desorption occurred at mix ratios below 1:4. The desorbed PCB concentration was 0.02 µg/ℓ with no measurable contribution from the interstitial water.

81. The amount of dieldrin desorbed was 0.002 µg/ℓ with the contribution from dispersal of interstitial water not significant. The percent organic in the soluble form actually decreased slightly for all equilibrium tests, as was observed for Fall River equilibrium tests. Although the decrease in soluble TOC was not large enough to show any adsorption trends, it clearly indicates that no significant TOC desorption occurred.

82. Settling test results - The Memphis sediment settling test results presented in Table 31 clearly demonstrate the decrease in PCB concentration with decreasing suspended solids concentrations seen with Chicago and Green Bay settling tests. The oil concentrations were again very near the lower limit for analysis and are subject to the same variations noted for Houston. The Memphis water column with a PCB concentration of 0.02 µg/ℓ may be used as a reference as it was in the Green Bay settling tests to illustrate the contribution of PCBs associated with the suspended sediment as a function of time. After a 30-min settling time, the effluent PCB concentration was 8.5 times the initial water column value; after 3 hr it was 4 times greater;

after 7 hr it was 3 times greater; and after 24 hr, twice as great. The final suspended solids concentration after 24 hr was 78 percent of the initial water column value. Dieldrin and t-DDT were also present in the settling test effluents. Dieldrin was detected in both the 30-min and 3-hr test effluents. The concentration at 3 hr was at the level reported for the water column. The concentration of t-DDT after 30-min settling (0.13 µg/l) was about half the concentration of dieldrin although the ratio of t-DDT to dieldrin in the sediment was 1.3:1. One possible explanation for the reversal was the presence of dieldrin on the water column suspended solids. Desorption at the mixing ratio used for the settling tests was not a significant factor in the concentrations of chlorinated hydrocarbons. The organic fraction of the suspended solids did not increase with settling time, and, although the soluble TOC did increase slightly with time, its role in affecting the migration of chlorinated hydrocarbons was not readily apparent.

Discussion of Results

Sediment Characteristics

83. Occurrence of pesticide materials - PCBs were found in measurable quantity in 59 of the 64 sediment samples analyzed in this project (Table 32). Aroclor 1254 was found in 54 of the samples; Aroclor 1242 in only 8 samples, all from Green Bay. Of the pesticides, dieldrin and the DDT compounds were the next most common. Dieldrin was found at all five sampling sites at Fall River and Memphis, and DDT compounds were found at all Memphis sites. Dieldrin was found in at least one site for all locations except Green Bay. DDT compounds were present in at least one sampling site at all locations. Aldrin was only found at two of five sites in Fall River and 2,4-D compounds were only found at two of five sites at Houston. Lindane, endrin, and toxaphene were not present in measurable concentrations in any of the sediment samples analyzed.

84. Concentration of pesticide materials - All parameters measured (TOC, oil and grease, and pesticide material) showed a wide range of variation in concentration between segments from a single sampling site, between sampling sites at one location, and between locations. The variation in concentration between the segments of each core sample can be seen by comparing values listed in Tables 3, 6, 9, 12, and 15. It is apparent that high concentrations of these parameters were distributed at various depths and various locations within the area sampled. Values for several parameters were calculated to determine the concentrations that would have been measured if the entire core from each site been analyzed as one sample. These values appear in Table 33.

85. During dredging operations, considerable mixing of the sediment being removed is expected to take place. The values in Table

33 may more closely resemble the concentrations of contaminants in the material discharged by a dredge than the values reported for each sample segment. The high variability of pesticide material concentration between sampling sites indicates that a large number of samples are necessary for an accurate estimate of concentration of contaminants in an area to be dredged.

86. Relationship between measured parameters - Adsorption of pesticide materials by clays, organic matter, and oil has been reported by many investigators.^{5,6,7,8,9} Possible correlations between PCB, oil and grease, organic carbon, and silt and clay fraction were investigated using values from all samples. No statistically significant (10 percent significance level) correlation was found between PCB concentration and the other three parameters. Limiting the correlations to the samples taken at one location (e.g., Chicago) did not improve the correlation. The lack of correlation can be easily recognized by comparing the bar graphs in Figure 7. The Chicago migration test sediment had the highest PCB content, as expected from the literature. Green Bay, however, had the lowest levels of TOC, oil, and silt and clay fraction but had the second highest PCB concentration. The levels of TOC, oil, and silt and clay fraction of the Houston sediment were about midway between the highest and lowest; yet the PCB content was lowest.

87. It is obvious, of course, that, in a system as heterogeneous as the sediments sampled, the concentration of PCB in the sediment depends to a very great degree on the source of the deposited solids and the opportunity these solids had to sorb PCB. It is quite likely that suspended matter with a high potential for sorbing pesticide materials may have had little or no contact with PCBs. Similarly, sediments with a relatively low sorptive capacity may contain large amounts of PCB simply because the solids had contact with PCB prior to settling. Lack of correlation between PCB content and TOC, oil, and silt and clay fraction, then, can be expected.

88. Comparison of dredged and undredged areas - Four of the five locations sampled are routinely dredged. The sediment samples obtained are of relatively recent origin. Variation in rainfall, winds, currents, and tides may be expected to cause contaminated material to be present in locally high concentrations within the sediment. The locations of these pockets may vary as to depth or horizontal position in the sediment depending on conditions during deposition. Such variation can be seen in the data in Tables 3, 9, 12, and 15. The samples from Green Bay are from a previously undredged area (Table 6). It was expected that oil, organic carbon, and pesticide materials would be found primarily in the upper portion of the sediments because these sediments were probably of much more recent origin than the deeper sediments. The high TOC in the bottom segment of the site 1 sample can be explained by the presence of vegetative matter. The oil and PCB contents of the lower segments at most Green Bay sites were

surprising, however. The low PCB values at site 1 (near the mouth of the Fox River) were also unexpected.

89. Parameter variations with depth - A vertical distribution of the parameters measured was not expected in the samples from the areas that are routinely dredged because these sediments are assumed to have been deposited at irregular intervals since the previous dredging activity. Some stratification was apparent, however, particularly with the pesticide materials. To facilitate comparison, the values of the parameters in each core segment were converted to the percent of the total amount in that core sample. An analysis of variance (AOV) test was then used to determine whether the observed differences were significant at the 5 percent significance level. The data for each dredged area were analyzed separately.

90. The percent TOC, PCB, dieldrin and t-DDT contained in each core segment was determined for each dredged area sampled. The average value for the five sites sampled at each dredged area are presented in Table 34. The parameters that have a statistically significant variation with depth are indicated by an asterisk next to the percent value for the top segment. In no case was there a significant variation of TOC with depth. The only significant variation of oil with depth was at Houston where the bottom segments contained more oil. PCB materials were concentrated in the upper portion of the sediment at Chicago and Green Bay and in the lower portion of the sediment at Memphis. Although PCBs were in higher concentrations in the upper portion of 3 of 4 sites at Fall River and 4 of 5 sites at Houston, the AOV test indicated that the variation was not significant when considering all sites. The higher concentration of dieldrin in the upper portion of the Fall River sediment was significant, however. Variations with depth for PCB, dieldrin, and t-DDT were significant for the Memphis samples. Each material, however, appeared to be concentrated in a different portion of the core sample. PCB, for example, was measured in the highest concentration in the lower portion of the sediment; dieldrin, on the other hand, was concentrated at the top, and t-DDT was concentrated in the center section of the core.

91. Interstitial water - Measurable amounts of PCB were found in all interstitial water samples except that from Memphis (Table 16). DDT was found in the Chicago interstitial water; 2,4-D in Houston interstitial water; and dieldrin in Memphis interstitial water. No correlation was found between concentration of pesticide material in the sediment and the amount in the interstitial water. The Fall River and Houston migration test sediments contained about the same amount of PCB, but the interstitial water concentrations were quite different. Although dieldrin was present in the Houston sediment and t-DDT was found in the Memphis sediment, neither material was found in the respective interstitial water samples. The DDT content of the Chicago interstitial water was greater than the PCB concentration - yet the sediment PCB concentration

was thirty times greater than the DDT value. The Memphis sediment also contained DDT, but none was found in the interstitial water.

92. The lack of correlation between amount of PCB in the sediment and the factors affecting sorption (sediment organic carbon, oil, and silt and clay fraction) was discussed in paragraph 86. A similar lack of correlation between these parameters and PCB content of the interstitial water exists. The Chicago sediment, high in TOC, oil, and silt and clay fraction, might be expected to have a lower PCB concentration in its interstitial water than the Green Bay sediment, which was low in TOC, oil, and silt and clay fraction. The interstitial water from both sediments, however, contained the same amount of PCB material. Assuming that the interstitial water PCB materials were the result of desorption from the sediment, greater desorption might have been expected from the Green Bay sediment.

93. The one correlation that was significant was between interstitial water PCB content and TOC. The correlation coefficient of -0.97 was significant at the 1 percent significance level. In tests involving adsorption of lindane and dieldrin on sand, Boucher and Lee¹² found a decrease in adsorption when the adsorbate solution contained natural dissolved organics. They also found that less dieldrin was desorbed from sand by water containing organic material than by distilled water. In this work, it appears that natural dissolved organics may inhibit desorption of PCB. More data, from interstitial water samples having a wider range of TOC and PCB values, are needed to evaluate this relationship.

94. Although measurable amounts of PCB, t-DDT, 2,4-D, and dieldrin were found in the interstitial water samples, the concentrations were very low. The highest concentration of PCB was 0.15 µg/l, well below the reported solubility level of Aroclor 1254 of about 56 µg/l⁶. The DDT concentration of 0.15 µg/l was also below the solubility levels of 1.2 to 37 µg/l reported for p,p'-DDT⁹.

95. The dispersal of interstitial water during dredging is expected to have a small effect on the amount of soluble pesticide material. During hydraulic dredging, one volume of bottom sediment may be mixed with four volumes of water. Assuming that 2/3 of the bottom sediment volume is interstitial water, the addition of four volumes of water results in a seven-fold dilution of the interstitial water ($4.67/0.67 = 7$). The highest PCB and DDT concentration measured in the interstitial water was 0.15 µg/l. Dilution with the water needed for hydraulic dredging would reduce the concentration to about 0.02 µg/l. During aquatic disposal of dredged material, the dilution of the sediment would be much greater, resulting in lower levels.

Water Column Water Characteristics

96. The only pesticide materials found in the water column

samples were associated with the suspended solids. No soluble pesticide materials were found in any of the water column samples at the detection limits used in this work. No pesticide materials were found in the water from Chicago, Fall River, or Houston. The Green Bay water contained 0.04 μg Aroclor 1242/ ℓ , μg Aroclor 1254/ ℓ , and 0.004 μg dieldrin/ ℓ . The Memphis sample contained 0.02 μg Aroclor 1254/ ℓ and 0.002 μg dieldrin/ ℓ .

Interfacial Water Characteristics

97. The only chlorinated hydrocarbon found in the interfacial water samples were the PCB compounds. These were found at all locations except Fall River. Both Aroclor 1242 (0.01 $\mu\text{g}/\ell$) and Aroclor 1254 (0.08 $\mu\text{g}/\ell$) were found in the Green Bay interfacial water. Only Aroclor 1254 was found at Chicago, Houston, and Memphis. Concentrations ranged from 0.08 $\mu\text{g}/\ell$ at Chicago to 0.04 and 0.02 $\mu\text{g}/\ell$ at Houston and Memphis. Whether the PCB compounds were soluble or associated with suspended solids was not determined.

Migration Test Results

98. Equilibrium test results - The emphasis in most previous work on sorption has been with the adsorption of pesticides from water by various materials with a view toward defining the role of these substances in the transport and accumulation of pesticides in an aquatic system.⁵⁻¹² It appears, however, that the results of the adsorption work cannot be generally applied to the desorption process. Huang and Liao⁵ studying the adsorption of dieldrin on montmorillonite clay found that desorption did not follow the Freundlich isotherm adsorption curve. Veith and Lee¹¹ were unable to desorb toxaphene from natural lake sediments where it had accumulated. These results suggest that desorption equilibria do not coincide with the adsorption equilibria, but rather tend to favor sorption on the particulates.

99. The chlorinated hydrocarbon most abundant and most widely found in this work was the PCB Aroclor 1254. The conclusions derived from these desorption studies, therefore, most directly apply to PCBs.

100. Factors affecting desorption - The absence of measurable amounts of soluble pesticide materials in many of the desorption tests greatly restricts the use of mathematical analysis of the desorption data. Use of the Freundlich model or correlations between desorbed material and the independent variables is not meaningful given the limited desorption which occurred. The factors affecting desorption are: solids-to-liquid ratio; PCB concentration in the sediment; particle size with its related organic fraction; and oil and grease content.

- a. Solids-to-liquid ratio - The most superficial review of the desorption data indicates the importance of the ratio of sediment solids to water column water. No desorption was measured for any chlorinated hydrocarbon with any of the sediments below the highest mix ratios of 1:4 or 1:5 despite the fact that a linear relationship predicts detectable concentrations for the Chicago and Green Bay sites at the next lowest ratios. Lotse *et al.*¹⁰, in a stepwise regression equation, demonstrated the sediment concentration in the water column as the most important independent variable for the adsorption of lindane. Similar results were reported by Huang and Liao⁵ for the adsorption of dieldrin on mineral clay systems. Lee and Plumb¹⁷ also discussed the importance of the solids-to-liquid ratio in the development of the elutriate test to evaluate the effect of a suspended sediment on water column quality.
- b. Sediment PCB concentration - The bar graph in Figure 7 provides a visual summary of the relative initial PCB concentrations of the five sediments used in the study. Presented in order of decreasing PCB concentrations (on a dry weight basis) are sediments from Chicago > Green Bay > Memphis > Houston > Fall River. In decreasing order of PCBs desorbed, the ranking is Chicago, Green Bay > Memphis > Houston > Fall River (no desorption). The relative amounts desorbed range from 1.8 percent of the total PCB concentration for the Houston sediment to 0.4 percent for the Memphis sediment. Boucher and Lee,¹² in a study of the sorptive properties of aquifer sand, showed increased lindane and dieldrin adsorption with increased concentrations. They reported about 4 percent of the sorbed dieldrin could be leached by a single wash with Lake Mendota water. The relationship between the solids-to-liquid ratio and the sediment PCB concentration together constitute the most important variables affecting desorption.
- c. Particle size and organic content - Although some investigators have studied the sorptive capacities of homogeneous substrates,^{5,6,8,9} a more complete approach would include the effects of interrelated

parameters such as solids-to-liquid ratio, sediment pesticide concentration, particle size fractions, and organic contents. In this work, a correlation coefficient relating TOC and silt and clay fraction of the sediments was calculated to be 0.88 (significant at the 5 percent level). Other studies have shown organic matter to be effective sorbers of pesticide materials. The regression equation of Lotse *et al.*¹⁰ ranked organic matter second in importance of independent variables affecting sorption. Hague, Schmedding, and Freed⁶ working with Aroclor 1254 found that Woodburn soil (organic content 3.1 percent) sorbed relatively more PCB than pure clays or sand. The desorption of dieldrin from pure montmorillonite clay using distilled water was 25 percent as reported by Huang and Liao⁵. The only dieldrin desorption measured in the study reported herein occurred with the Memphis sediment (a TOC value of 9,300 mg/kg and 47 percent silt and clay). It was found that 0.2 percent of the total dieldrin in the 1:4 system desorbed after 24 hr, a decrease by two orders of magnitude from the dieldrin-montmorillonite clay system of Huang and Liao.

The effect of soluble organic carbon on desorption is apparently minor and, as mentioned previously in the section on equilibrium test results, no general trend relating soluble TOC increase and PCB desorption was discernable. Boucher and Lee,¹² however, reported that the amount of dieldrin desorbed from aquifer sand decreased from 6 percent to 4 percent of the total sorbed dieldrin when distilled water was replaced with Lake Mendota water containing soluble organics. In the study reported herein, the concentration of PCB in the interstitial water, assumed to be the result of desorption from the sediment solids, was inversely proportioned to the interstitial water TOC. In the desorption tests, however, this effect was not noted.

The role the interstitial water played in the release of chlorinated hydrocarbons was relatively minor, with the exception of Houston, where theoretically half of the final soluble concentration (0.02 µg/ℓ) may have been due to interstitial water at the 1:4 mix ratio. For all other tests the theoretical contribution was less than 10 percent; in the case of the Chicago sediment, apparent adsorption of initially soluble t-DDT

occurred. This study also indicates caution should be used when trying to estimate the amount of soluble material transferred to the water column based on interstitial water characteristics. The Fall River sediment had the highest percent of soluble PCBs (0.85 percent) although it showed the least relative transfer upon being mixed with the overlying water column.

- d. Oil and grease - The significance of sedimented oil in accumulating DDT was studied by Hartung and Klingler⁹, who determined the partition coefficient between sedimented oils and the overlying water column to be on the order of 1.08×10^6 to 1.45×10^6 . The partition coefficient calculated for PCB from this study yielded values ranging from 0.1×10^6 for Houston to 6.1×10^6 for Green Bay. However, as with the other parameters investigated, the partitioning equilibrium is apparently not linear, i.e., PCBs were not measured at lower sediment-to-liquid ratios although the partition equation predicted their presence at detectable concentrations.

One of the problems in performing desorption tests on pesticide-containing materials is the difficulty in obtaining a sample for analysis containing only soluble material. Nonsoluble material cannot be removed by filtration because of the possibility of also removing soluble pesticide materials by adsorption on the filter. As an alternative, high-speed centrifugation was used in this work to remove particulates. Since specific gravity rather than particle size determines the material removed by centrifugation, the soluble fraction obtained by centrifuge may contain different materials than that obtained by filtration. Substances with a specific gravity very near that of the liquid portion will remain in suspension and materials with lower specific gravities will rise to the surface. In centrifuging samples in this study, the centrate was clear, indicating that the particulates were effectively removed. In some of the samples from the desorption tests and in most of the interstitial water samples, however, an oil sheen or iridescence was observed on the surface of the samples after centrifuging. No attempt was made to exclude this oil sheen from the samples analyzed. Since the amount of oil needed to produce a surface sheen is

very small, probably less than 0.1 mg/l in the samples analyzed, the effect on organic carbon measurements is negligible. Because of the high solubility of pesticide materials in oil, however, the actual concentration in true water solution may be lower than the values reported for the desorption tests and interstitial water. For example, the Fall River interstitial water contained 0.15 µg PCB/l. Assuming the interstitial water sample contained as much as 0.1 mg oil/l and assuming a partition coefficient of 1×10^6 , the concentration of PCB in the water phase would be about 0.14 µg/l instead of the 0.15 µg/l reported. It should be noted that Hartung and Klingler⁹ also reported some difficulty in the complete removal of oil from samples used in their partition coefficient test.

Settling Test Results

101. Development of a descriptive relationship - The increase in soluble PCBs in a water column due to mixing with sediments under the conditions outlined in the previous section were relatively minor. Settling tests were performed to investigate another possible method of transfer of PCBs to the water column. The parameters of TOC, soluble TOC, oil and grease, and pesticide material concentration in the supernatant were measured for various settling times. The solids-to-liquid ratios used did not yield measurable soluble pesticide concentrations during the desorption tests except in the case of the Green Bay system. The results of the settling tests (Tables 19, 22, 25, 28, and 31) were subjected to a correlation analysis¹⁸. The resultant correlation-probability matrix¹⁸ is summarized in the following tabulation.

| | Suspended Solids (SS) | SS-TOC | SS-Clay | Oil & Grease | PCBs |
|--------------|--------------------------|--------|---------|-----------------|-------|
| SS | **** | 0.844 | 0.990 | 0.018 | 0.377 |
| SS-TOC | 0% | **** | 0.833 | 0.306 | 0.488 |
| SS-Clay | 0% | 0% | **** | -0.064 | 0.273 |
| Oil & Grease | 50% | 19.9% | 50% | **** | 0.867 |
| PCBs | 12% | 3.8% | 27.3% | 0% | **** |

The values in the upper right portion of the matrix are the correlation coefficients, those in the lower left represent the probability that the corresponding correlation coefficient is due to chance. For example, the correlation between suspended solids and oils and grease is 0.018 but there is a 50/50 probability (50 percent) that this correlation is due to chance, therefore very little meaning could be attributed to the correlation coefficient. In general, the higher the probability (50 percent is maximum) the less significant the correlation coefficient.

102. The results of the settling tests given in Tables 19, 22, 25, 28, and 31 were subjected to a correlation analysis.¹⁸ The resultant correlation-probability matrix is summarized in the above tabulation.

103. The values in the upper right portion of the matrix are the correlation coefficients; those in the lower left represent the probability that the corresponding correlation coefficient is due to chance. For example, the correlation between suspended solids and oil and grease is 0.018, but there is a 50/50 probability (50 percent) that this correlation is due to chance; therefore, very little meaning could be attributed to the correlation coefficient. In general, the higher the probability (50 percent is maximum), the less significant the correlation coefficient.

104. The total organic carbon associated with the suspended solids (SS-TOC) was calculated by subtracting the soluble TOC value from the TOC value. The SS-Clay fraction was calculated by multiplying the suspended solids value times the percent particle size in suspension smaller than 4 μm in diameter. A stepwise regression was then performed on the data designating the PCB concentration in the supernatant as the dependent variable and the parameters of oil and grease, suspended solids, SS-TOC, and SS-Clay as independent variables. The stepwise regression procedure adds the independent variables to the equation in order of importance. Variables which do not contribute significantly to the description of the relationship are not included. The resulting regression equation containing the variables of oil and grease and suspended solids is presented in the following tabulation.

| | <u>Oil and Grease</u> | <u>Suspended Solids</u> |
|---------------------------------|-----------------------|-------------------------|
| Equation Coefficient | 0.0045 | 0.0002 |
| Partial F-ratio* | 94.3 | 16.7 |
| Partial Correlation Coefficient | 0.867 | 0.377 |
| Multiple Correlation | 0.867 | 0.939 |

* Significant at the 1% significance level.

