

DREDGED MATERIAL RESEARCH PROGRAM



CONTRACT REPORT D-76-7

EFFECT OF SEDIMENT ORGANIC MATTER ON MIGRATION OF VARIOUS CHEMICAL CONSTITUENTS DURING DISPOSAL OF DREDGED MATERIAL