Note: Regression Constant = 0.0033
Index of Determination = 0.882

105. The multiple regression coefficient shows that 88 percent of PCB variation was related to variations in oil and grease and suspended solids. The significance of the rejection of the other two independent variables will be discussed in a later section. A scatter diagram of actual and calculated data presented in Figure 9 graphically demonstrates the fit of the regression equation.

106. Effect of oil and grease - The work of Hartung and Klingler⁹ with sedimented oils established the oils as powerful concentrators of DDT in sediments. The regression equation substantiates this for oils in suspended sediment, indicating the oils are about 20 times more important in describing the concentration of PCBs in suspension than suspended solids alone. The most dramatic demonstration of the effect of oils on PCBs found in the supernatant is the comparison of the Houston and the Fall River settling tests. The Fall River site, which was initially lower in oils than Houston, had measurable PCBs and oils for the first 30 min of settling; whereas Houston had measurable oils and PCBs through 24 hr.

107. It should be pointed out that the oil and grease parameter includes all materials that are soluble in hexane and are not volatile at 80°C. In natural sediments this could include not only oils and greases but also waxes, soaps, sulfur, bio-fats, and lipids, all of which (except sulfur) would be excellent solvents for the nonpolar PCB molecules. Hartung and Klingler⁹ analyzed the hexane soluble extract of the bottom sediment from the Detroit River and found it to be very similar to petroleum oil. Although the hexane extractable values may define a wide variety of chemicals, they are largely nonpolar and organic in nature and would act as very powerful "accumulators" of PCBs.

108. Prior to performing the settling tests, it was expected that oil and grease values would be correlated with either suspended solids or the suspended solids-clay fraction. This was true for the Chicago and Green Bay tests. In the Fall River, Houston, and Memphis tests, however, the oil content remained relatively constant for the various settling times while the suspended solids levels decreased with time. This resulted in a poor correlation between the values for oil and suspended solids that permitted the evaluation of the relative effect of each parameter. The high probability that the correlation coefficient is due to chance, however, can be attributed to the difference between the Chicago and Green Bay test results and the results from the Fall River, Memphis, and Houston tests. The low correlation between oils and SS-TOC (0.316) indicates the contribution of non-oil organic species to the TOC values. This is interesting in light of the relatively high correlation (0.84) oils had with TOC in the five sediments used for the settling tests, pointing out the difficulty of extrapolating bulk sediment parameters to their effect on the water column after mixing.

109. Effect of suspended solids - The regression equation did not include the SS-clay and SS-TOC parameters because, as indicated by their high correlation coefficients (paragraph 101), they are very closely related to suspended solids. The term SS-Clay may be a misnomer; for as discussed earlier, these fine particles include some organic material, possibly as an organoclay complex⁷. Leland, Bruce and Shimp¹ performed a regression on the clay-size fraction of Lake Michigan bottom sediments against organic carbon and were able to demonstrate a significant relationship (correlation coefficient of 0.65). Suspended organic matter and organoclays may be expected to have a lower specific gravity than clay and a lower settling rate. Evidence of this was the increasing organic fraction of the suspended solids after longer settling times.

110. The net effect of the suspended solids term in the regression equation is that because of its high correlation to SS-TOC and SS-Clay it includes the effects of clay-sized particles and organics associated with the suspended solids. This is secondary in importance to oil and grease suspended particulates in acting as a vehicle for PCBs.

111. Effect of settling time on suspended PCB material - Table 35 shows the amount of PCB material remaining in the water column after various periods of settling. The largest decrease occurred within the first three hours of the test; thereafter the decrease was less pronounced. Both Green Bay and Memphis returned to approximately their pretest water column PCB values after 24 hr. The Green Bay tests are the only ones that had the same sediment-to-water ratio for both settling and desorption tests. After 24 hr of mixing, 0.16 $\mu\text{g PCB}/\ell$ were found in the soluble form from the desorption test, while only 0.08 $\mu\text{g}/\ell$ were found in the settling test. The rate of desorption in a natural sediment may not be instantaneous as suggested by Huang and Liao⁵ but appears to be a function of both contact time and agitation.

112. Transfer of pesticide materials to water column - The implication of the desorption and settling test results is that transfer of pesticide material from bottom sediments to the soluble portion of the water column during dredging and disposal operations is not significant. The sediment solids that remain suspended in the water column, however, may contain significant amounts of sorbed, pesticide materials. Those suspended solids characterized by high nonpolar organic hydrocarbon concentrations are about 20 times as effective in accumulating pesticides as suspended solids characterized by total organic carbon and clay concentrations. The concentration of pesticides associated with suspended solids returned to near water column background levels after 24 hr of settling under quiescent conditions.

Summary and Conclusions

113. On the basis of analyses by gas chromatography, the most prevalent pesticide material found in the sediments at five locations

sampled were polychlorinated biphenyls. Aroclor 1254 isomers were the most common PCBs found. DDT compounds and dieldrin were found in about half the sampling sites. Aldrin and 2,4-D were also found. Concentrations of toxaphene, lindane, or endrin were less than the analytical detection limits (1 µg/kg for toxaphene and 0.1 µg/kg for lindane and endrin). Concentrations of the pesticide materials were highly variable within the sediment. The high variability should be considered when planning sampling in similar areas.

114. A lack of correlation between sediment PCB concentrations and organic carbon, oil, and silt and clay content was found. This was probably the result of the lack of opportunity for some of the solids in the sediment to sorb PCB materials.

115. The concentration of pesticide materials often varied with depth within a sediment. This variation with depth did not occur for TOC at any of the dredging areas or for oil concentration at four of five dredging areas. Usually, the pesticide material concentration was highest in the upper portion of the sediment. At Memphis, however, three pesticide materials were concentrated in the middle or lower portions.

116. PCB materials were found in four of five interstitial water samples. Pesticides found in the interstitial water samples were DDT (Chicago), 2,4-D (Houston), and dieldrin (Memphis). No correlation was found between the concentration of materials in the sediment and the interstitial water pesticide material concentration. Sediments having widely different values for parameters reported to affect pesticide adsorption (organic carbon, oil, and silt and clay fraction) contained similar amounts of PCB in the interstitial water. The only correlation found was an inverse relationship between PCB and TOC content of the interstitial water.

117. Measurable amounts of pesticide material were found in the water column water from two of the five dredge areas sampled. The Green Bay sample contained 0.08 µg PCB/ℓ, and the Memphis sample contained 0.02 µg PCB/ℓ and 0.002 µg dieldrin/ℓ. These concentrations were associated with the suspended solids in the water.

118. The only chlorinated hydrocarbons found in the interfacial water samples were PCB compounds. These were found in waters from all areas except Fall River. Whether these compounds were soluble or associated with suspended solids was not determined.

119. The desorption of pesticide materials was studied by mixing sediment with water column water at several ratios. Ratios typically used ranged from 1:4 to 1:50 sediment to water (weight/weight basis). Desorption occurred only at the highest ratio of sediment to water tested. No desorption was measured at ratios of sediment to water of

1:10 or lower. At the ratios where desorption occurred, the amount desorbed was directly related to the amount of pesticide material initially present. Sediment particle size and organic content, reported by others as important variables in adsorption work, had a less important role in these desorption tests. The effect of the soluble organic carbon content of the water column water was minor. The amount of PCB material desorbed was related to the sediment oil and grease concentration by partition coefficients ranging from 0.1×10^6 to 6.1×10^6 . These ratios were not applicable at sediment-to-water ratios lower than 1:5. The sediment interstitial water contributed a negligible amount of pesticide material to the soluble portion of the dilution water.

120. Settling tests were performed on mixtures of sediment and water column water to determine the amount of pesticide materials added to the water column by resuspension of sediment solids. It was found in these tests that the amount of PCB remaining in the water column was directly proportional to the amount of oil and grease remaining in suspension and the suspended solids concentration. The role of oil and grease was about 20 times more important than the role of suspended solids. About 88 percent of the variation in PCB remaining in the water column could be associated with changes in the oil and grease and suspended solids values. The suspended solids variable includes, to some extent the effect of suspended organic matter and suspended clay. The amount of PCB material remaining in suspension decreased with increased settling times. In systems where both suspended solids and oil and grease levels decreased with time, the decrease in PCB level was rapid, with the largest reductions occurring within the first three hr of settling. In systems where the suspended solids concentration decreased with time but the oil content changed little, the decrease in PCB content was slower. In all settling tests, the amount of PCB material remaining in suspension ranged from water column background level to $0.03 \mu\text{g}/\ell$ above the background level after settling period ranging from 5 to 24 hr.

121. Based on these tests, the dredging and aquatic disposal of sediments containing pesticide materials may affect the water column in the following manner:

- a. The amount of soluble pesticide material added to the water column by dispersion of the sediment interstitial water is negligible at sediment-to-water ratios of 1:10 or less.
- b. The amount of pesticide material desorbed from resuspended sediment is negligible at sediment-to-water ratios of 1:10 or less.
- c. Pesticide materials are transferred to the water column by means of the resuspended solids. Reduction of the suspended solids concentration by settling results in a decrease in pesticide material concentration.

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Table 1. Chicago Water Sample Analysis

| Parameter | Water Column | Interfacial Water | | | | | |
|------------------------|--------------|-------------------|--------|--------|--------|--------|--------|
| | | 2-3 | 1 | 2 | 3 | 4 | 5 |
| Site | -- | 2-3 | 1 | 2 | 3 | 4 | 5 |
| Sampling date | 1/7/75 | 1/7/75 | 8/8/74 | 8/8/74 | 8/8/74 | 8/8/74 | 8/8/74 |
| pH | 7.76 | -- | 7.90 | 7.70 | 7.85 | 7.75 | 7.30 |
| Suspended solids, mg/l | 9 | 103 | 135 | 1,140 | 98 | 49 | 12,000 |
| TOC, mg/l | 9 | 7 | 12 | 14 | 8 | 6 | 260 |
| Soluble TOC, mg/l | 10 | 6 | 8 | 6 | 3 | 4 | 6 |
| PCB, µg/l** | <0.02 | 0.08* | <1 | <1 | <1 | <1 | <1 |
| Aldrin, µg/l† | <0.002 | <0.002 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Dieldrin, µg/l† | <0.002 | <0.002 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Endrin, µg/l† | <0.002 | <0.002 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Lindane, µg/l† | <0.002 | <0.002 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| t-DDT, µg/l† | <0.002 | <0.002 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| 2,4-D, µg/l** | <0.02 | <0.02 | <1 | <1 | <1 | <1 | <1 |
| Toxaphene, µg/l** | <0.02 | <0.02 | <1 | <1 | <1 | <1 | <1 |

* Aroclor 1254

** detection limit 0.02 µg/l

† detection limit 0.002 µg/l

Table 2. Chicago Sediment Characteristics

| Sample Site | Depth Sampled m | Core Length m | Core Segment | Density g/cc | Particle-Size Analysis | | | |
|-----------------------|--------------------|------------------|--------------|-----------------|------------------------|---------------|------|-------------|
| | | | | | Median Diameter mm | Grain Size, % | | |
| | | | | | | Gravel | Sand | Silt & Clay |
| 1 | 0.30 | 0.20 | Top | 1.49 | 0.049 | 0 | 36 | 64 |
| | | | 2nd | - | - | - | - | - |
| | | | 3rd | - | - | - | - | - |
| | | | Bottom | - | - | - | - | - |
| 2 | 1.22 | 0.68 | Top | 1.47 | <0.044 | 0 | 28 | 72 |
| | | | 2nd | 1.45 | <0.044 | 0 | 28 | 72 |
| | | | 3rd | 1.70 | <0.044 | 0 | 24 | 76 |
| | | | Bottom | 1.63 | <0.044 | 0 | 24 | 76 |
| 3 | 1.83 | 0.79 | Top | 1.42 | <0.044 | 0 | 17 | 83 |
| | | | 2nd | 1.34 | <0.044 | 0 | 9 | 91 |
| | | | 3rd | 1.44 | <0.044 | 0 | 12 | 88 |
| | | | Bottom | 1.46 | <0.044 | 0 | 24 | 76 |
| 4 | 1.02 | 0.41 | Top | 1.80 | 0.086 | 2 | 58 | 40 |
| | | | 2nd | 1.81 | 0.062 | 0 | 50 | 50 |
| | | | 3rd | 2.14 | 0.066 | 3 | 49 | 48 |
| | | | Bottom | 1.94 | 0.064 | 2 | 49 | 49 |
| 5 | 0.91 | 0.61 | Top | 1.53 | <0.044 | 0 | 22 | 78 |
| | | | 2nd | 1.40 | <0.044 | 0 | 22 | 78 |
| | | | 3rd | 1.38 | 0.062 | 0 | 50 | 50 |
| | | | Bottom | 1.90 | 0.054 | 0 | 30 | 70 |
| Migration Test Sample | -- | -- | -- | 1.40 | 0.032 | 0 | 33 | 67 |

Table 3. Chicago Sediment Analyses

| Sample Site | Core Segment | Total Solids, % | TOC mg/kg | Oil mg/kg | PCB* µg/l | t-DDT µg/kg | Dieldrin µg/kg |
|-----------------------|--------------|-----------------|-----------|-----------|-----------|-------------|----------------|
| 1 | Top | 52.9 | 8,490 | 1,840 | 186 | <0.2 | <0.2 |
| | 2nd | -- | -- | -- | -- | -- | -- |
| | 3rd | -- | -- | -- | -- | -- | -- |
| | Bottom | -- | -- | -- | -- | -- | -- |
| 2 | Top | 52.2 | 15,700 | 2,360 | 306 | 1.0 | <0.2 |
| | 2nd | 51.3 | 15,600 | 4,010 | 334 | <0.2 | <0.2 |
| | 3rd | 56.2 | 18,700 | 2,400 | 33 | <0.2 | <0.2 |
| | Bottom | 67.2 | 18,900 | 2,370 | 27 | <0.2 | <0.2 |
| 3 | Top | 50.2 | 17,400 | 1,090 | 280 | <0.2 | 2.6 |
| | 2nd | 45.3 | 25,100 | 3,110 | 88 | <0.2 | <0.2 |
| | 3rd | 48.3 | 29,800 | 3,490 | 52 | <0.2 | <0.2 |
| | Bottom | 46.4 | 26,500 | 5,410 | 4 | <0.2 | <0.2 |
| 4 | Top | 72.3 | 4,710 | 541 | 82 | <0.2 | <0.2 |
| | 2nd | 71.3 | 6,450 | 1,200 | 50 | <0.2 | <0.2 |
| | 3rd | 78.9 | 5,580 | 329 | <1 | <0.2 | <0.2 |
| | Bottom | 82.0 | 9,280 | 549 | 7 | <0.2 | <0.2 |
| 5 | Top | 44.4 | 22,600 | 2,760 | 296 | 0.9 | <0.2 |
| | 2nd | 46.2 | 30,200 | 3,050 | 871 | 1.7 | <0.2 |
| | 3rd | 64.4 | 12,000 | 1,580 | 344 | 3.8 | <0.2 |
| | Bottom | 76.6 | 7,640 | 2,040 | 24 | <0.2 | <0.2 |
| Migration Test Sample | -- | 48.5 | 25,200 | 5,400 | 223 | 7.4** | <0.1 |

Note: mg/kg and µg/kg units are in terms of dry solids

* As Aroclor 1254

** 4.7 µg/kg p,p'-DDE
 1.5 µg/kg p,p'-DDD
 1.2 µg/kg p,p'-DDT

Table 4. Green Bay Water Sample Analyses

| Parameter | Water Column | Interfacial Water | | | | | |
|-----------------------|--------------|-------------------|--------|--------|--------|--------|--------|
| | | 4-5 | 1 | 2 | 3 | 4 | 5 |
| Site | -- | 4-5 | 1 | 2 | 3 | 4 | 5 |
| Sampling date | 1/18/75 | 4/8/75 | 9/9/74 | 9/9/74 | 9/9/74 | 9/9/74 | 9/9/74 |
| pH | | | | | | | |
| Suspended solids mg/l | 52 | 43 | 45 | 42 | 45 | 37 | 67 |
| TOC, mg/l | 26 | 17 | 24 | 25 | 25 | 26 | 26 |
| Soluble TOC, mg/l | 16 | 15 | -- | 25 | 24 | 27 | 23 |
| Oil and grease, mg/l | 25 | -- | -- | -- | -- | -- | -- |
| PCB, µg/l, total* | 0.08 | 0.09 | <1 | <1 | <1 | <1 | <1 |
| Aroclor #1242, µg/l | 0.04 | 0.01 | <1 | <1 | <1 | <1 | <1 |
| Aroclor #1254, µg/l | 0.04 | 0.08 | <1 | <1 | <1 | <1 | <1 |
| Soluble PCB, µg/l* | <0.02 | -- | -- | -- | -- | -- | -- |
| Aldrin, µg/l** | <0.002 | <0.002 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Dieldrin, µg/l** | 0.004 | <0.002 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Endrin, µg/l** | <0.002 | <0.002 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Lindane, µg/l** | <0.002 | <0.002 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| t-DDT, µg/l** | <0.002 | <0.002 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| 2,4-D, µg/l** | <0.02 | <0.02 | <1 | <1 | <1 | <1 | <1 |
| Toxaphene, µg/l* | <0.02 | <0.02 | <1 | <1 | <1 | <1 | <1 |

* detection limit 0.02 µg/l

** detection limit 0.002 µg/l

Table 5. Green Bay Sediment Characteristics

| Sample Site | Depth Sampled m | Core Length m | Core Segment | Density g/cc | Particle-Size Analysis | | | |
|----------------------------|--------------------|------------------|--------------|-----------------|------------------------|---------------|------|----------------|
| | | | | | Median Diameter m | Grain Size, % | | |
| | | | | | | Gravel | Sand | Silt % Clay |
| 1 | 0.30 | 0.28 | Top | 1.90 | 0.070 | 0 | 63 | 37 |
| | | | Bottom | 1.63 | 0.051 | 0 | 41 | 59 |
| 2 | 0.30 | 0.30 | Top | 1.80 | 0.089 | 0 | 75 | 25 |
| | | | Bottom | 1.92 | 0.184 | 0 | 94 | 6 |
| 3 | 0.30 | 0.25 | Top | 1.93 | 0.113 | 0 | 96 | 4 |
| | | | Bottom | 1.86 | 0.117 | 0 | 98 | 2 |
| 4 | 0.30 | 0.30 | Top | 1.99 | 0.140 | 0 | 98 | 2 |
| | | | Bottom | 1.94 | 0.116 | 0 | 96 | 4 |
| 5 | 0.38 | 0.25 | Top | 1.85 | 0.110 | 0 | 95 | 5 |
| | | | Bottom | 1.90 | 0.110 | 0 | 97 | 3 |
| Migration Test Sample-- | -- | -- | -- | 1.87 | 0.100 | 0 | 96 | 4 |

Table 6. Green Bay Sediment Analysis

| Sample Site | Core Segment | Total Solids, % | TOC mg/kg | Oil mg/kg | t-DDT* $\mu\text{g/kg}$ | PCB, $\mu\text{g/kg}$ | | |
|--------------------------|--------------|-----------------|-----------|-----------|-------------------------|-----------------------|-------|-------|
| | | | | | | Total | #1242 | #1254 |
| 1 | Top | 78.5 | 1,650 | 136 | 0.2 | 33 | 33 | <1 |
| | Bottom | 46.5 | 17,600 | 740 | <0.1 | 6 | <1 | 6 |
| 2 | Top | 76.5 | 3,790 | 380 | <0.1 | 96 | 96 | <1 |
| | Bottom | 83.9 | 1,440 | 390 | <0.1 | <1 | <1 | <1 |
| 3 | Top | 77.5 | 1,920 | 260 | <0.1 | 301 | 242 | 59 |
| | Bottom | 80.0 | 1,240 | 250 | <0.1 | 12 | 12 | <1 |
| 4 | Top | 81.8 | 670 | 96 | <0.1 | 18 | 14 | 4 |
| | Bottom | 82.0 | 610 | 240 | <0.1 | 6 | 6 | <1 |
| 5 | Top | 76.3 | 1,950 | 850 | <0.1 | 517 | 517 | <1 |
| | Bottom | 79.9 | 1,770 | 630 | <0.1 | 163 | 150 | 13 |
| Migration Test Sample -- | | 77.9 | 159 | 233 | <0.1 | 184 | 177 | 7 |

Note: mg/kg and $\mu\text{g/kg}$ values are in terms of dry solids.

* o,p - DDE

Table 7. Fall River Water Sample Analyses

| Parameter | Water Column | Interfacial Water | | | | | |
|------------------------|--------------|-------------------|---------|---------|---------|---------|---------|
| | | 4 | 1 | 2 | 3 | 4 | 5 |
| Site | -- | 4 | 1 | 2 | 3 | 4 | 5 |
| Sampling date | 1/9/75 | 1/9/75 | 10/7/74 | 10/7/74 | 10/7/74 | 10/7/74 | 10/7/74 |
| pH | 7.60 | -- | 7.45 | 7.45 | 7.40 | 7.45 | 7.40 |
| Suspended solids, mg/l | 60 | 543 | 52 | 98 | 295 | 119 | 107 |
| TOC, mg/l | 11 | 10 | 9 | 12 | 12 | 9 | 6 |
| Soluble TOC, mg/l | 11 | 11 | 9 | 12 | 11 | 9 | 6 |
| PCB, µg/l* | <0.02 | <0.02 | <1 | <1 | <1 | <1 | <1 |
| Aldrin, µg/l ** | <0.002 | <0.002 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Dieldrin, µg/l ** | <0.002 | <0.002 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Endrin, µg/l** | <0.002 | <0.002 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Lindane, µg/l** | <0.002 | <0.002 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| t-DDT, µg/l** | <0.002 | <0.002 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| 2,4-D, µg/l* | <0.02 | <0.02 | <1 | <1 | <1 | <1 | <1 |
| Toxaphene, µg/l* | <0.02 | <0.02 | <1 | <1 | <1 | <1 | <1 |

* detection limit 0.02 µg/l

** detection limit 0.002 µg/l

Table 8. Fall River Sediment Characteristics

| Sample Site | Depth Sampled m | Core Length m | Core Segment | Density g/cc | Particle-Size Analysis | | | |
|-----------------------|--------------------|------------------|--------------|-----------------|------------------------|---------------|------|----------------|
| | | | | | Median Diameter mm | Grain Size, % | | |
| | | | | | | Gravel | Sand | Silt % Clay |
| 1 | 0.3 | 0.3 | Top | 1.87 | 0.135 | 0 | 61 | 39 |
| | | | 2nd | - | - | - | - | - |
| | | | 3rd | - | - | - | - | - |
| | | | Bottom | - | - | - | - | - |
| 2 | 0.3 | 0.3 | Top | 1.57 | 0.068 | 0 | 51 | 49 |
| | | | 2nd | 1.85 | 0.205 | 0 | 82 | 18 |
| | | | 3rd | - | - | - | - | - |
| | | | Bottom | - | - | - | - | - |
| 3 | 0.3 | 0.3 | Top | 1.64 | <0.044 | 0 | 31 | 69 |
| | | | 2nd | 1.77 | 0.204 | 0 | 75 | 25 |
| | | | 3rd | - | - | - | - | - |
| | | | Bottom | - | - | - | - | - |
| 4 | 0.8 | 0.8 | Top | 1.58 | 0.102 | 0 | 60 | 40 |
| | | | 2nd | 1.54 | 0.075 | 0 | 54 | 46 |
| | | | 3rd | 1.59 | 0.102 | 0 | 59 | 41 |
| | | | Bottom | - | - | - | - | - |
| 5 | 1.1 | 0.4 | Top | 1.57 | 0.125 | 2 | 65 | 33 |
| | | | 2nd | 1.72 | 0.280 | 12 | 70 | 18 |
| | | | 3rd | 1.63 | 0.125 | 0 | 63 | 37 |
| | | | Bottom | 1.62 | 0.157 | 5 | 64 | 31 |
| Migration Test Sample | - | - | - | 1.65 | 0.215 | <1 | 73 | 27 |

Table 9. Fall River Sediment Analyses

| Sample Site | Core Segment | Total Solids, % | TOC mg/kg | Oil mg/kg | PCB* ² µg/kg | Dieldrin µg/kg | Aldrin µg/kg | t-DDT µg/kg |
|-----------------------|--------------|-----------------|-----------|-----------|-------------------------|----------------|--------------|-------------|
| 1 | Top | 74.6 | 7,030 | 362 | <1 | 0.7 | <0.1 | <0.1 |
| | 2nd | -- | -- | -- | -- | -- | -- | -- |
| | 3rd | -- | -- | -- | -- | -- | -- | -- |
| | Bottom | -- | -- | -- | -- | -- | -- | -- |
| 2 | Top | 62.4 | 12,900 | 1,260 | 25 | 2.8 | <0.1 | <0.1 |
| | 2nd | 62.6 | 11,800 | 431 | 25 | 1.5 | <0.1 | <0.1 |
| | 3rd | -- | -- | -- | -- | -- | -- | -- |
| | Bottom | -- | -- | -- | -- | -- | -- | -- |
| 3 | Top | 63.0 | 9,900 | 458 | 13 | 1.1 | <0.1 | <0.1 |
| | 2nd | 58.1 | 14,100 | 480 | <1 | 0.5 | <0.1 | <0.1 |
| | 3rd | -- | -- | -- | -- | -- | -- | -- |
| | Bottom | -- | -- | -- | -- | -- | -- | -- |
| 4 | Top | 62.1 | 12,100 | 845 | 33 | 49 | 13.7 | 31.0 |
| | 2nd | 61.6 | 12,100 | 324 | 24 | 0.7 | 1.5 | 3.9 |
| | 3rd | 60.4 | 12,100 | 233 | 4 | 0.1 | 5.8 | <0.1 |
| | Bottom | -- | -- | -- | -- | -- | -- | -- |
| 5 | Top | 62.4 | 7,800 | 1,570 | 19 | 2.9 | 0.9 | <0.1 |
| | 2nd | 61.3 | 12,100 | 357 | 4 | <0.1 | 0.7 | <0.1 |
| | 3rd | 58.6 | 9,500 | 1,450 | 2 | <0.1 | 0.3 | <0.1 |
| | Bottom | 57.7 | 12,400 | 407 | 1 | <0.1 | 0.1 | <0.1 |
| Migration Test Sample | | 58.4 | 13,710 | 344 | 12.5 | <0.1 | <0.1 | <0.1 |

* Aroclor 1254

Note: mg/kg and µg/kg values are in terms of dry solids.

Table 10. Houston Water Samples Analyses

| Parameter | Water Column | Interfacial Water | | | | |
|------------------------|--------------|-------------------|---------|---------|---------|---------|
| | | 1 | 2 | 3 | 4 | 5 |
| Site | -- | 1 | 2 | 3 | 4 | 5 |
| Sampling date | 1/30/75 | 1/30/75 | 1/30/75 | 1/30/75 | 1/30/75 | 1/30/75 |
| pH | 7.50 | 7.15 | 7.05 | 7.35 | 7.10 | 7.30 |
| Suspended solids, mg/l | 41 | 42 | 238 | 117 | 64 | 79 |
| TOC, mg/l | 11 | 9 | 16 | 16 | 10 | 17 |
| Soluble TOC, mg/l | 7 | 7 | 8 | 10 | 7 | 9 |
| Oil and grease, mg/l | <1 | - | - | - | - | - |
| PCB, µg/l*,** | <0.02 | 0.04 | 0.04 | <0.02 | <0.02 | <0.02 |
| Aldrin, µg/l† | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| Dieldrin, µg/l† | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| Endrin, µg/l† | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| Lindane, µg/l† | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| t-DDT, µg/l† | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| 2,4-D, µg/l*** | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Toxaphene, µg/l*** | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |

* Aroclor 1254

** Detection limit 0.02 µg/l

† Detection limit 0.002 µg/l

Table 11. Houston Sediment Characteristics

| Sample Site | Depth Sampled m | Core Length m | Core Segment | Density g/cc | Particle-Size Analysis | | | |
|----------------------------|--------------------|------------------|--------------|-----------------|------------------------|---------------|------|----------------|
| | | | | | Median Diameter mm | Grain Size, % | | |
| | | | | | | Gravel | Sand | Silt % Clay |
| 1 | 1.22 | 0.51 | Top | 1.38 | 0.142 | 0 | 69 | 31 |
| | | | Bottom | 1.37 | 0.102 | 0 | 62 | 38 |
| 2 | 1.22 | 0.55 | Top | 1.38 | 0.117 | 0 | 68 | 32 |
| | | | Bottom | 1.54 | 0.087 | 0 | 64 | 36 |
| 3 | 1.22 | 0.61 | Top | 1.45 | 0.075 | 0 | 55 | 45 |
| | | | Bottom | 1.51 | 0.094 | 0 | 58 | 42 |
| 4 | 0.96 | 0.61 | Top | 1.28 | 0.074 | 0 | 57 | 43 |
| | | | Bottom | 1.35 | 0.086 | 0 | 58 | 42 |
| 5 | 0.96 | 0.66 | Top | 1.35 | 0.074 | 0 | 53 | 47 |
| | | | Bottom | 1.40 | 0.064 | 0 | 51 | 49 |
| Migration Test Sample-- | -- | -- | -- | 1.37 | 0.125 | 0 | 72 | 28 |

Table 12. Houston Sediment Analysis

| Sample Site | Core Segment | Total Solids, % | TOC mg/kg | Oil mg/kg | PCB* µg/kg | 2,4-D µg/kg | t,-DDT µg/kg | Dieldrin µg/kg |
|-------------|--------------|-----------------|-----------|-----------|------------|-------------|--------------|----------------|
| 1 | Top | 44.2 | 9,280 | 113 | 16.6 | <1 | <0.1 | <0.1 |
| | Bottom | 42.2 | 8,780 | 356 | 0.5 | <1 | <0.1 | <0.1 |
| 2 | Top | 46.3 | 7,720 | 690 | 4.0 | <1 | <0.1 | <0.1 |
| | Bottom | 45.9 | 8,330 | 1,470 | 0.9 | <1 | <0.1 | <0.1 |
| 3 | Top | 47.4 | 7,200 | 506 | 10.5 | <1 | <0.1 | <0.1 |
| | Bottom | 43.1 | 16,700 | 3,220 | 15.0 | <1 | <0.1 | <0.1 |
| 4 | Top | 38.4 | 8,100 | 495 | 19.6 | 37 | 1.3 | 0.5 |
| | Bottom | 49.4 | 9,720 | 3,030 | 1.6 | 58 | 0.7 | 2.4 |
| 5 | Top | 40.0 | 12,800 | 750 | 12.9 | 28 | 1.3 | 7.8 |
| | Bottom | 43.3 | 14,200 | 1,960 | 7.9 | 30 | 1.0 | 4.0 |
| Composite | -- | 45.6 | 9,200 | 1,555 | 12.0 | 1.3 | <0.1 | 0.2 |

Note: mg/kg and µg/kg units are in terms of dry solids.

* Aroclor 1254

Table 13. Memphis Water Sample Analyses

| Parameter | Water Column | Interfacial Water | | | | |
|-------------------------|--------------|-------------------|---------|---------|---------|---------|
| | | 1 | 2 | 3 | 4 | 5 |
| Site | -- | 1 | 2 | 3 | 4 | 5 |
| Sample date | 2/11/75 | 2/11/75 | 2/11/75 | 2/11/75 | 2/11/75 | 2/11/75 |
| pH | 7.55 | 7.15 | 7.60 | 6.95 | 6.90 | 6.70 |
| Suspended solids, mg/l | 59 | 69 | 54 | 70 | 115 | 55 |
| TOC, mg/l | 15 | 7 | 8 | 43 | 27 | 15 |
| Soluble TOC, mg/l | 11 | 7 | 9 | 26 | 20 | 14 |
| Oil and grease, mg/l | 1 | -- | -- | -- | -- | -- |
| PCB, µg/l *, ** | <0.02 | <0.02 | 0.02 | 0.02 | <0.02 | <0.02 |
| Soluble PCB, µg/l** | <0.02 | -- | -- | -- | -- | -- |
| Aldrin, µg/l† | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| Dieldrin, µg/l† | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| Soluble Dieldrin, µg/l† | <0.002 | -- | -- | -- | -- | -- |
| Endrin, µg/l† | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| Lindane, µg/l† | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| t-DDT, µg/l† | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| 2,4-D, µg/l** | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Toxaphene, µg/l** | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |

* Aroclor #1254

** Detection limits 0.02 µg/l

† Detection limits 0.002 µg/l

Table 14. Memphis Sediment Characteristics

| Sample Site | Depth Sampled m | Core Length m | Core Segment | Density g/cc | Particle-Size Analysis | | | |
|-------------|--------------------|------------------|--------------|-----------------|------------------------|---------------|------|----------------|
| | | | | | Median Diameter mm | Grain Size, % | | |
| | | | | | | Gravel | Sand | Silt % Clay |
| 1 | -- | 0.71 | Top | 1.48 | <0.044 | 0 | 29 | 71 |
| | | | 2nd | 1.52 | <0.044 | 0 | 28 | 72 |
| | | | Bottom | 1.54 | 0.046 | 0 | 36 | 64 |
| 2 | -- | 0.71 | Top | 1.54 | <0.044 | 0 | 38 | 62 |
| | | | 2nd | 1.53 | 0.080 | 0 | 54 | 46 |
| | | | Bottom | 1.63 | 0.054 | 0 | 45 | 55 |
| 3 | -- | 0.71 | Top | 1.43 | <0.044 | 0 | 38 | 62 |
| | | | 2nd | 1.49 | <0.044 | 0 | 33 | 67 |
| | | | Bottom | 1.55 | <0.044 | 0 | 39 | 71 |
| 4 | -- | 0.71 | Top | 1.39 | 0.080 | 0 | 55 | 45 |
| | | | 2nd | 1.51 | 0.096 | 0 | 73 | 27 |
| | | | Bottom | 1.54 | 0.190 | 0 | 73 | 27 |
| 5 | -- | 0.71 | Top | 1.40 | 0.076 | 0 | 55 | 45 |
| | | | 2nd | 1.46 | <0.044 | 0 | 52 | 48 |
| | | | Bottom | 1.42 | 0.072 | 0 | 35 | 65 |
| Composite | -- | -- | -- | 1.43 | 0.070 | 0 | 53 | 47 |

Table 15. Memphis-Mississippi River Sediment Analyses

| Sample Site | Core Segment | Total Solids, % | TOC mg/kg | Oil mg/kg | PCB* µg/kg | t-DDT µg/kg | Dieldrin µg/kg |
|--------------------------|--------------|-----------------|-----------|-----------|------------|-------------|----------------|
| 1 | Top | 49.7 | 13,600 | 291 | 86 | 15 | 17 |
| | 2nd | 55.9 | 12,600 | 240 | 227 | 18 | 5 |
| | Bottom | 57.6 | 9,810 | 171 | 148 | 12 | 2 |
| 2 | Top | 46.4 | 10,500 | 642 | 36 | 5.1 | 7.0 |
| | 2nd | 59.2 | 11,000 | 568 | 61 | 8.5 | 3.0 |
| | Bottom | 55.9 | 9,600 | 644 | 86 | 8.9 | <0.1 |
| 3 | Top | 54.6 | 12,800 | 581 | 88 | 4.6 | 3 |
| | 2nd | 55.2 | 10,600 | 671 | 145 | 10.9 | 1.8 |
| | Bottom | 53.8 | 13,200 | 768 | 187 | 12.0 | 0.8 |
| 4 | Top | 50.6 | 13,800 | 365 | 26 | 15.8 | 3.0 |
| | 2nd | 56.2 | 11,200 | 467 | 73 | 27.3 | 1.2 |
| | Bottom | 69.6 | 6,500 | 575 | 51 | 6.9 | 0.5 |
| 5 | Top | 43.4 | 18,000 | 1,020 | 164 | 15.6 | 4.8 |
| | 2nd | 50.7 | 16,400 | 310 | 130 | 24.5 | 3.8 |
| | Bottom | 49.0 | 20,500 | 780 | 198 | 17.7 | 4.6 |
| Migration Test Sample -- | | 49.6 | 9,300 | 329 | 78 | 5.1 | 3.9 |

Note: mg/kg and µg/kg units are in terms of dry solids

* Aroclor 1254

Table 16. Characteristics of Migration Test Sediments
and Interstitial Water

| | <u>Chicago</u> | <u>Green Bay</u> | <u>Fall River</u> | <u>Houston</u> | <u>Memphis</u> |
|----------------------------|----------------|------------------|-------------------|----------------|----------------|
| ORP, mv | 0 | -234 | +65 | -151 | -48 |
| Density, g/cc | 1.40 | 1.87 | 1.65 | 1.37 | 1.43 |
| Total solids, % | 48.5 | 77.9 | 58.4 | 45.6 | 49.6 |
| Total volatile solids, % | 2.1 | 0.5 | 1.0 | 2.3 | 2.8 |
| TOC, mg/kg | 25,200 | 159 | 13,700 | 9,200 | 9,300 |
| Oil and grease, mg/kg | 5,400 | 233 | 344 | 1,555 | 329 |
| PCB, µg/kg | 223* | 184** | 12.5* | 12* | 78* |
| 2,4-D, µg/kg | <1 | <1 | <1 | 1.3 | <1 |
| Toxaphene, µg/kg | <10 | <10 | <10 | <10 | <10 |
| t-DDT, µg/kg | 7.4 | <0.1 | <0.1 | <0.1 | 5.1 |
| Aldrin, µg/kg | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Dieldrin, µg/kg | <0.1 | <0.1 | <0.1 | 0.20 | 3.9 |
| Endrin, µg/kg | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Lindane, µg/kg | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| <u>Particle-Size Data:</u> | | | | | |
| Median diameter, mm | 0.032 | 0.100 | 0.215 | 0.125 | 0.070 |
| % Gravel | 0 | 0 | <1 | 0 | 0 |
| % Sand | 33 | 96 | 73 | 72 | 53 |
| % Silt and clay | 67 | 4 | 27 | 28 | 47 |
| <u>Interstitial Water:</u> | | | | | |
| TOC, mg/l | 25 | 16 | 22 | 38 | 90 |
| PCB, µg/l | 0.13 | 0.13 | 0.15 | 0.08 | <0.02 |
| 2,4-D, µg/l | <0.02 | <0.02 | <0.02 | 0.02 | <0.02 |
| Toxaphene, µg/l | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| t-DDT, µg/l | 0.151 | <0.002 | <0.002 | <0.002 | <0.002 |
| Aldrin, µg/l | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| Dieldrin, µg/l | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| Endrin, µg/l | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| Lindane, µg/l | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |

Note: mg/kg and g/kg values are in terms of dry solids.

* Aroclor 1254

** 177 µg/kg Aroclor 1242
7 µg/kg Aroclor 1254

Table 17. Chicago Equilibrium Test
Conditions and Results

Sediment Characteristics:

| | |
|----------------------------------|--------|
| Total solids, % by wt | 48.5 |
| Total volatile solids, % by wt | 2.1 |
| Specific gravity, g/cc | 1.4 |
| TOC, mg/kg dry solids | 25,200 |
| Oil and grease, mg/kg dry solids | 5,400 |
| PCB, µg/kg dry solids | 233 |
| t-DDT, µg/kg dry solids | 7.4 |

Sediment Interstitial Water Characteristics:

| | |
|-------------|-------|
| TOC, mg/l | 25 |
| PCB, µg/l | 0.13 |
| t-DDT, µg/l | 0.151 |

Water Column Water Characteristics:

| | |
|------------------------|--------|
| Suspended solids, mg/l | 9 |
| TOC, mg/l | 9 |
| Soluble TOC, mg/l | 9 |
| PCB, µg/l | <0.02 |
| t-DDT, µg/l | <0.002 |

Ratio Wet Sediment/Water:

1:5 1:15 1:50

Concentration of Solubles

After 24 hr:

| | | | |
|-----------------------|--------|--------|--------|
| TOC, mg/l | 51 | 33 | 6 |
| PCB, µg/l | 0.15 | <0.02 | <0.02 |
| t-DDT, µg/l | <0.002 | <0.002 | <0.002 |
| Aldrin-dieldrin, µg/l | <0.002 | <0.002 | <0.002 |
| Endrin, µg/l | <0.002 | <0.002 | <0.002 |
| Lindane, µg/l | <0.002 | <0.002 | <0.002 |
| 2,4-D (esters), µg/l | <0.02 | <0.02 | <0.02 |
| Toxaphene, µg/l | <0.02 | <0.02 | <0.02 |

Table 18. Chicago Equilibrium Test Evaluation

| Ratio - Sediment/Water | 1:5 | 1:15 | 1:50 |
|-------------------------------|------------------|------------------|------------------|
| Initial Concentrations | | | |
| Grams wet sediment/ℓ | <u>175</u> | <u>64</u> | <u>20</u> |
| Grams dry sediment/ℓ | <u>85</u> | <u>31</u> | <u>10</u> |
| ml interstitial water/ℓ | <u>90</u> | <u>33</u> | <u>10</u> |
| ml dilution water/ℓ | <u>894</u> | <u>955</u> | <u>986</u> |
| TOC Values, mg/ℓ | | | |
| Due to sediment solids | <u>2,142</u> | <u>781</u> | <u>252</u> |
| Due to dilution water | <u>8</u> | <u>9</u> | <u>9</u> |
| Total TOC | <u>2,150</u> | <u>790</u> | <u>261</u> |
| Soluble TOC, mg/ℓ | | | |
| Due to interstitial water | <u>2</u> | <u>1</u> | <u><1</u> |
| Due to dilution water | <u>8</u> | <u>9</u> | <u>9</u> |
| Total soluble TOC | <u>10</u> | <u>10</u> | <u>9</u> |
| TOC after mixing 24 hr | <u>51</u> | <u>33</u> | <u>6</u> |
| TOC desorbed | <u>41</u> | <u>23</u> | <u>-3</u> |
| Total PCB, μg/ℓ | | | |
| Due to sediment solids | <u>19.81</u> | <u>7.22</u> | <u>2.33</u> |
| Due to dilution water | <u><0.02</u> | <u><0.02</u> | <u><0.02</u> |
| Total PCB's | <u>19.81</u> | <u>7.22</u> | <u>2.33</u> |
| Soluble PCB, μg/ℓ | | | |
| Due to interstitial water | <u><0.02</u> | <u><0.02</u> | <u><0.02</u> |
| Due to dilution water | <u><0.02</u> | <u><0.02</u> | <u><0.02</u> |
| Total initial soluble PCB's | <u><0.02</u> | <u><0.02</u> | <u><0.02</u> |
| After mixing soluble PCB's | <u>0.15</u> | <u><0.02</u> | <u><0.02</u> |
| PCB's desorbed | <u>0.15</u> | <u><0.02</u> | <u><0.02</u> |
| Total DDT, μg/ℓ | | | |
| Due to sediment solids | <u>0.629</u> | <u>0.229</u> | <u>0.074</u> |
| Due dilution water | <u><0.002</u> | <u><0.002</u> | <u><0.002</u> |
| Total DDT | <u>0.629</u> | <u>0.229</u> | <u>0.074</u> |
| Soluble t-DDT | | | |
| Due to interstitial water | <u>0.014</u> | <u>0.005</u> | <u>0.001</u> |
| Due to dilution water | <u><0.002</u> | <u><0.002</u> | <u><0.002</u> |
| Total initial soluble t-DDT | <u>0.014</u> | <u>0.005</u> | <u>0.001</u> |
| After mixing t-DDT | <u><0.002</u> | <u><0.002</u> | <u><0.002</u> |
| t-DDT desorbed | <u>---</u> | <u>---</u> | <u>---</u> |

Underlined numbers are calculated values.

Table 20. Green Bay Equilibrium Test
Conditions and Results

Sediment Characteristics:

| | |
|----------------------------------|------|
| Total solids, % by wt | 77.9 |
| Total volatile solids, % by wt | 0.5 |
| Specific gravity, g/cc | 1.87 |
| TOC, mg/kg, dry solids | 159 |
| Oil and grease, mg/kg dry solids | 233 |
| Total PCB, µg/kg dry solids | 184 |
| PCB (Aroclor #1242) | 177 |
| PCB (Aroclor #1254) | 7 |

Sediment Interstitial Water Characteristics:

| | |
|---------------------|------|
| TOC mg/ℓ | 25 |
| Total PCB's, µg/ℓ | 0.13 |
| PCB (Aroclor #1242) | 0.05 |
| PCB (Aroclor #1254) | 0.08 |

Water Column Characteristics:

| | |
|------------------------|--------|
| Suspended solids, mg/ℓ | 52 |
| TOC, mg/ℓ | 26 |
| Soluble TOC, mg/ℓ | 16 |
| Oil and grease, mg/ℓ | 25 |
| Total PCB's, µg/ℓ | 0.08 |
| PCB (Aroclor #1242) | 0.04 |
| PCB (Aroclor #1254) | 0.04 |
| Soluble PCB µg/ℓ | <0.02 |
| Total Dieldrin µg/ℓ | 0.004 |
| Soluble Dieldrin µg/ℓ | <0.002 |

| | | | |
|---------------------------|-----|------|------|
| Ratio Wet Sediment/Water: | 1:4 | 1:10 | 1:30 |
|---------------------------|-----|------|------|

Concentration of Solubles

After 24 hr:

| | | | |
|-----------------------|--------|--------|--------|
| TOC mg/ℓ | 19 | 17 | 22 |
| Total PCB, µg/ℓ | 0.16 | <0.02 | <0.02 |
| PCB (Aroclor #1242) | 0.02 | <0.02 | <0.02 |
| PCB (Aroclor #1254) | 0.14 | <0.02 | <0.02 |
| t-DDT, µg/ℓ | <0.002 | <0.002 | <0.002 |
| Aldrin-dieldrin, µg/ℓ | <0.002 | <0.002 | <0.002 |
| Endrin, µg/ℓ | <0.002 | <0.002 | <0.002 |
| Lindane, µg/ℓ | <0.002 | <0.002 | <0.002 |
| 2,4-D (esters), µg/ℓ | <0.02 | <0.02 | <0.02 |
| Toxaphene, µg/ℓ | <0.02 | <0.02 | <0.02 |

Table 21. Green Bay Equilibrium Test Evaluation

| Ratio - Sediment/Water | 1:4 | 1:10 | 1:30 |
|--------------------------------|-----------------|-----------------|-----------------|
| Initial Concentrations | | | |
| Grams wet sediment/ℓ | <u>220</u> | <u>95</u> | <u>33</u> |
| Grams dry sediment/ℓ | <u>172</u> | <u>74</u> | <u>26</u> |
| ml interstitial/ℓ | <u>48</u> | <u>21</u> | <u>7</u> |
| ml dilution water/ℓ | <u>882</u> | <u>949</u> | <u>982</u> |
| TOC Values, mg/ℓ | | | |
| Due to sediment solids | <u>27</u> | <u>12</u> | <u>4</u> |
| Due to dilution water | <u>23</u> | <u>25</u> | <u>26</u> |
| Total TOC | <u>50</u> | <u>37</u> | <u>30</u> |
| Soluble TOC Values mg/ℓ | | | |
| Due to interstitial water | <u>1.2</u> | <u>0.5</u> | <u>0.2</u> |
| Due to dilution water | <u>14.1</u> | <u>15.2</u> | <u>15.7</u> |
| Total soluble TOC | <u>15.3</u> | <u>15.7</u> | <u>15.9</u> |
| TOC after mixing 24 hr | <u>19</u> | <u>17</u> | <u>22</u> |
| TOC desorbed | <u>3.7</u> | <u>1.3</u> | <u>6.1</u> |
| Total PCB, µg/ℓ | | | |
| Due to sediment solids (total) | <u>31.65</u> | <u>13.62</u> | <u>4.78</u> |
| (Aroclor #1242) | <u>30.45</u> | <u>13.10</u> | <u>4.60</u> |
| (Aroclor #1254) | <u>1.20</u> | <u>0.52</u> | <u>0.18</u> |
| Due to dilution water (total) | <u>0.07</u> | <u>0.08</u> | <u>0.08</u> |
| (Aroclor #1242) | <u>0.035</u> | <u>0.04</u> | <u>0.04</u> |
| (Aroclor #1254) | <u>0.035</u> | <u>0.04</u> | <u>0.04</u> |
| Total PCB | <u>31.75</u> | <u>13.70</u> | <u>4.86</u> |
| (Aroclor #1242) | <u>30.48</u> | <u>13.14</u> | <u>4.64</u> |
| (Aroclor #1254) | <u>1.24</u> | <u>0.056</u> | <u>0.22</u> |
| Soluble PCB, µg/ℓ | | | |
| Due to interstitial water | <u>0.006</u> | <u>0.003</u> | <u>0.001</u> |
| Due to dilution water | <u><0.02</u> | <u><0.02</u> | <u><0.02</u> |
| Total initial soluble | <u><0.02</u> | <u><0.02</u> | <u><0.02</u> |
| After mixing soluble PCB | <u>0.16</u> | <u><0.02</u> | <u><0.02</u> |
| (Aroclor #1242) | <u>0.02</u> | <u><0.02</u> | <u><0.02</u> |
| (Aroclor #1254) | <u>0.14</u> | <u><0.02</u> | <u><0.02</u> |
| PCB desorbed | <u>0.16</u> | <u><0.02</u> | <u><0.02</u> |
| (Aroclor #1242) | <u>0.02</u> | <u><0.02</u> | <u><0.02</u> |
| (Aroclor #1254) | <u>0.14</u> | <u><0.02</u> | <u><0.02</u> |

Underlined numbers are calculated values.

Table 22. Green Bay Settling Test Results

Ratio - Sediment:Water = 1:4

Initial Concentrations:

| | |
|------------------------|----------------|
| Wet mud added, g/ℓ | 220 |
| Suspended solids, mg/ℓ | <u>171,380</u> |
| TOC, mg/ℓ | <u>50</u> |
| Oil and grease, mg/ℓ | <u>62</u> |
| PCB, μg/ℓ | <u>31.72</u> |
| PCB (Aroclor #1242) | <u>30.48</u> |
| PCB (Aroclor #1254) | <u>1.24</u> |

Settling Times:

0.5 hr 1 hr 3 hr 24 hr

Supernatant Concentrations:

| | | | | |
|------------------------|------|------|------|------|
| Suspended Solids, mg/ℓ | 324 | 295 | 170 | 71 |
| Turbidity, FTU | 150 | 150 | 95 | 60 |
| Oil and grease, mg/ℓ | 137 | 74 | 41 | 14 |
| TOC, mg/ℓ | 44 | 49 | 31 | 33 |
| Soluble TOC, mg/ℓ | 18 | 24 | 23 | 15 |
| PCB, μg/ℓ | 1.07 | 0.70 | 0.22 | 0.08 |
| PCB (Aroclor #1242) | 0.68 | 0.39 | 0.15 | 0.05 |
| PCB (Aroclor #1254) | 0.39 | 0.31 | 0.07 | 0.03 |

Underlined numbers are calculated values.

Table 23. Fall River Equilibrium Test
Conditions and Results

| | | |
|---|--------|--------|
| Sediment Characteristics: | | |
| Total solids, % by wt | 58.4 | |
| Total volatile solids, % by wt | 1.0 | |
| Specific gravity, g/cc | 165 | |
| TOC, mg/kg dry solids | 13,700 | |
| Oil and grease, mg/kg dry solids | 344 | |
| PCB, µg/kg dry solids | 13 | |
| Sediment Interstitial Water Characteristics: | | |
| TOC, mg/l | 22 | |
| PCB, µg/l | 0.15 | |
| Water Column Water Characteristics: | | |
| Suspended solids, mg/l | 60 | |
| TOC, mg/l | 11 | |
| Soluble TOC, mg/l | 11 | |
| PCB, µg/l | <0.02 | |
| Ratio Wet Sediment/Water: | 1:4 | 1:10 |
| Concentration of Solubles | | |
| after 24 hr: | | |
| TOC, mg/l | 5 | 5 |
| PCB, µg/l | <0.02 | <0.02 |
| t-DDT, µg/l | <0.002 | <0.002 |
| Aldrin-dieldrin, µg/l | <0.002 | <0.002 |
| Endrin, µg/l | <0.002 | <0.002 |
| Lindane, µg/l | <0.002 | <0.002 |
| 2,4-D (esters), µg/l | <0.02 | <0.02 |
| Toxaphene, µg/l | <0.02 | <0.02 |

Table 24. Fall River Equilibrium Test Evaluation

| Ratio - Sediment/Water: | 1:4 | 1:10 |
|---------------------------------|-----------------|-----------------|
| Initial Concentrations | | |
| Wet sediment added, g | <u>217</u> | <u>94</u> |
| Water column water used, ml | <u>868</u> | <u>943</u> |
| Sediment dry solids, g | <u>127</u> | <u>55</u> |
| Sediment interstitial water, ml | <u>90</u> | <u>39</u> |
| TOC Values, mg/l | | |
| Sediment solids portion | <u>1,740</u> | <u>754</u> |
| Dilution water portion | <u>10</u> | <u>10</u> |
| Total amount of TOC | <u>1,750</u> | <u>764</u> |
| Soluble TOC - mg/l | | |
| Due to interstitial water | <u>2</u> | <u>1</u> |
| Due to dilution water | <u>10</u> | <u>10</u> |
| Total initial soluble | <u>12</u> | <u>11</u> |
| After mixing 24 hr | <u>5</u> | <u>5</u> |
| Change in soluble TOC | <u>-7</u> | <u>-6</u> |
| PCB Values, µg/l | | |
| Sediment solids portion | <u>1.65</u> | <u>0.72</u> |
| Dilution water portion | <u><0.02</u> | <u><0.02</u> |
| Total amount of PCB | <u>1.65</u> | <u>0.72</u> |
| Soluble PCB, µg/l | | |
| Due to interstitial water | <u>0.014</u> | <u>0.006</u> |
| Due to dilution water | <u><0.02</u> | <u><0.02</u> |
| Total initial soluble | <u>0.014</u> | <u>0.006</u> |
| After mixing 24 hr | <u>0.02</u> | <u>0.02</u> |
| Change in soluble PCB | -- | -- |

Underlined numbers are calculated values.

Table 25. Fall River Settling Test Results

Ratio - Sediment:Water = 1:10

| | | | | |
|------------------------------------|---------------|-------|--------|-------|
| Initial Concentrations | | | | |
| Wet mud added, g/l | 94 | | | |
| Suspended solids, mg/l | <u>54,896</u> | | | |
| TOC, mg/l | <u>754</u> | | | |
| Oil and grease, mg/l | <u>19</u> | | | |
| PCB, µg/l | <u>0.72</u> | | | |
| Settling Time: | 0.5 hr | 2 hr | 5.5 hr | 24 hr |
| Supernatant Concentrations: | | | | |
| Suspended solids, mg/l | 398 | 143 | 46 | 15 |
| Turbidity, FTU | 190 | 60 | 30 | 8 |
| Oil and grease, mg/l | 1 | <1 | <1 | <1 |
| TOC, mg/l | 17 | 13 | 11 | 9 |
| Soluble TOC, mg/l | 8 | 7 | 7 | 6 |
| PCB, µg/l | 0.06 | <0.02 | <0.02 | <0.02 |

Underlined numbers are calculated values.

Table 26. Houston Equilibrium Test
Conditions and Results

| | | |
|---|--------|--------|
| Sediment Characteristics: | | |
| Total solids, % by wt | 45.6 | |
| Total volatile solids, % by wt | 2.3 | |
| Specific gravity, g/cc | 1.37 | |
| TOC, mg/kg dry solids | 9,200 | |
| Oil and grease, mg/kg dry solids | 1,555 | |
| PCB, µg/kg dry solids | 12 | |
| Dieldrin, µg/kg dry solids | 0.2 | |
| 2,4-D (esters) µg/kg dry solids | 1.3 | |
| Sediment Interstitial Water Characteristics: | | |
| TOC, mg/l | 38 | |
| PCB, µg/l | 0.08 | |
| Dieldrin, µg/l | <0.002 | |
| 2,4-D (esters), µg/l | 0.02 | |
| Water Column Water Characteristics: | | |
| Suspended solids, mg/l | 41 | |
| TOC, mg/l | 11 | |
| Soluble TOC, mg/l | 7 | |
| PCB, µg/l | 0.02 | |
| Dieldrin, µg/l | <0.002 | |
| 2,4-D (esters), µg/l | <0.02 | |
| Soluble PCB, µg/l | <0.02 | |
| Ratio Wet Sediment/Water | 1:4 | 1:10 |
| Concentration of Solubles after 24 hr: | | |
| TOC, mg/l | 93 | 16 |
| PCB, µg/l | 0.02 | <0.02 |
| t-DDT, µg/l | <0.002 | <0.002 |
| Aldrin-dieldrin µg/l | <0.002 | <0.002 |
| Endrin, µg/l | <0.002 | <0.002 |
| Lindane, µg/l | <0.002 | <0.002 |
| 2,4-D (esters), µg/l | <0.02 | <0.02 |
| Toxaphene, µg/l | <0.02 | <0.02 |

Table 27. Houston Equilibrium Test Evaluation

| Ratio - Sediment/Water | 1:4 | 1:10 |
|-----------------------------------|-----------------|-----------------|
| Initial Concentrations | | |
| Wet sediment added, g/ℓ | <u>211</u> | <u>93</u> |
| Water column water used, ml/ℓ | <u>846</u> | <u>932</u> |
| Sediment dry solids, g/ℓ | <u>96</u> | <u>42.4</u> |
| Sediment interstitial water, mg/ℓ | <u>115</u> | <u>50.6</u> |
| TOC Values, mg/ℓ | | |
| Sediment solids portion | <u>883</u> | <u>390</u> |
| Water column portion | <u>9</u> | <u>10</u> |
| Total amount of TOC | <u>892</u> | <u>400</u> |
| Soluble TOC, mg/ℓ | | |
| Due to interstitial water | <u>4</u> | <u>2</u> |
| Due to water column water | <u>6</u> | <u>6</u> |
| Total initial soluble TOC | <u>10</u> | <u>8</u> |
| After mixing 24 hr | <u>93</u> | <u>16</u> |
| Change in soluble TOC | <u>+83</u> | <u>+8</u> |
| PCB Values, µg/ℓ | | |
| Sediment solids portion | <u>1.15</u> | <u>0.50</u> |
| Water column portion | <u><0.02</u> | <u>0.02</u> |
| TOTAL | <u>1.15</u> | <u>0.52</u> |
| Soluble PCB, µg/ℓ | | |
| Due to interstitial water | <u>0.009</u> | <u>0.004</u> |
| Due to water column water | <u><0.02</u> | <u><0.02</u> |
| Total initial soluble PCB | <u><0.02</u> | <u><0.02</u> |
| After mixing 24 hr | <u>0.02</u> | <u><0.02</u> |
| Change in soluble PCB | <u>+0.011</u> | <u>--</u> |
| 2,4-D Values, µg/ℓ | | |
| Sediment solids portion | <u>0.12</u> | <u>0.06</u> |
| Water Column portion | <u><0.02</u> | <u><0.02</u> |
| TOTAL | <u>0.12</u> | <u>0.06</u> |
| Soluble 2,4-D, µg/ℓ | | |
| Due to interstitial water | <u>0.002</u> | <u>0.001</u> |
| Due to water column water | <u><0.02</u> | <u><0.02</u> |
| Total initial soluble 2,4-D | <u><0.02</u> | <u><0.02</u> |
| After mixing 24 hr | <u><0.02</u> | <u><0.02</u> |
| Change in soluble 2,4-D | <u>--</u> | <u>--</u> |

Underlined numbers are calculated values.

Table 28. Houston Settling Test Results

Ratio - Sediment:Water = 1:10

| Initial Concentrations | | | |
|-----------------------------|---------------|--------|--------|
| Wet mud added, g/l | 93 | | |
| Suspended solids, mg/l | <u>42,408</u> | | |
| TOC, mg/l | <u>390</u> | | |
| Oil and grease, mg/l | <u>65</u> | | |
| PCB, µg/l | <u>0.51</u> | | |
| Dieldrin, µg/l | <u>0.008</u> | | |
| 2,4-D (esters) µg/l | <u>0.05</u> | | |
| Settling Time: | 1 hr | 5.5 hr | 24 hr |
| Supernatant Concentrations: | | | |
| Suspended solids, mg/l | 80 | 40 | 30 |
| Oil and grease, mg/l | 3 | 4 | 3 |
| TOC, mg/l | 12 | 13 | 11 |
| Soluble TOC, mg/l | 13 | 13 | 12 |
| PCB, µg/l | 0.05 | 0.05 | 0.02 |
| Dieldrin, µg/l | <0.002 | <0.002 | <0.002 |
| 2,4-D (esters), µg/l | <0.02 | <0.02 | <0.02 |

Underlined numbers are calculated values.

Table 29. Memphis Sediment Equilibrium Test
Conditions and Results

| | | | |
|---|----------------------------|------------|-------------------------|
| Sediment Characteristics: | | | |
| Total solids, % by wt | 49.6 | | |
| Total volatile solids, % by wt | 2.8 | | |
| Specific gravity, g/cc | 1.43 | | |
| TOC, mg/kg dry solids | 9,300 | | |
| Oil and grease, mg/kg dry solids | 329 | | |
| PCB, µg/kg dry solids | 78 | | |
| Dieldrin, µg/kg dry solids | 3.9 | | |
| t-DDT, µg/kg dry solids | 5.1 | | |
| Sediment Interstitial Water Characteristics: | | | |
| TOC, mg/l | 90 | | |
| PCB, µg/l | <0.02 | | |
| Dieldrin, µg/l | 0.002 | | |
| t-DDT, µg/l | <0.002 | | |
| Water Column Water Characteristics: | | | |
| Suspended solids, mg/l | 59 | | |
| TOC, mg/l | 15 | | |
| Soluble TOC, mg/l | 11 | | |
| PCB, µg/l | 0.02 | | |
| Dieldrin, µg/l | 0.002 | | |
| Ratio | Wet sediment/water: | 1:4 | 1:10 1:30 |
| Concentration of Solubles | | | |
| after 24 hr: | | | |
| TOC, mg/l | 16 | 11 | 11 |
| PCB, µg/l | 0.03 | <0.02 | <0.02 |
| t-DDT, µg/l | <0.002 | <0.002 | <0.002 |
| Aldrin-dieldrin, µg/l | 0.003 | <0.002 | <0.002 |
| Endrin, µg/l | <0.002 | <0.002 | <0.002 |
| Lindane, µg/l | <0.002 | <0.002 | <0.002 |
| 2,4-D (esters) µg/l | <0.02 | <0.02 | <0.02 |
| Toxaphene µg/l | <0.02 | <0.02 | <0.02 |

Table 30. Memphis Equilibrium Test Evaluation

| Ratio - Sediment/water | 1:4 | 1:10 | 1:30 |
|-----------------------------------|-----------------|------------------|------------------|
| Initial Concentration | | | |
| Wet sediment added, g/l | <u>213</u> | <u>93</u> | <u>33</u> |
| Water column water used, ml/l | <u>851</u> | <u>935</u> | <u>977</u> |
| Sediment dry solids, g/l | <u>106</u> | <u>46</u> | <u>16</u> |
| Sediment interstitial water/ mg/l | <u>107</u> | <u>47</u> | <u>17</u> |
| TOC Values, mg/l | | | |
| Sediment solids portion | <u>986</u> | <u>428</u> | <u>149</u> |
| Dilution water portion | <u>13</u> | <u>14</u> | <u>15</u> |
| Total TOC | <u>999</u> | <u>442</u> | <u>164</u> |
| Soluble TOC, mg/l | | | |
| Due to interstitial water | <u>9.6</u> | <u>4.2</u> | <u>1.5</u> |
| Due to water column water | <u>9.4</u> | <u>10.3</u> | <u>10.7</u> |
| Total initial soluble TOC | <u>19</u> | <u>14</u> | <u>12</u> |
| After mixing 24 hr | <u>16</u> | <u>11</u> | <u>11</u> |
| Change in soluble TOC | <u>-3</u> | <u>-3</u> | <u>-1</u> |
| PCB Values, µg/l | | | |
| Sediment solids portion | <u>8.27</u> | <u>3.59</u> | <u>1.25</u> |
| Water column portion | <u><0.02</u> | <u><0.02</u> | <u><0.02</u> |
| Total PCB | <u>8.27</u> | <u>3.59</u> | <u>1.25</u> |
| Soluble PCB, µg/l | | | |
| Due to interstitial water | <u><0.02</u> | <u><0.02</u> | <u><0.02</u> |
| Due to water column water | <u><0.02</u> | <u><0.02</u> | <u><0.02</u> |
| Total initial soluble PCB | <u><0.02</u> | <u><0.02</u> | <u><0.02</u> |
| After mixing 24 hr | <u>0.03</u> | <u><0.02</u> | <u><0.02</u> |
| Change in soluble PCB | <u>+0.03</u> | <u>--</u> | <u>--</u> |
| Dieldrin Values, µg/l | | | |
| Sediment solids portion | <u>0.413</u> | <u>0.179</u> | <u>0.062</u> |
| Water column portion | <u>0.002</u> | <u>0.002</u> | <u>0.002</u> |
| Total Dieldrin | <u>0.415</u> | <u>0.181</u> | <u>0.064</u> |
| Soluble Dieldrin, µg/l | | | |
| Due to interstitial water | <u>0.0002</u> | <u>0.0001</u> | <u>0.0001</u> |
| Due to water column water | <u>0.002</u> | <u>0.002</u> | <u>0.002</u> |
| Total initial soluble dieldrin | <u>0.002</u> | <u>0.002</u> | <u>0.002</u> |
| After mixing 24 hr | <u>0.003</u> | <u><0.002</u> | <u><0.002</u> |
| Change in soluble dieldrin | <u>+0.001</u> | <u>--</u> | <u>--</u> |

Underlined numbers are calculated values.

Table 31. Memphis Settling Tests
Ratio - Sediment:Water = 1:10

| Initial Concentrations | | | | |
|-----------------------------|---------------|--------|--------|--------|
| Wet mud added, g/l | 93 | | | |
| Suspended solids, mg/l | <u>46,128</u> | | | |
| TOC, mg/l | <u>428</u> | | | |
| Oil and grease, mg/l | <u>15</u> | | | |
| PCB, µg/l | <u>3.59</u> | | | |
| Settling Times: | 0.5 hr | 3 hr | 7 hr | 24 hr |
| Supernatant Concentrations: | | | | |
| Suspended solids, mg/l | 1,375 | 514 | 329 | 46 |
| Oil and grease, mg/l | 2 | 3 | 2 | 8 |
| TOC, mg/l | 70 | 21 | 19 | 11 |
| Soluble TOC, mg/l | 8 | 10 | 10 | 12 |
| PCB, µg/l | 0.17 | 0.08 | 0.06 | 0.04 |
| Dieldrin, µg/l | 0.029 | 0.002 | <0.002 | <0.002 |
| t-DDT, µg/l | 0.013 | <0.002 | <0.002 | <0.002 |

Underlined numbers are calculated values.

Table 32 - Occurrence of Pesticide Materials in Sediment Samples

| Pesticide Material | Number of Samples Containing Pesticide Materials | | | | | Total (64 Samples) |
|--------------------|--|---------------------------|----------------------------|-------------------------|-------------------------|-----------------------|
| | Chicago (17 Samples) | Green Bay (10 Samples) | Fall River (12 Samples) | Houston (10 Samples) | Memphis (15 Samples) | |
| Aroclor 1242 | 0 | 8 | 0 | 0 | 0 | 8 |
| Aroclor 1254 | 16 | 4 | 9 | 10 | 15 | 54 |
| Total PCB | 16 | 9 | 9 | 10 | 15 | 59 |
| t-DDT | 4 | 1 | 2 | 4 | 16 | 26 |
| Dieldrin | 1 | 0 | 8 | 4 | 14 | 27 |
| Aldrin | 0 | 0 | 7 | 0 | 0 | 7 |
| 2,4-D | 0 | 0 | 0 | 4 | 0 | 4 |

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| Pesticide Material | Number of Sampling Sites Containing Pesticide Materials | | | | | Total (25 Sites) |
|--------------------|---|------------------------|-------------------------|----------------------|----------------------|---------------------|
| | Chicago (5 Sites) | Green Bay (5 Sites) | Fall River (5 Sites) | Houston (5 Sites) | Memphis (5 Sites) | |
| Aroclor 1242 | 0 | 5 | 0 | 0 | 0 | 5 |
| Aroclor 1254 | 5 | 4 | 5 | 5 | 5 | 24 |
| Total PCB | 5 | 5 | 5 | 5 | 5 | 25 |
| t-DDT | 2 | 1 | 1 | 2 | 5 | 11 |
| Dieldrin | 1 | 0 | 5 | 2 | 5 | 13 |
| Aldrin | 0 | 0 | 2 | 0 | 0 | 2 |
| 2,4-D | 0 | 0 | 0 | 2 | 0 | 2 |

Table 33 - Chemical Characteristics of Entire Sediment Depth at
Each Sampling Site and Location

| <u>Site</u> | <u>Parameter*</u> | <u>Site 1</u> | <u>Site 2</u> | <u>Site 3</u> | <u>Site 4</u> | <u>Site 5</u> |
|-------------|---------------------|---------------|---------------|---------------|---------------|---------------|
| Chicago | | | | | | |
| | TOC, mg/kg | 8,490 | 17,500 | 24,600 | 6,580 | 15,400 |
| | Oil, mg/kg | 1,840 | 2,724 | 3,230 | 627 | 2,240 |
| | PCB, µg/kg | 186 | 153 | 108 | 31 | 301 |
| | t-DDT, µg/kg | <0.2 | 0.2 | <0.2 | <0.2 | 1.4 |
| | Dieldrin, µg/kg | <0.2 | <0.2 | 0.7 | <0.2 | <0.2 |
| Green Bay | | | | | | |
| | TOC, mg/kg | 7,026 | 2,520 | 1,580 | 640 | 1,860 |
| | Oil, mg/kg | 340 | 385 | 255 | 167 | 736 |
| | PCB, µg/kg | 24 | 44 | 157 | 12 | 333 |
| | Aroclor 1242, µg/kg | 22 | 44 | 127 | 10 | 327 |
| | Aroclor 1254, µg/kg | 2 | 0 | 30 | 2 | 6 |
| | t-DDT, g/kg | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Fall River | | | | | | |
| | TOC, mg/kg | 7,030 | 12,300 | 12,000 | 12,100 | 10,500 |
| | Oil, mg/kg | 362 | 811 | 469 | 362 | 938 |
| | PCB, µg/kg | <1 | 25 | 6 | 20 | 6 |
| | Dieldrin, µg/kg | 0.7 | 2.1 | 0.8 | 16.9 | 0.7 |
| | Aldrin, µg/kg | <0.1 | <0.1 | <0.1 | 7.1 | 0.5 |
| | t-DDT, µg/kg | <0.1 | <0.1 | <0.1 | 11.8 | <0.1 |
| Houston | | | | | | |
| | TOC, mg/kg | 9,040 | 8,040 | 11,800 | 9,040 | 13,500 |
| | Oil, mg/kg | 231 | 1,100 | 1,830 | 1,960 | 1,390 |
| | PCB, g/kg | 9 | 2 | 13 | 10 | 10 |
| | 2,4-D, µg/kg | <1 | <1 | <1 | 49 | 29 |
| | t-DDT, µg/kg | <0.1 | <0.1 | <0.1 | 0.9 | 1.1 |
| | Dieldrin, µg/kg | <0.1 | <0.1 | <0.1 | 1.6 | 5.8 |
| Memphis | | | | | | |
| | TOC, mg/kg | 11,900 | 10,400 | 12,200 | 9,980 | 18,300 |
| | Oil, mg/kg | 230 | 616 | 675 | 484 | 681 |
| | PCB, µg/kg | 157 | 63 | 141 | 51 | 163 |
| | t-DDT, µg/kg | 15 | 7.7 | 9.2 | 15.9 | 19.5 |
| | Dieldrin, µg/kg | 7 | 3.0 | 1.8 | 1.4 | 4.4 |

* Calculated from concentrations in each sample. Units per kg dry solids.

Table 34. Analysis of Significant Variation
of Contaminant with Depth

| Parameter | Core Segment | Average Percent of Total Core Used for Analysis & | | | | |
|-----------|--------------|---|-----------|------------|---------|---------|
| | | Chicago | Green Bay | Fall River | Houston | Memphis |
| TOC | Top | 20 | 50 | 44 | 44 | 33 |
| | 2nd | 24 | 50 | 56 | 56 | 34 |
| | 3rd | 26 | -- | -- | -- | 33 |
| | Bottom | 30 | -- | -- | -- | -- |
| Oil | Top | 18 | 42 | 68 | 22* | 32 |
| | 2nd | 29 | 58 | 32 | 78 | 30 |
| | 3rd | 21 | -- | -- | -- | 38 |
| | Bottom | 32 | -- | -- | -- | -- |
| PCB | Top | 47* | 88* | 72 | 75 | 19* |
| | 2nd | 38 | 12 | 28 | 25 | 39 |
| | 3rd | 12 | -- | -- | -- | 42 |
| | Bottom | 4 | -- | -- | -- | -- |
| Dieldrin | Top | -- | -- | 82* | -- | 59* |
| | 2nd | -- | -- | 18 | -- | 27 |
| | 3rd | -- | -- | -- | -- | 14 |
| | Bottom | -- | -- | -- | -- | -- |
| DDT | Top | -- | -- | -- | -- | 23* |
| | 2nd | -- | -- | -- | -- | 44 |
| | 3rd | -- | -- | -- | -- | 33 |
| | Bottom | -- | -- | -- | -- | -- |

* Starred values indicate that variation of parameter with depth was significant at 5% significance level.

Table 35. PCB Remaining in the Water Column
After Various Settling Times*

| Settling Time, hrs | Chicago | | Green Bay | | Fall River | | Houston | | Memphis | |
|--|--------------------|-----|--------------------|-----|--------------------|-----|--------------------|-----|--------------------|-----|
| | $\mu\text{g}/\ell$ | % | $\mu\text{g}/\ell$ | % | $\mu\text{g}/\ell$ | % | $\mu\text{g}/\ell$ | % | $\mu\text{g}/\ell$ | % |
| 0 | 7.22 | 100 | 31.7 | 100 | 0.72 | 100 | 0.51 | 100 | 3.59 | 100 |
| 0.5 | 0.42 | 5.8 | 1.07 | 3.4 | 0.06 | 8.3 | 0.05 | 9.8 | 0.17 | 4.8 |
| 1.0 | 0.19 | 2.6 | 0.70 | 2.2 | -- | -- | -- | -- | -- | -- |
| 2.0 | -- | -- | -- | -- | <0.02 | <3 | -- | -- | -- | -- |
| 3.0 | -- | -- | 0.22 | 0.7 | -- | -- | -- | -- | 0.08 | 2.3 |
| 5.0 | 0.05 | 0.7 | -- | -- | -- | -- | -- | -- | -- | -- |
| 5.5 | -- | -- | -- | -- | <0.02 | <3 | 0.05 | 9.8 | -- | -- |
| 7.0 | -- | -- | -- | -- | -- | -- | -- | -- | 0.06 | 1.7 |
| 24 | -- | -- | 0.08 | 0.3 | <0.02 | <3 | 0.02 | 3.9 | 0.04 | 1.1 |
| Initial Water Column Concen- tration | 0.02 | -- | 0.08 | -- | <0.02 | -- | 0.02 | -- | 0.02 | -- |

* Two columns for each site represent concentration and percent of initial amount remaining in suspension, respectively.

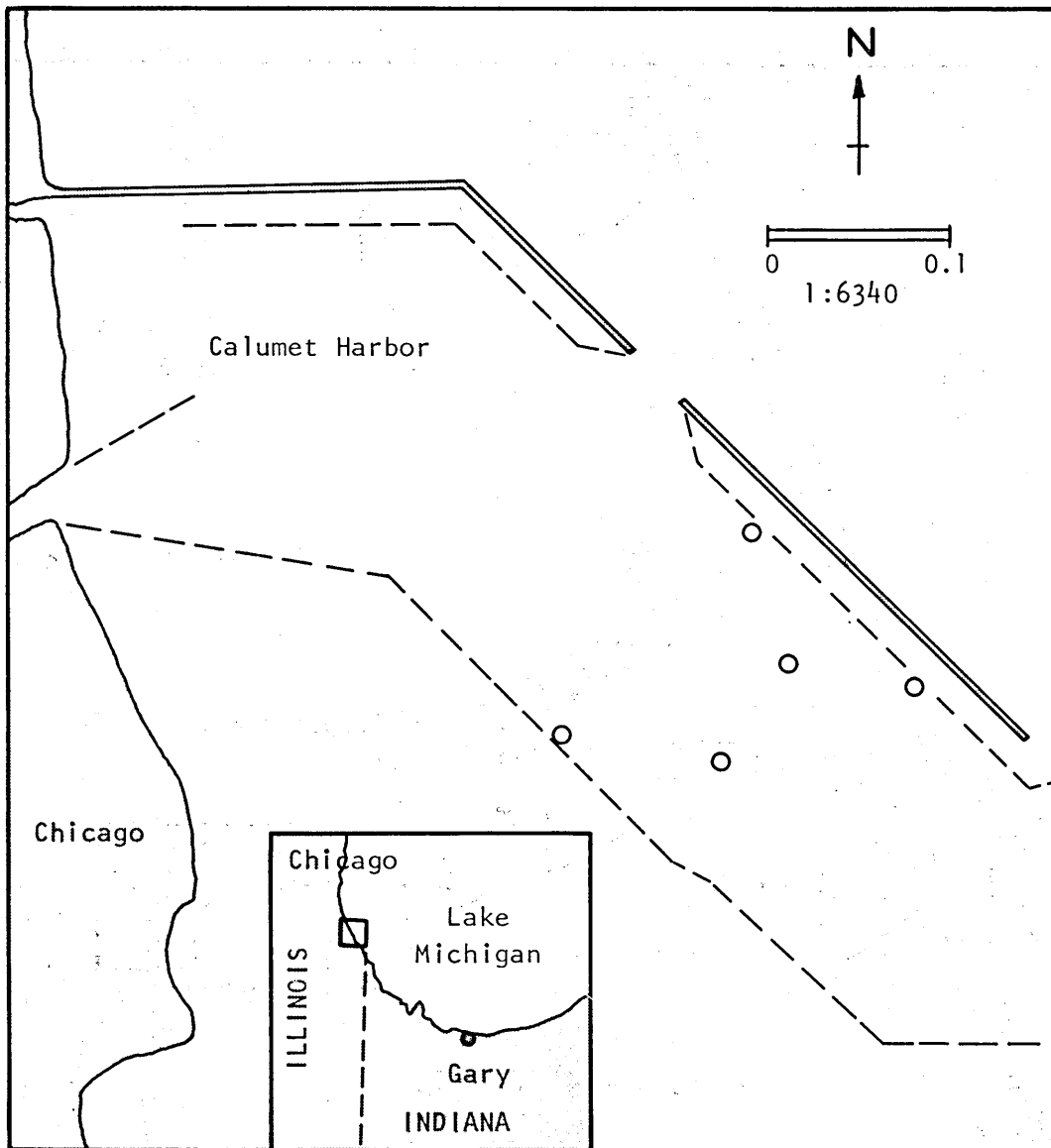


Figure 1. Chicago Sampling Sites

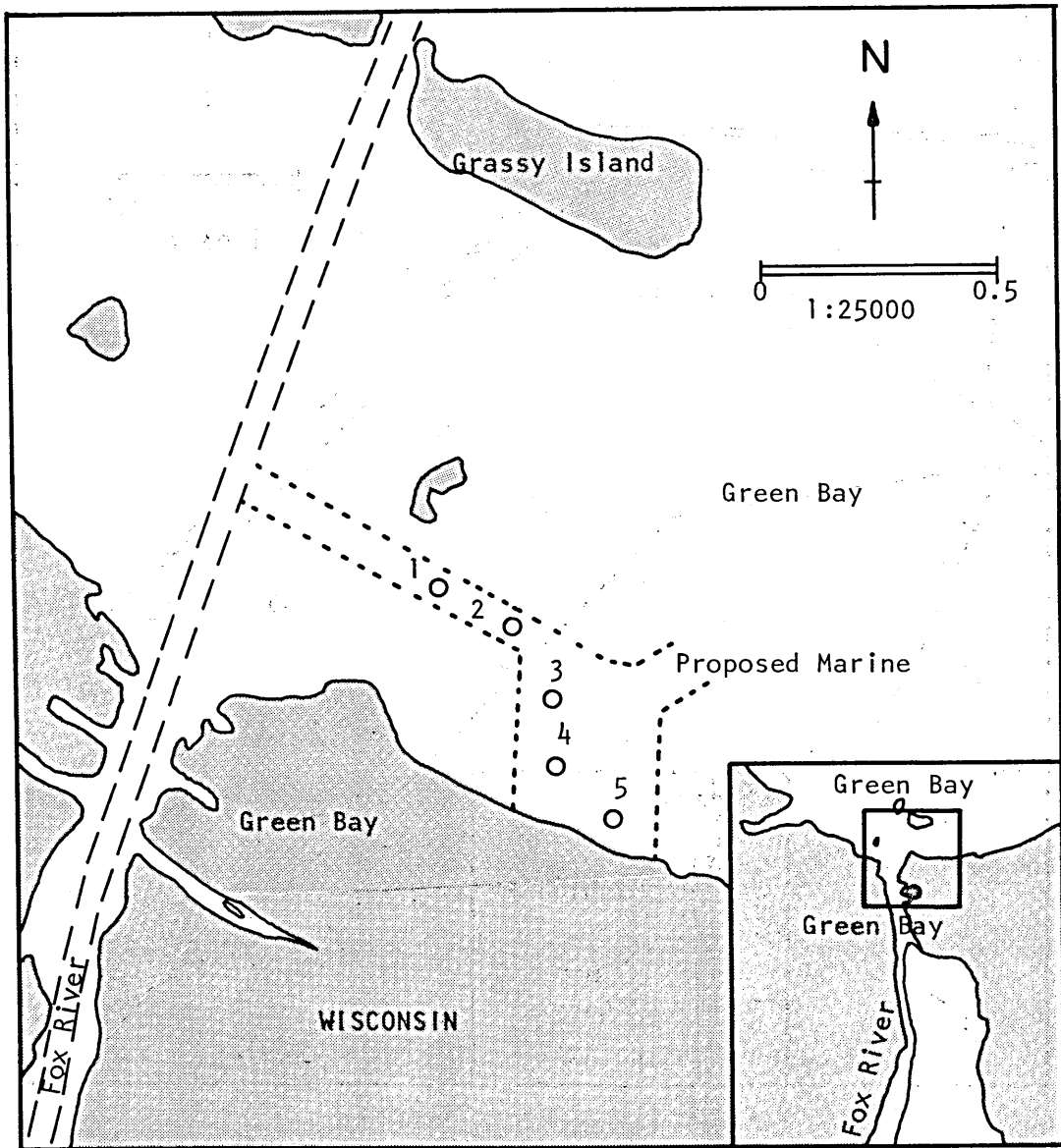


Figure 2. Green Bay Sampling Sites

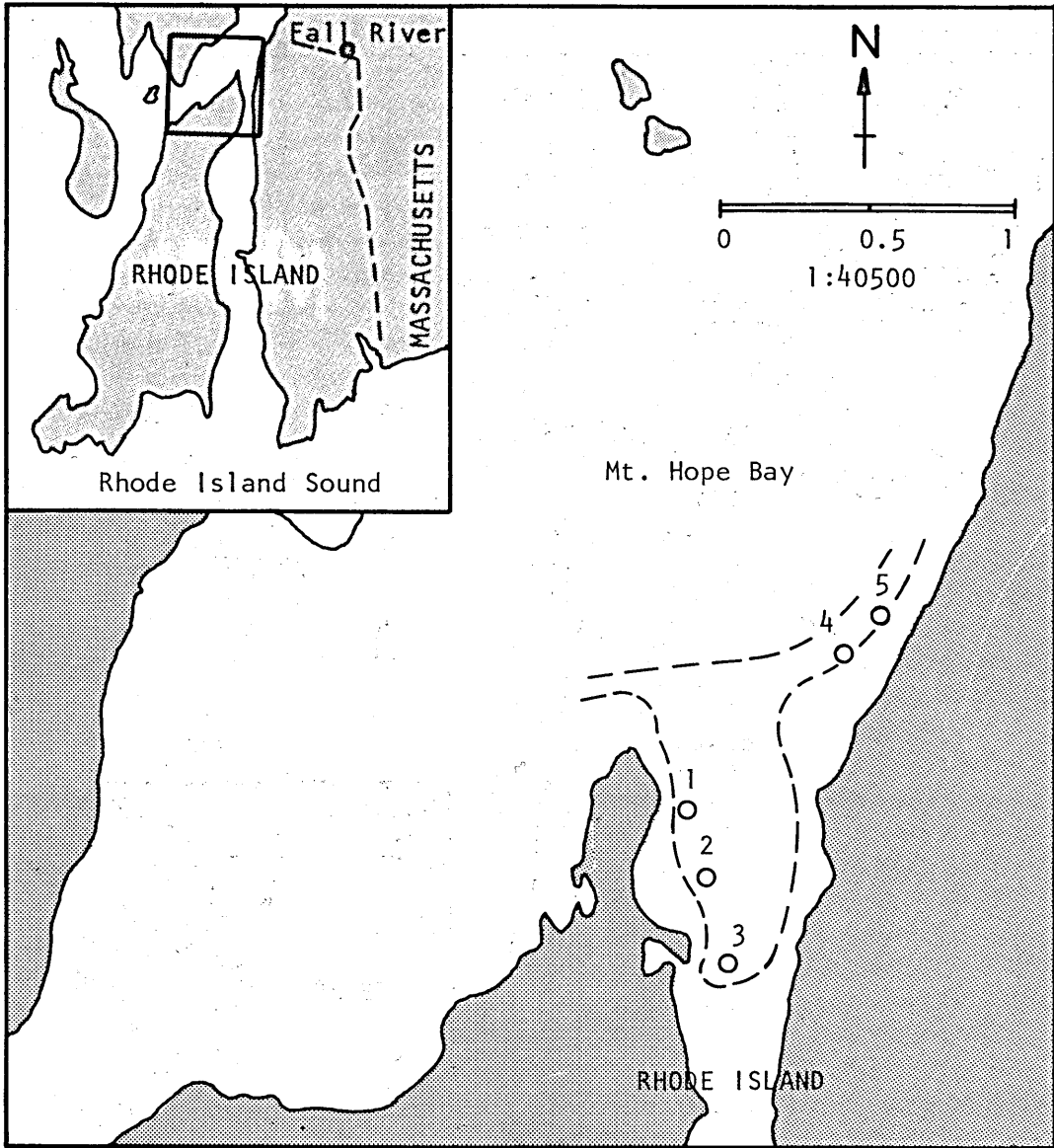


Figure 3. Fall River Sampling Sites

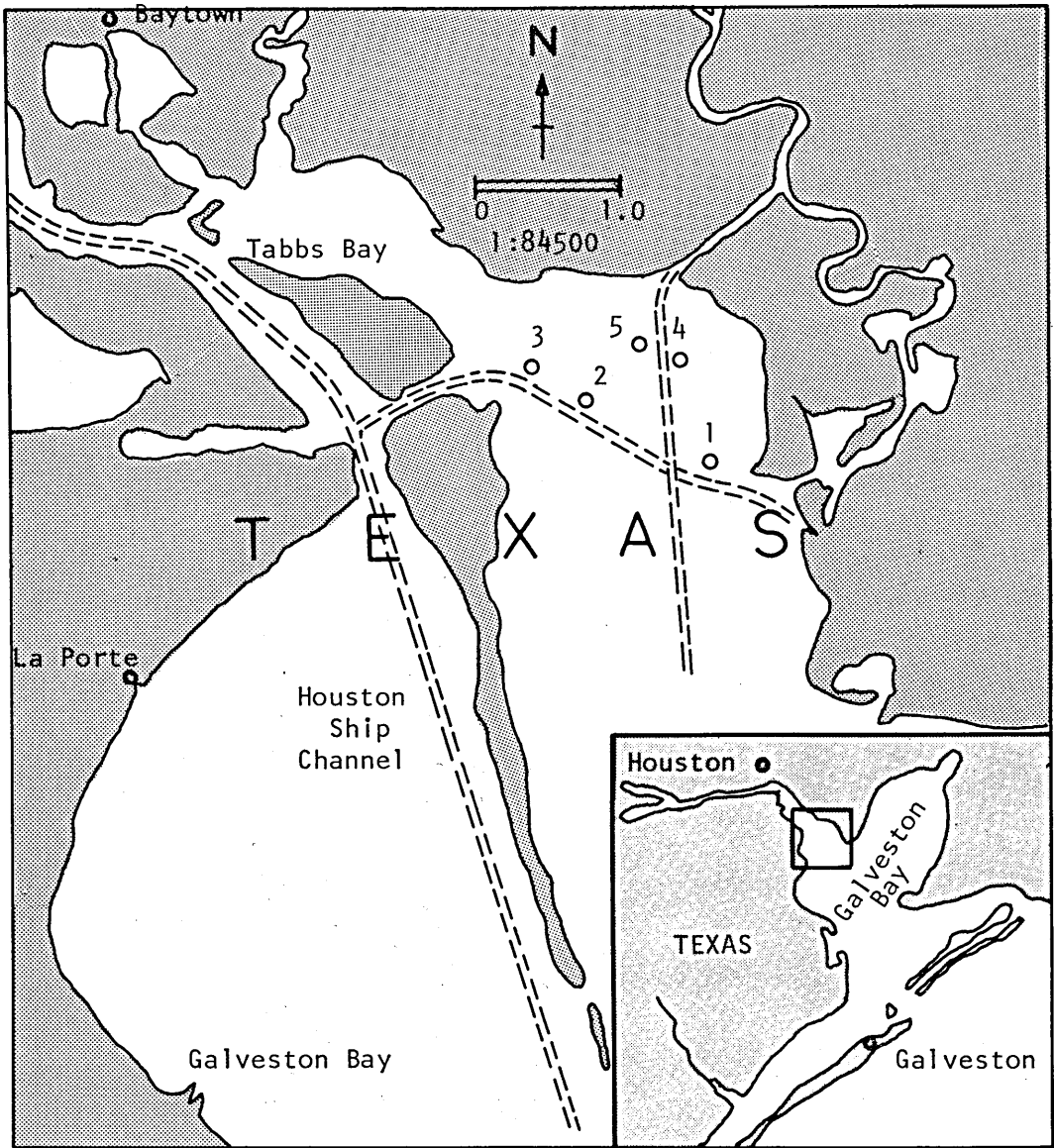


Figure 4. Houston Sampling Sites

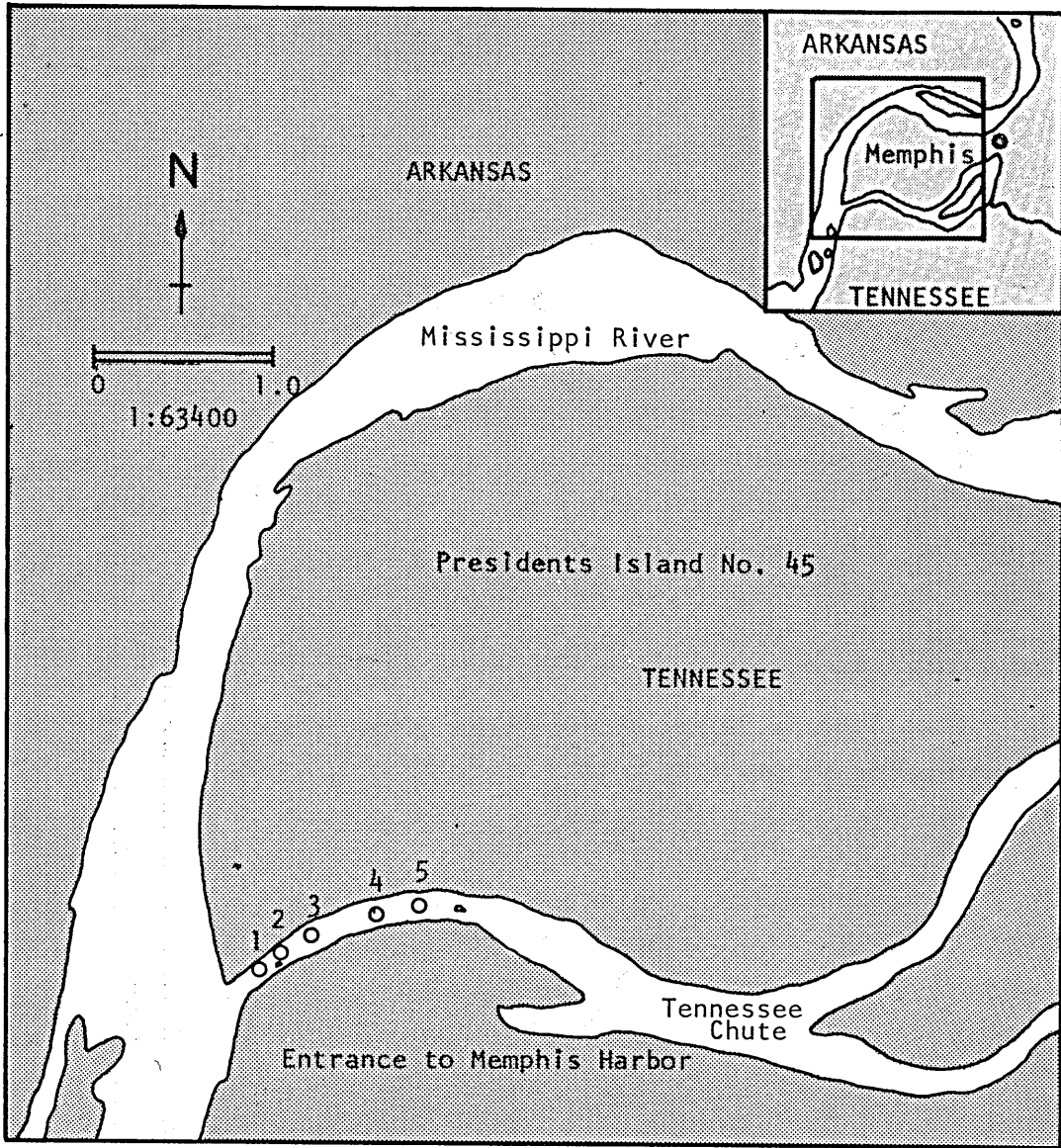


Figure 5. Memphis Sampling Sites

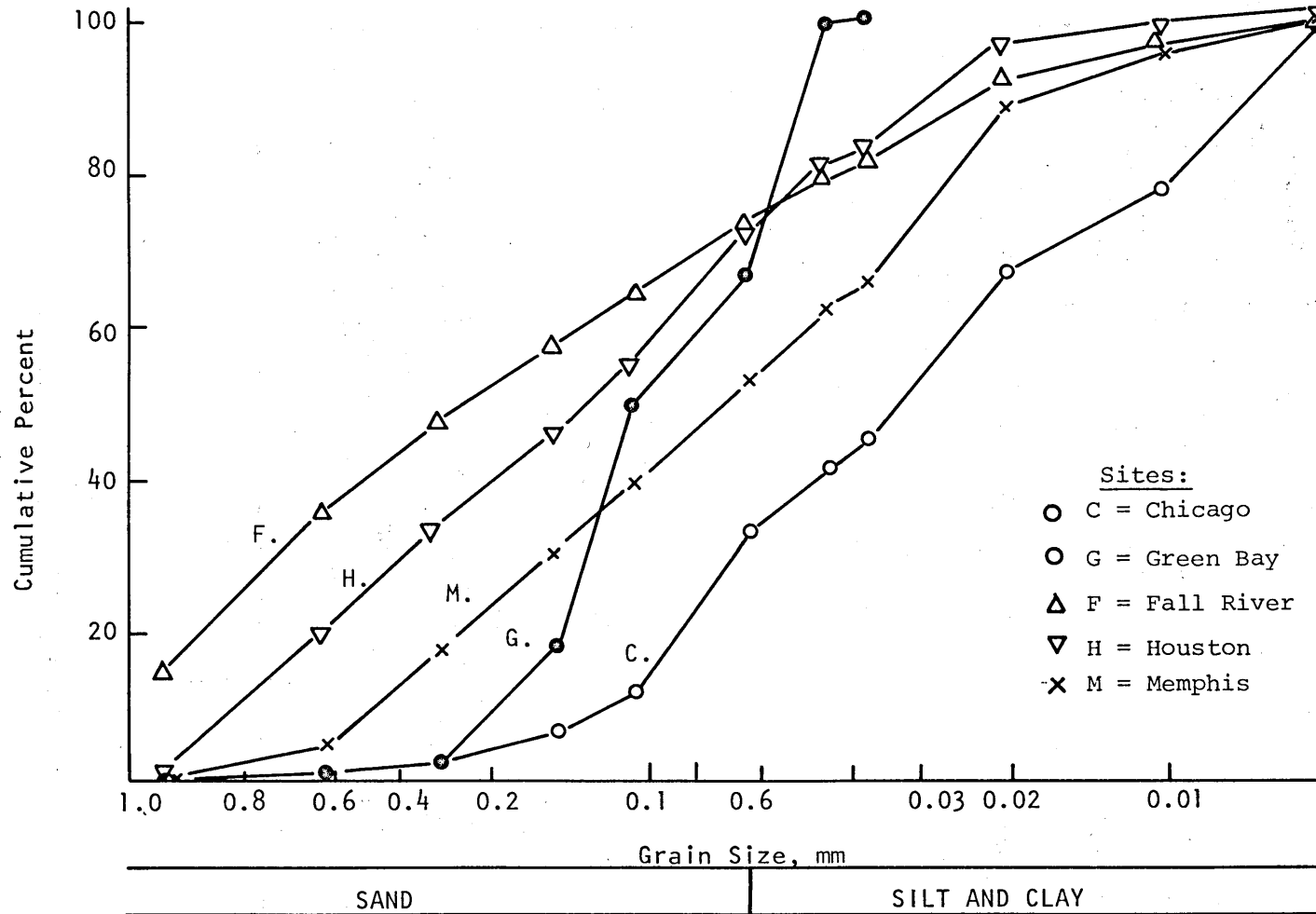


Figure 6. Particle Size Distribution of Migration Test Sediments

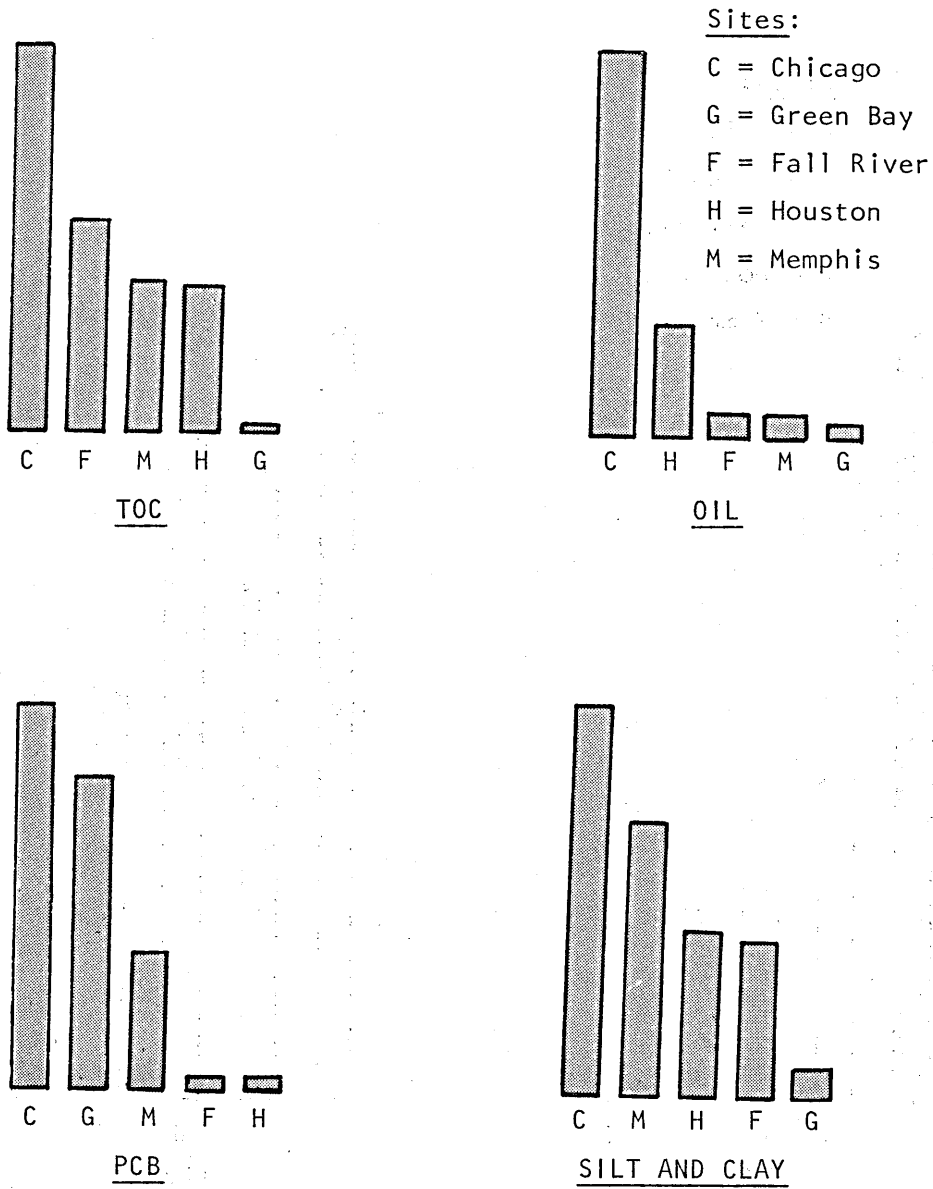


Figure 7. Relative Amounts of TOC, Oil, PCB, and Silt and Clay in Migration Test Samples

Sites:

C = Chicago

G = Green Bay

F = Fall River

H = Houston

M = Memphis

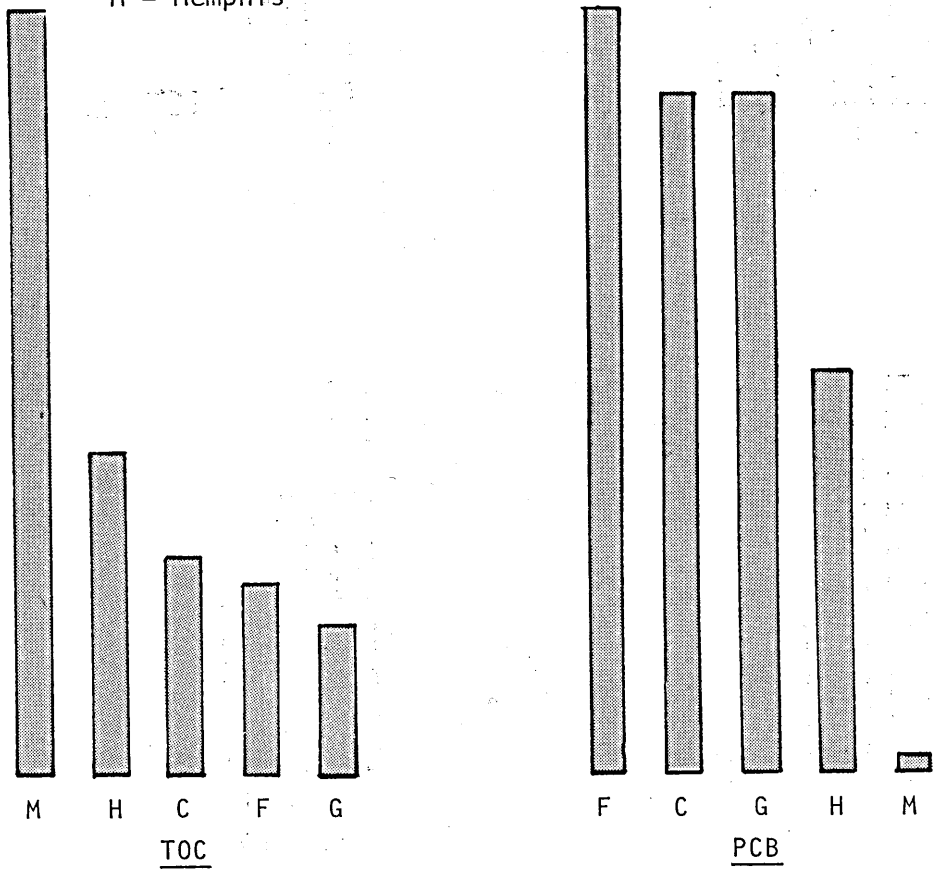


Figure 8. Relative Amounts of TOC and PCB in Migration Test Sediment Interstitial Water

Appendix A

Common and Chemical Names of Chlorinated Hydrocarbons

Used In This Report

| <u>Common Name</u> | <u>Chemical Name</u> |
|--------------------|---|
| Aldrin | 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4- <u>endo,exo</u> -5,8-dimethanonaphthalene |
| Dieldrin | 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4- <u>endo,exo</u> -5,8-dimethanonaphthalene |
| pcp'-DDD | 2,2-bis(p-chlorophenyl)-1,1-dichloroethane |
| o,p'-DDD | 2,2-bis(o-chlorophenyl)-1,1-dichloroethane |
| p,p'-DDE | 2,2-bis(p-chlorophenyl)-1,1-dichloroethylene |
| o,p'-DDE | 2,2-bis(o-chlorophenyl)-1,1-dichloroethylene |
| p,p'-DDT | 2,2-bis(p-chlorophenyl)-1,1,1-trichloroethane |
| o,p'-DDT | 2,2-bis(p-chlorophenyl)-1,1,1-trichloroethane |
| t-DDT | Summed concentration of the six DDT analogs |
| Endrin | 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4 <u>endo, endo</u> -5, 8-dimethanonaphthalene |
| Lindane | gamma 1, 2, 3, 4, 5, 6-hexachlorocyclohexane |
| PCB | Polychlorinated biphenyl |
| Aroclor #1242 | PCB manufactured by Monsanto Chemical Co. - contains 42% Chlorine |
| Aroclor #1254 | PCB manufactured by Monsanto Chemical Co. - contains 54% Chlorine |
| 2,4-D, BE I | 2,4 dichlorophenoxyacetic acid, butyl esters |
| 2,4-D, BE II | 2,4 dichlorophenoxyacetic acid, butoxy ethanol ether esters |
| Toxaphene | Mixture of chlorinated camphene compounds |

THE UNIVERSITY OF CHICAGO

PHYSICS DEPARTMENT

PHYSICS 230

LECTURE 1

MECHANICS

1.1 Kinematics

1.2 Dynamics

1.3 Energy

Appendix B

Analytical Procedures

General Analytical Methods

Procedures
Precision and Recovery Data

Pesticide Analysis

Procedure
Recovery Data

1. This appendix includes a description of analytical procedures used and reports results of the recovery and precision tests performed using samples and procedures from this project.

General Analytical Methods

Procedures

2. The procedures described in the EPA Manual for Chemical Analysis of Water and Wastes, 1971¹⁵ and Standard Methods for the Examination of Water and Wastewater, 13th Ed.¹⁶ were used to analyze for the following parameters*. The page number of the manual where the analytical procedure is found is included for ready reference.

- a. Total solids (EPA Manual Page 280) - Evaporation of water at 105°C.
- b. Total volatile solids (EPA Manual Page 282) - Ignition at 550°C.
- c. Suspended solids (EPA Manual Page 278) - filtration through glass fiber filter and drying at 105°C.
- d. Oil and grease (Standard Methods Page 412) - Sediment samples were mixed with anhydrous magnesium sulfate and extracted with hexane in a Soxhlet apparatus. Water samples were extracted with hexane using a separatory funnel (Standard Methods Page 254).
- e. Total organic carbon (EPA Manual Page 221) - Combustion-infra-red method using a Beckman Model 915 Total Organic Carbon Analyzer.
- f. pH (EPA Manual Page 230) - Beckman SS-2 pH Meter
- g. Soluble TOC - Samples were filtered through prewashed 0.45 micron filters to remove suspended solids. TOC measurements were then made on the filtrate.
- h. Soluble pesticides - Samples were centrifuged to remove suspended solids. Pesticide analyses were performed on the centrate.
- i. Chloride analysis (EPA Manual Page 24) - titration with mercuric nitrate.

*References are given in the References Section following the main text.

- j. Turbidity (EPA Manual Page 308) - measurement using a Hach 2100-A Turbidimeter.

Precision and Recovery

3. Precision and recovery data were obtained from several analytical procedures using samples obtained in this project. This data was obtained using procedures recommended in the EPA Handbook for Analytical Quality Control in Water and Wastewater Laboratories.¹⁹

4. TOC and Soluble TOC - A wide variability in soluble TOC results at low levels prompted the determination of precision and recovery data for soluble TOC. The same data were obtained for TOC for comparison. These tests were run using 7 replicates of water column water from the Chicago sampling site. The precision results are listed below:

| <u>Sample</u> | <u>TOC, mg/l</u> | <u>Soluble TOC, mg/l</u> |
|--------------------|------------------|--------------------------|
| 1 | 9 | 15 |
| 2 | 9 | 15 |
| 3 | 10 | 9 |
| 4 | 10 | 8 |
| 5 | 9 | 6 |
| 6 | 8 | 13 |
| 7 | 8 | 8 |
| Average | 9 | 10 |
| Standard Deviation | 0.8 | 3.7 |

5. After the addition of 4 mg TOC/l, the analyses were repeated. The results are listed below:

| <u>Sample</u> | <u>TOC, mg/l</u> | <u>Soluble TOC, mg/l</u> |
|------------------|------------------|--------------------------|
| 1 | 13 | 11 |
| 2 | 12 | 7 |
| 3 | 12 | 13 |
| 4 | 11 | 16 |
| 5 | 11 | 24 |
| 6 | 11 | 14 |
| 7 | 11 | 14 |
| Average | 11.6 | 14.1 |
| Percent Recovery | 89 | 101 |

6. On the basis of these tests, the following statements may be made. In a single laboratory, using water column water from Chicago containing 9 mg TOC/l and 10 mg soluble TOC/l, the standard deviations were

± 0.8 mg/l and ± 3.7 mg/l respectively and the recoveries were 89 percent and 101 percent respectively.

7. Oil and Grease - Water Samples - The precision and recovery of the separatory funnel method of analysis for low levels of oil in water was also determined. Four replicate samples of interfacial water from the Chicago sampling site were analyzed for precision and for recovery. The results follow:

| <u>Sample</u> | <u>Oil and Grease mg/l</u> | <u>Oil and Grease, mg/l (Added 19.2 mg oil/liter)</u> |
|--------------------|--------------------------------|---|
| 1 | 0.4 | 20.8 |
| 2 | 2.0 | 24.8 |
| 3 | 4.2 | 18.0 |
| 4 | 5.0 | 14.8 |
| Average | 2.9 | 19.6 |
| Standard Deviation | 2.1 | -- |
| Percent Recovery | -- | 85 |

8. In a single laboratory, using a sample of interfacial water at a concentration of 3 mg oil/l, the standard deviation was ± 2 mg/l and the recovery was 85 percent.

9. Oil and Grease - Sediments - The precision and recovery for oil and grease analysis of fine grained sediments by the Soxhlet procedure was determined using sediment samples from Memphis. The results are listed below:

| <u>Sample</u> | <u>Oil mg/kg</u> | <u>Oil, mg/kg (Added 706 mg oil/kg)</u> |
|-----------------------|----------------------|---|
| 1 | 394 | 682 |
| 2 | 327 | 893 |
| 3 | 271 | 872 |
| 4 | 327 | 985 |
| 5 | 327 | 830 |
| Average | 329 | 852 |
| Standard Deviation | 44 | -- |
| Percent Recovery | -- | 82 |

10. In a single laboratory, using a sample of sediment from Memphis harbor containing 329 mg oil and grease/l, the standard deviation was ± 44 mg/l and the recovery was 82 percent.

Pesticide Analysis

Procedure

11. After extraction, the extracts were concentrated and interferences removed using cleanup procedures including Florisil column separation, silicic acid column separation, micro-alkali dehydrochlorination, and sulfur removal by reaction with elemental copper or mercury. Identification and quantitation were done using gas liquid chromatography with a ^{63}Ni electron capture detector. Derivation procedures and relative retention times on columns of different polarities were employed as confirming procedures. A flow diagram of the analytical scheme is shown in Figure B-1.

Extraction

12. Sediment samples - The thawed core sediment was mixed with anhydrous sodium sulfate (pre-extracted with acetone) in a mortar and pestle until a free-flowing state was achieved. The sample was then placed in glass extraction thimbles and extracted with 1:1 hexane-acetone mixture for 24 hr in a 250-ml Soxhlet apparatus operating at 8 to 10 cycles per hour. Hexane washings from the mortar and pestle were also placed in the Soxhlet. The 100-g aliquot used usually required three to four Soxhlets to accommodate the sample after mixing with the sodium sulfate. The extractants were combined and transferred with hexane washings to a Kuderna-Danish concentrator and concentrated to about 5 mls. The sample was passed through a 7-10 cm sodium sulfate column in preparation for Florisil cleanup.

13. Water samples - Chlorinated hydrocarbons were extracted from water samples by liquid-liquid partition. Two 1.0 liter aliquots were extracted by shaking with three 60-ml portions of 15 percent methylene chloride in hexane in a 2-liter separatory funnel. All solvent layers were passed through a 7-10 cm sodium sulfate column, collected in a Kuderna-Danish apparatus and concentrated to 1 ml. An exploratory injection was made to determine if further cleanup were necessary.

Removal of Interferences and Cleanup

14. Florisil Column Cleanup - A charge of activated Florisil (the weight of the charge was determined by its Lauric Acid Value according to Mills.²⁰) was placed in a Chromaflex column and settled by gentle tapping. A 1-cm layer of anhydrous sodium sulfate was added and 50 to 60 ml of petroleum ether was passed through the column. When the petroleum ether was about 5 mm from the sodium sulfate surface, the sample extract was transferred by a long stem funnel (with petroleum ether washings) to the column and eluted with the following mixed ethers at 5 ml/min. (NOTE: For both column chromatography procedures,

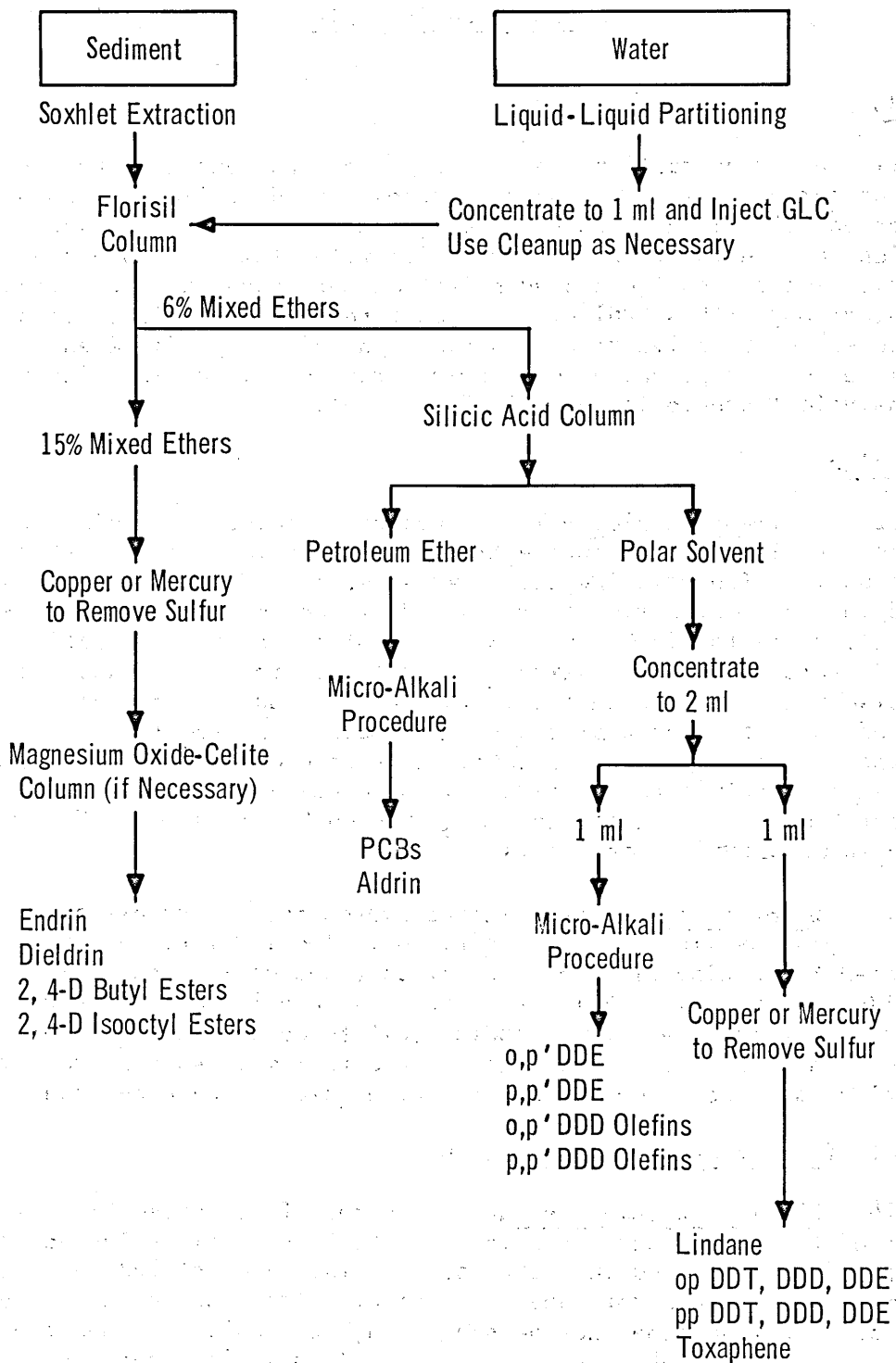


Figure B1. Flow diagram of the analytical scheme

the elution rate is important. To quickly adjust this rate, the lower part of a broken 25 ml burette equipped with a Teflon stopcock was placed between the Chromaflex column and the receiving vessel to make repetitive flow adjustments without losing eluate. See Figure B-2) The sample was washed through the column by first adding 200 ml of 6 percent (volume/volume) ethyl ether in petroleum ether followed by 200 ml of 15 percent (volume/volume) ethyl ether in petroleum ether. The first eluate (6 percent eluate) may be expected to contain aldrin, lindane, toxaphane, DDD, DDE, DDT, and PCBs. The second eluate (15 percent eluate) may be expected to contain endrin, dieldrin, and 2,4-D butyl esters.

15. Silicic Acid Column Separation Procedure - Celite 545 was oven dried and acid washed. Silicic acid was oven dried for a minimum of seven hr at 130°C to remove water. The silicic acid was cooled and weighted into a glass-stoppered bottle to which a small amount of water was added (3-g water/100-g silicic acid. The bottle was stoppered and shaken. Fifteen hr were allowed for equilibrium to occur. Separation achieved was determined as described below by loading 40 g of Aroclor #1254 and p,p'DDE in hexane on the column. Inadequate separation required readjustment of the water content of the silicic acid in recommended increments of 0.5 percent. More water was required when the DDE eluted in the petroleum ether portion. Standardization was required for each new lot of silicic acid purchased. Once a batch of silicic acid was hydrated, activity remained for about 5 days.

16. Five g of Celite and 20 g of silicic acid were weighed, and combined in a 250-ml beaker, and immediately slurried with 80 ml of petroleum ether. The slurry was transferred to the chromatographic column, with the stopcock kept open. The slurry in the column was stirred to remove air bubbles; then air pressure was applied to force the petroleum ether through the column. The column was not allowed to crack or go dry; the stopcock was closed when air pressure was not being applied. The flow was stopped when the petroleum ether level was 3 mm above the surface of the silicic acid.

17. Large amounts of PCBs or pesticides placed on the column would result in incomplete separation. The extracted sample placed on the column contained no polar solvents and was 5 ml in volume. A 250-ml volumetric flask was placed beneath the column and a suitable aliquot of the 6 percent Florisil eluate was added, taking care not to disturb the surface of the silicic acid. (A long-stem funnel was useful for this purpose.) Slight air pressure was applied until the solvent level was about 3 mm from the surface of the silicic acid. The 250-ml separatory funnel containing 250 ml of petroleum ether was carefully placed on the column, and the petroleum ether was allowed to run down the side of the column until the space above the silicic acid was half filled. Air pressure was applied and the flow rate was adjusted to 5 ml/min. When exactly 250 ml was collected, the volumetric flask was replaced with a 500-ml Kuderna-Danish flask and the pesticides eluted at a rate of 5 ml/min with 200 ml of methylene chloride, hexane, and acetonitrile (90:19:1).

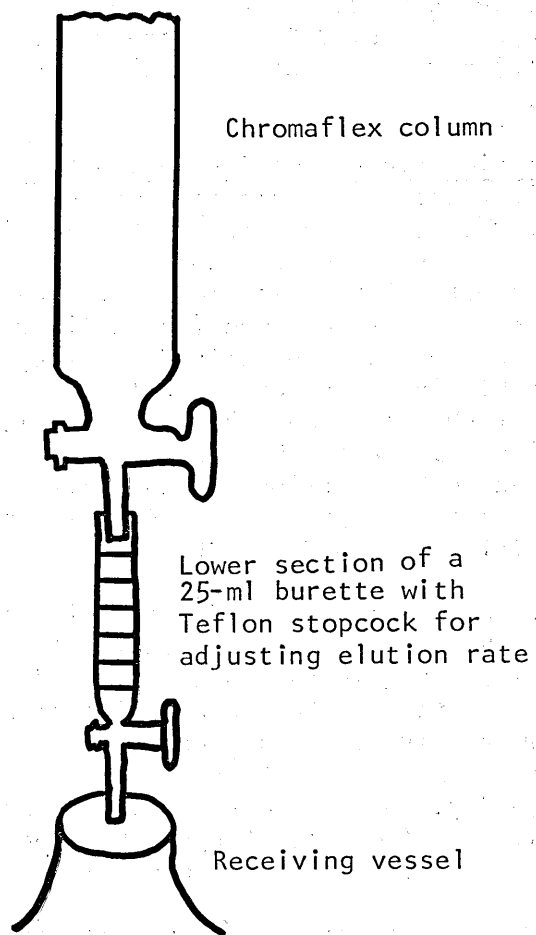


Figure B2. Drawing of a Recommended Procedure for Obtaining Proper Elution Rates

18. The petroleum ether eluate containing the PCBs was quantitatively transferred to a 500-ml Kuderna-Danish and both eluates were concentrated to 5 ml. The petroleum ether eluate contained aldrin and the following Aroclors: 1221, 1248, 1252, 1258, 1260, and 1262. The polar eluate (acetonitrile, methylene chloride, hexane) contained the o,p' and p,p' isomers of DDT, DDE, and DDT; toxaphane; and Aroclors 1221, 1242, and 1248. Aroclors 1221, 1242, 1248, 1252, and 1258 divided between the two eluates with the earliest eluting peaks in the polar eluate.

19. The separation between the PCBs and the p,p'DDE is very narrow; therefore great care was exercised in adjusting the elution flow rate and volume of the petroleum ether portion.

20. Sulfur Interference - Elemental sulfur is encountered in most sediment samples, marine algae, and some industrial wastes. The solubility of sulfur in various solvents is very similar to the organochlorine and organophosphate pesticides; therefore, the sulfur interference follows along with the pesticides through the normal extraction and cleanup techniques. The sulfur is quite evident in gas chromatograms obtained from electron capture detectors. If the gas chromatograph is operated at the normal conditions for pesticide analysis, the sulfur interference can completely mask the region from the solvent peak through p,p'DDE. Method (a) was used for sediments of very high sulfur content, while method (b) was used effectively for lower sulfur concentrations.

Method a. A small drop of metallic mercury was added to about 5 ml of the concentrated extract and shaken for 5 minutes. The mercury reacted with the sulfur forming mercury sulfide, a black precipitate. If the sulfur content was very high, both the silicic acid polar eluate and the Florisil 15 percent mixed ethers eluate required treatment.²¹

Method b. This technique eliminated sulfur by the formation of copper sulfide on the surface of the copper. There are two critical steps that were followed to remove all the sulfur: (1) the copper must be highly reactive; all oxides were removed so that the copper had a shiny, bright appearance; and (2) the sample extract was vigorously agitated with the reactive copper for at least one minute. It was usually necessary to treat both the 6 percent and 15 percent Florisil eluate with copper if sulfur crystallized out upon concentration of the 6 percent eluate.

21. If the presence of sulfur was indicated by an exploratory injection from the final extract concentrate (usually 5 ml) into the

gas chromatograph, removal proceeded as follows:

- a. Under a nitrogen stream at ambient temperature, the extract was concentrated in the concentrator tube to exactly 1.0 ml.
- b. If the sulfur concentration was such that crystallization occurred, 500 μl of the supernatant extract (or a lesser volume if sulfur deposit was too heavy) was carefully transferred by syringe into a glass-stoppered, 12-ml graduated, conical centrifuge tube. Five hundred μl of isooctane was added.
- c. About 2 mg of bright copper powder was added; the tube was stoppered and agitated vigorously 1 minute on a Vortex mixer. (Note: The copper powder as received from the supplier must be treated for removal of surface oxides with 6N HNO_3 . After about 30 seconds of exposure, decant off acid, rinse several times with distilled water and finally with acetone. Dry under a nitrogen stream.)
- d. Five hundred of the supernatant treated extract was carefully transferred to a 10-ml graduated evaporator concentrator tube. An exploratory injection into the gas chromatograph at this point provided information as to whether further quantitative dilution of the extract was required.
NOTE: If the volume transfers given above were followed, a final extract volume of 1.0 ml was of equal sample concentration to a 4 ml concentrate of the Florisil cleanup fraction.

22. Microalkali Treatment - The procedure outlined by Young and Burke²² was employed as both a chemical derivative-confirming technique and sample cleanup. The procedure, as described by Young and Burke, is listed in the following paragraphs.

23. One ml of 2 percent ethanolic KOH and a few carborundum chips were added to 2 ml of a petroleum ether solution of pesticides (suitable for subsequent GLC analysis) in a 10 ml-Mills tube. The tube was connected to a micro-condenser and heated over a steam bath so that gentle boiling occurred. When the volume was reduced to 1 ml, the tube was heated vigorously with steam for 15 min or until the volume was reduced to 0.2 ml and then removed from the steam bath. If the concentrated sample contained a precipitate, several drops of 2 percent potassium hydroxide in ethanol were added and the tube warmed gently until the precipitate was dissolved. After cooling the tube slightly, 2 ml of

1:1 ethanol-water mixture was added. The tube was cooled to room temperature and 1 or 2 ml hexane were added by pipet. The tube was stoppered and shaken vigorously 30 sec and the solvent layer allowed to separate. Separation of the phases should be sharp. An aliquot of the hexane layer was removed with a microliter syringe for GLC injection.

23. This method converts DDT to its DDE analogs, p,p'DDD to p,p'DDD olefin and o,p'DDD to cis and trans o,p'DDD olefin. Toxaphene and lindane peaks were completely altered. Endrin, dieldrin, and aldrin were recovered 70-90 percent and PCBs were recovered 100 percent. In addition the method removed many interfering substances (including sulfur) that interfered with chromatography.

24. Magnesium Oxide-Celite Column - The following procedure was used to aid in the cleanup of particularly contaminated sediments. It is a modification of the magnesium oxide-celite procedure outlined in the Pesticide Analytical Manual of the Food and Drug Administration²³ and the method described by Hughes, et al.²⁴

25. A column of approximately 2 cm height of a 1:1 mixture of magnesium oxide-celite 545 was formed in a 3.3 cm diameter glass extraction thimble with a medium fritted glass base. This column was pre-eluted with 50 mls of petroleum ether and placed between the Florisil column and the receiving vessel, allowing the 15 percent mixed ethers eluate to pass slowly through the magnesium oxide-celite. At an elution rate of 5 ml/min, the minicolumn built a 2 to 5-cm head of the eluting ethers above the surface of the column bed. Once the Florisil column and magnesium oxide column had drained, the magnesium oxide was rinsed with 30 to 50 mls of petroleum ether and the rinsings were added to the receiving flask. Sediment eluates so treated generally did not require treatment with mercury to remove elemental sulfur.

Gas Chromatographic Conditions

26. Instrument - Injections were made on a Barber-Colman Series 5000 gas chromatograph equipped with a ⁶³Ni electron capture detector. Coiled glass columns 183 cm long and 0.4 cm diameter were used. One column contained 3 percent OV-210 on Chromosorb W-HP (80/100 mesh) and the other contained 1.5 percent OV-17/1.95 percent QF-1 on Chromosorb W-HP (80/100 mesh).

27. Quantitation - The relative retention times of the sample peaks (relative to aldrin) were compared against the peaks produced by standards supplied by the EPA Pesticide and Toxic Substances Laboratory, Triangle Park, N.C. All pesticide and Aroclor standards, both working standards and stock standards, were prepared using 2, 2, 4 trimethyl pentane and stored in a freezer at -10°C when not being used. To be quantitated the chlorinated hydrocarbon of interest must

correspond to the proper relative retention time on both columns and appear in the proper chromatographic column eluate. Quantitation was done by comparing peak areas of known standards against those of the suspected substance using a Varian model 485 integrator or by triangulation. The quantity of chlorinated hydrocarbon material (in nanograms) so determined was then used to calculate concentrations in parts per billion according to the following formula:

$$\frac{\text{ng of pesticides x ml of extract}}{\mu\text{l injected x l of original sample}} = \mu\text{g/l}$$

$$\frac{\text{ng of pesticide x ml of extract}}{\mu\text{l injected x kg oven dry weight of sediment}} = \mu\text{g/l}$$

Recovery Data

28. Sediments - Composite sediment samples were analyzed in duplicate with one replicate spiked to determine recovery of the pesticides and PCBs of interest.

29. A 200-g aliquot of sediment (natural moisture content) was split in half; one half was analyzed according to the previously outlined procedure and the other half was spiked with known amounts of various pesticides made up in 2,3,4 trimethyl pentane. The concentrations were adjusted to allow microliter additions to the sediment using a 10 μl syringe, thus minimizing any solvent effect. After the addition of the pesticides, the sample was thoroughly mixed with a glass rod, covered with foil, and placed in a refrigerator for 4 to 10 days for equilibration. The sample was then analyzed by the method outlined. The values determined for chlorinated hydrocarbons, when present, in the unspiked sample were subtracted from those in the spiked sample and the result divided by the amount originally added. Some recovery tests were performed with toxaphene added at levels of 100 parts added toxaphene to 1 part added pesticide.

30. The results of the recovery tests are listed in Table B-1. Generally, recoveries of pesticides in the presence of high concentration of toxaphene were low. High toxaphene concentrations have not been found in the sediments analyzed in this project, however.

31. Recovery Data - Water Samples - A one-liter aliquot of Chicago water column water was spiked at appropriate levels with chlorinated hydrocarbons of interest. The chlorinated hydrocarbons were made from stock solutions using acetone as a bridging solvent. The samples were extracted by the method previously outlined immediately after spiking. The recovery data are presented in Table B-2.

Table B-1. Pesticide Recovery Data: Sediments

| Pesticide | Sample | Amount Added µg/kg | Equilization | | Recovery % | Average % | Literature Values % |
|------------------------|--------------|-----------------------|--------------|--|---------------|--------------|---------------------------|
| | | | Time days | | | | |
| Endrin | Chicago | 0.5 | 10 | | 80 | | About 90 |
| | Green Bay | 0.5 | 4 | | 92 | 74 | |
| | Fall River | 0.6 | 4 | | 50 | | |
| Dieldrin | Chicago | 0.5 | 10 | | 80 | | 61-90 |
| | Green Bay | 0.5 | 4 | | 65 | 80 | |
| | Fall River | 0.6 | 4 | | 96 | | |
| Lindane | Chicago | 0.2 | 10 | | 75 | 54 | 65-111 |
| | Fall River | 0.2 | 4 | | 33 | | |
| 2,4-D Bu- tyl Ester | Fall River | 5.0 | 4 | | 78 | -- | -- |
| Toxaphene | Fall River | 12.1 | 4 | | 83 | -- | 61-89 |
| Aroclor 1242 | Green Bay | 25 | 4 | | 110 | -- | -- |
| Aroclor 1254 | Chicago | 14 | 10 | | 96 | 96 | >80 |
| | Fall River | 30 | 4 | | 96 | | |
| p,p'-DDT, p,p'-DDE | Fall River** | 1.4 | 4 | | 50 | -- | -- |
| p,p'-DDT p,p'-DDE | Fall River** | 1.4 | 4 | | 73 | -- | -- |
| p,p'-DDT | Chicago | 1.6 | 10 | | 69 | 77 | 68-99 |
| | Green Bay | 2.8 | 4 | | 86 | | |
| o,p'-DDT | Chicago | 1.6 | 10 | | 93 | 91 | 77-111 |
| | Green Bay | 2.8 | 4 | | 90 | | |
| p,p'-DDE | Chicago | 1.6 | 10 | | 69 | 84 | 68-99 |
| | Green Bay | 1.4 | 4 | | 93 | | |
| o,p'-DDE | Chicago | 1.6 | 10 | | 93 | 94 | 77-111 |
| | Green Bay | 1.4 | 4 | | 95 | | |
| p,p'-DDD | Green Bay | 1.4 | 4 | | 85 | -- | -- |
| o,p'-DDD | Green Bay | 1.4 | 4 | | 83 | -- | -- |

* These values were obtained from the literature and reported by Chesters, Pionke, and Daniel²⁵

** Toxaphene added at a ratio of 100 parts to 1 part added pesticide.

Table B-2. Pesticide Recovery Data: Water

| <u>Pesticide</u> | <u>Amount Added µg/kg</u> | <u>Recovery %</u> |
|------------------------|-------------------------------|-----------------------|
| Endrin | 0.010 | 74 |
| Dieldrin | 0.010 | 81 |
| Lindane | 0.005 | 98 |
| 2,4-D butyl ester | 0.10 | 83 |
| 2,4-D iso-propyl ester | 0.10 | 67 |
| Aroclor 1254 | 0.50 | 67 |
| | 0.50 | 86 |
| p,p'-DDT | 0.02 | 108 |
| | 0.04 | 83 |
| p,p'-DDT | 0.04 | 113 |
| | 0.04 | 93 |
| p,p'-DDE | 0.02 | 105 |
| | 0.01 | 85 |
| o,p'-DDE | 0.01 | 85 |
| | 0.02 | 85 |
| p,p'-DDD | 0.04 | 88 |
| | 0.02 | 66 |
| o,p'-DDD | 0.04 | 80 |
| | 0.02 | 89 |

Appendix C

Results of Preliminary Work in Milwaukee Harbor

1. The work in Milwaukee Harbor was performed to test sampling procedures and to obtain samples for testing the planned laboratory procedures.

Test of Sampling Methods

2. It was originally intended that sediment samples would be taken using an Inter-Ocean piston core sampler. Tests in Milwaukee Harbor, however, showed that this sampler was unsatisfactory for the uncompacted type of sediments that were present. Observation of the sampler in operation by divers indicated that the slurry-like sediment was being lost from the sampler during retrieval, even though mechanically the sampler appeared to be functioning properly. The manual method using divers described in the Sampling Methods section of this report (paragraph 15) was used as a substitute method. This method allowed the samplers to have visual control of the sampler during penetration and retrieval. It also allowed the accurate comparison of penetration depth to sample core length for the determination of compaction occurring during sampling. This method of sampling was used at all locations tested except Memphis, where the high turbidity, currents, and possibility of snags made diving impractical and unsafe. A conventional gravity core sampler was successfully used instead.

Test of Laboratory Methods

3. Centrifugation was used to separate the interstitial water from the sediments. The Envirex centrifuge was not capable, however, of removing all the suspended solids; a large amount of colloidal material remained in suspension. Clarification procedures such as filtration and flocculation were considered and discarded because of the possibility of adsorption on filters and flocs. Arrangements were made with the University of Wisconsin-Milwaukee to use a high-speed centrifuge for the removal of suspended solids from interstitial water samples and equilibrium test effluents.

Results of Analysis

4. The results of the chemical analysis of the samples obtained from Milwaukee Harbor are listed in Table C-1. Results from the analysis of interstitial water and samples from equilibrium tests are not included because of the problem in removing suspended solids from the samples.

Table C-1. Chemical Characteristics of Milwaukee Harbor Samples

| <u>Characteristic</u> | <u>Harbor Water</u> | <u>Interfacial Water</u> | <u>Sediment Core*</u> | |
|-----------------------|---------------------|--------------------------|-----------------------|--------------------|
| | | | <u>Top Foot</u> | <u>Bottom Foot</u> |
| Total solids | -- | -- | 38.7% | 47.8% |
| Suspended solids | 7 mg/l | 1074 mg/l | -- | -- |
| TOC | 7 mg/l | 30 mg/l | 36,700 mg/kg | 9,800 mg/kg |
| Soluble TOC | 5 mg/l | 8 mg/l | -- | -- |
| Oil and grease | -- | -- | 9,550 mg/kg | 7,110 mg/kg |
| PCB | 0.01 µg/l | 1 µg/l | 6,420 µg/kg | 728 µg/kg |
| Aldrin-dieldrin | 0.01 µg/l | 0.1 µg/l | 0.1 µg/kg | 0.1 µg/kg |
| Endrin | 0.01 µg/l | 0.1 µg/l | 0.1 µg/kg | 0.1 µg/kg |
| t-DDT | 0.01 µg/l | 0.1 µg/l | 0.1 µg/kg | 0.1 µg/kg |
| Lindane | 0.01 µg/l | 0.1 µg/l | 0.1 µg/kg | 0.1 µg/kg |
| 2,4-D | 0.1 µg/l | 1 µg/l | 1 µg/kg | 1 µg/kg |
| Toxaphene | 0.1 µg/l | 10 µg/l | 10 µg/kg | 10 µg/kg |

* Concentrations reported in terms of weight of dry solids.

Appendix D

Water Temperatures and Dissolved Oxygen Measurements

Taken During Sampling of Sediments

| | |
|-----------|--|
| Table D-1 | Calumet Harbor Water Temperature and Dissolved Oxygen Measurements - August 8, 1974 |
| Table D-2 | Green Bay Water Temperatures and Dissolved Oxygen Measurements - September 9, 1974 |
| Table D-3 | Mt. Hope Bay Water Temperatures and Dissolved Oxygen Measurements - October 7, 1974 |
| Table D-4 | Tabbs Bay Water Temperatures and Dissolved Oxygen Measurements - January 30, 1975 |
| Table D-5 | Tennessee Chute Water Temperatures and Dissolved Oxygen Measurements - February 11, 1975 |

Table D-1. Calumet Harbor Water Temperature and
Dissolved Oxygen Measurements, August 8, 1974

| Water Depth,m | Temperature °C | | | | | Dissolved Oxygen, mg/l | | | | |
|------------------|----------------|-----------|-----------|-----------|-----------|------------------------|-----------|-----------|-----------|-----------|
| | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 |
| 0.30 | 21 | 22 | 22 | 22 | 22 | 8.7 | 8.6 | 8.2 | 8.6 | 8.4 |
| 0.61 | 21 | 22 | -- | -- | -- | 8.5 | 8.4 | -- | -- | -- |
| 0.91 | 21 | 22 | 21 | 22 | 22 | 8.4 | 8.3 | 8.0 | 8.6 | 8.3 |
| 1.22 | 21 | 21 | -- | -- | -- | 8.3 | 8.1 | -- | -- | -- |
| 1.52 | 21 | 21 | -- | -- | -- | 8.2 | 8.1 | -- | -- | -- |
| 1.83 | 21 | 21 | 21 | 21 | 21 | 8.1 | 8.0 | 7.9 | 8.6 | 8.3 |
| 2.13 | 21 | 21 | -- | -- | -- | 8.1 | 8.2 | -- | -- | -- |
| 2.44 | 21 | 21 | -- | -- | -- | 8.2 | 8.1 | -- | -- | -- |
| 2.74 | 21 | 21 | 21 | 21 | 21 | 8.0 | 8.2 | 7.6 | 8.4 | 8.1 |
| 3.05 | 21 | 21 | -- | -- | -- | 8.0 | 8.1 | -- | -- | -- |
| 3.35 | 21 | 21 | -- | -- | -- | 8.0 | 8.1 | -- | -- | -- |
| 3.66 | 21 | 21 | 21 | 21 | 21 | 7.9 | 8.0 | 7.6 | 8.1 | 8.0 |
| 3.96 | 21 | 21 | -- | -- | -- | 7.7 | 8.0 | -- | -- | -- |
| 4.27 | 21 | 20 | -- | -- | -- | 7.7 | 7.9 | -- | -- | -- |
| 4.57 | 21 | 20 | 19 | 20 | 20 | 7.7 | 7.7 | 7.4 | 7.1 | 7.7 |
| 4.88 | 20 | 19 | -- | -- | -- | 7.7 | 7.5 | -- | -- | -- |
| 5.18 | 20 | 19 | -- | -- | -- | 7.4 | 7.4 | -- | -- | -- |
| 5.49 | 18 | 19 | 19 | 19 | 19 | 7.1 | 7.3 | 7.3 | 6.7 | 7.6 |
| 5.79 | 18 | 18 | -- | -- | -- | 7.0 | 7.2 | -- | -- | -- |
| 6.10 | 18 | 18 | -- | -- | -- | 7.0 | 7.3 | -- | -- | -- |
| 6.40 | 18 | 18 | 18 | 18 | 18 | 7.0 | 7.3 | 7.2 | 6.7 | 7.3 |
| 6.70 | 17 | 17 | -- | -- | -- | 7.0 | 7.4 | -- | -- | -- |
| 7.01 | 17 | 17 | -- | -- | -- | 7.2 | 7.4 | -- | -- | -- |
| 7.31 | 17 | 17 | 17 | 17 | 18 | 7.1 | 7.4 | 7.2 | 6.7 | 6.8 |
| 7.62 | 17 | 17 | -- | -- | -- | 7.1 | 7.4 | -- | -- | -- |
| 7.92 | 16 | 17 | -- | -- | -- | 6.9 | 7.4 | -- | -- | -- |
| 8.23 | 16 | 17 | 17 | 17 | 17 | 6.9 | 7.4 | 7.0 | 6.7 | 6.7 |
| 8.53 | 16 | 17 | -- | -- | -- | 6.9 | 7.4 | -- | -- | -- |
| 8.84 | 16 | 17 | -- | -- | -- | 6.9 | 7.4 | -- | -- | -- |
| 9.14 | 16 | 16 | 17 | 17 | 17 | 6.9 | 7.3 | 0.8 | 6.8 | 5.2 |
| 9.45 | 16 | 16 | -- | -- | -- | 6.9 | 7.2 | -- | -- | -- |

Table D-2. Green Bay Water Column Temperature and
Dissolved Oxygen Measurements, September 9, 1974

| Water Depth,m | Temperature, °C | | | | | Dissolved Oxygen, mg/l | | | | |
|------------------|-----------------|-----------|-----------|-----------|-----------|------------------------|-----------|-----------|-----------|-----------|
| | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 |
| 0.30 | 22 | 21 | 21 | 21 | 22 | 5.7 | 6.0 | 6.2 | 6.5 | 9.0 |
| 0.61 | 21 | 20 | 20 | 21 | 21 | 5.7 | 5.0 | 5.4 | 6.2 | 8.0 |
| 0.91 | 21 | 19 | 20 | 21 | 21 | 5.5 | 4.6 | 5.3 | 5.9 | 6.8 |
| 1.22 | 21 | 19 | 20 | 21 | 20 | 4.7 | 4.6 | 4.8 | 6.1 | 6.8 |
| 1.52 | 19 | 18 | 20 | 21 | -- | 4.7 | 4.8 | 4.6 | 6.2 | -- |
| 1.83 | 19 | -- | 19 | -- | -- | 4.8 | -- | 4.5 | -- | -- |

Table D-3. Mt. Hope Bay Water Temperatures
and Dissolved Oxygen Measurements, October 7, 1974

| Water Depth,m | Temperature, °C | | | | | Dissolved Oxygen, mg/l | | | | |
|------------------|-----------------|-----------|-----------|-----------|-----------|------------------------|-----------|-----------|-----------|-----------|
| | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 |
| 0.30 | 16 | 16 | 16 | 16 | 15 | 7.2 | 7.1 | 6.5 | 6.8 | 7.0 |
| 0.61 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 0.91 | 16 | 16 | 16 | 16 | 15 | 7.2 | 7.1 | 6.6 | 6.8 | 7.0 |
| 1.22 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 1.52 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 1.83 | 16 | 15 | 16 | 16 | 16 | 7.2 | 7.2 | 6.2 | 7.0 | 7.0 |
| 2.13 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 2.44 | -- | 16 | -- | -- | 15 | -- | 7.2 | -- | -- | 7.0 |
| 2.74 | -- | -- | 16 | -- | -- | -- | -- | 6.2 | -- | -- |
| 3.05 | -- | -- | -- | 16 | -- | -- | -- | -- | 7.0 | -- |
| 3.35 | 16 | 16 | -- | -- | -- | 7.2 | 7.2 | -- | -- | -- |
| 3.66 | -- | -- | 16 | -- | 15 | -- | -- | 6.3 | -- | 7.1 |
| 3.96 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 4.27 | 16 | 16 | -- | 16 | -- | 7.2 | 7.4 | -- | 7.0 | -- |
| 4.57 | -- | -- | -- | -- | 15 | -- | -- | -- | -- | 7.0 |
| 4.88 | -- | -- | 15 | -- | -- | -- | -- | 6.4 | -- | -- |
| 5.18 | 16 | 15 | -- | 16 | -- | 7.5 | 7.3 | -- | 7.0 | -- |
| 5.49 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 5.79 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 6.10 | 15 | 15 | 15 | 16 | 15 | 7.6 | 7.4 | 6.7 | 7.0 | 7.2 |
| 6.40 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 6.70 | -- | 15 | 14 | -- | -- | -- | 7.6 | 6.7 | -- | -- |
| 7.01 | 15 | -- | -- | 15 | -- | 7.6 | -- | -- | 7.0 | -- |
| 7.31 | -- | -- | -- | -- | 14 | -- | -- | -- | -- | 7.6 |
| 7.62 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 7.92 | -- | -- | -- | 15 | -- | -- | -- | -- | 7.1 | -- |
| 8.23 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 8.53 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 8.84 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 9.14 | -- | -- | -- | 15 | -- | -- | -- | -- | 7.2 | -- |
| 9.45 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 9.75 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 10.06 | -- | -- | -- | 15 | -- | -- | -- | -- | 7.2 | -- |
| 10.36 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 10.67 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 10.97 | -- | -- | -- | 15 | -- | -- | -- | -- | 7.2 | -- |

Table D-4. Houston Water Temperature and Dissolved
Oxygen Measurements, January 30, 1975

| Water Depth,m | Temperature, °C | | | | | Dissolved Oxygen, mg/l | | | | |
|------------------|-----------------|-----------|-----------|-----------|-----------|------------------------|-----------|-----------|-----------|-----------|
| | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 |
| 0.30 | 19 | 19 | 19 | 20 | 20 | 10.6 | 11.0 | 10.6 | 10.6 | 10.6 |
| 0.61 | 18 | 19 | 19 | 20 | 20 | 10.7 | 11.0 | 11.0 | 10.8 | 10.9 |
| 0.91 | 18 | 19 | 20 | 20 | 20 | 10.8 | 11.0 | 11.2 | 11.0 | 11.0 |
| 1.22 | 18 | 18 | 20 | 19 | 20 | 10.8 | 11.1 | 11.2 | 11.0 | 11.0 |
| 1.52 | 18 | 18 | -- | 19 | 20 | 10.8 | 11.2 | -- | 11.0 | 11.1 |
| 1.83 | 18 | -- | -- | -- | 20 | 10.8 | -- | -- | -- | 11.1 |

Table D-5. Memphis Water Temperatures and
Dissolved Oxygen Measurements, February 11, 1975

| Water Depth m | Temperature °C | | | | | Dissolved Oxygen, mg/l | | | | |
|---------------------|----------------|-----------|-----------|-----------|-----------|------------------------|-----------|-----------|-----------|-----------|
| | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 |
| 0.30 | 7.5 | 7.0 | 7.0 | 4.5 | 4.5 | 8.2 | 8.8 | 11.6 | 10.8 | 10.7 |
| 0.61 | 7.0 | -- | -- | -- | -- | 8.8 | -- | -- | -- | -- |
| 0.91 | 6.5 | -- | -- | -- | -- | 9.2 | -- | -- | -- | -- |
| 1.22 | 6.0 | -- | -- | -- | -- | 9.2 | -- | -- | -- | -- |
| 1.51 | 6.0 | 6.5 | 5.0 | 4.5 | 4.5 | 9.5 | 9.6 | 10.8 | 10.8 | 10.8 |
| 1.83 | 5.5 | -- | -- | -- | -- | 9.8 | -- | -- | -- | -- |
| 2.13 | 5.5 | -- | -- | -- | -- | 9.9 | -- | -- | -- | -- |
| 2.44 | 5.0 | -- | -- | -- | -- | 10.0 | -- | -- | -- | -- |
| 2.74 | 5.0 | -- | -- | -- | -- | 10.1 | -- | -- | -- | -- |
| 3.05 | 5.0 | 5.0 | 5.0 | 4.5 | 4.5 | 10.2 | 9.8 | 10.7 | 10.8 | 10.7 |
| 3.35 | 4.5 | -- | -- | -- | -- | 10.3 | -- | -- | -- | -- |
| 3.66 | 4.5 | -- | -- | -- | -- | 10.4 | -- | -- | -- | -- |
| 3.96 | 4.0 | -- | -- | -- | -- | 10.4 | -- | -- | -- | -- |
| 4.27 | 4.0 | -- | -- | -- | -- | 10.4 | -- | -- | -- | -- |
| 4.57 | 4.0 | 5.0 | 4.0 | 4.0 | 4.5 | 10.4 | 10.0 | 10.6 | 10.8 | 10.7 |
| 4.88 | 4.0 | -- | -- | -- | -- | 10.5 | -- | -- | -- | -- |
| 5.18 | 4.0 | -- | -- | -- | -- | 10.5 | -- | -- | -- | -- |
| 5.49 | 4.0 | -- | -- | -- | -- | 10.6 | -- | -- | -- | -- |
| 5.79 | 4.0 | -- | -- | -- | -- | 10.6 | -- | -- | -- | -- |
| 6.10 | 4.0 | 4.5 | 4.0 | 4.0 | 4.5 | 10.6 | 10.1 | 10.6 | 10.8 | 10.7 |
| 6.40 | 4.0 | -- | -- | -- | -- | 10.6 | -- | -- | -- | -- |
| 6.70 | 4.0 | -- | -- | -- | -- | 10.6 | -- | -- | -- | -- |
| 7.01 | 4.0 | -- | -- | -- | -- | 10.6 | -- | -- | -- | -- |
| -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 7.62 | -- | 4.5 | 4.0 | 4.0 | 4.5 | -- | 10.2 | 10.8 | 10.8 | 10.6 |
| -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 9.14 | -- | 4.0 | 4.0 | 4.0 | 4.5 | -- | 10.3 | 10.8 | 10.8 | 10.6 |
| -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 10.67 | -- | 4.0 | 4.0 | 4.0 | 4.5 | -- | 10.4 | 10.8 | 10.8 | 10.6 |
| -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 12.2 | -- | -- | -- | 4.0 | 4.0 | -- | -- | -- | 10.8 | 10.5 |

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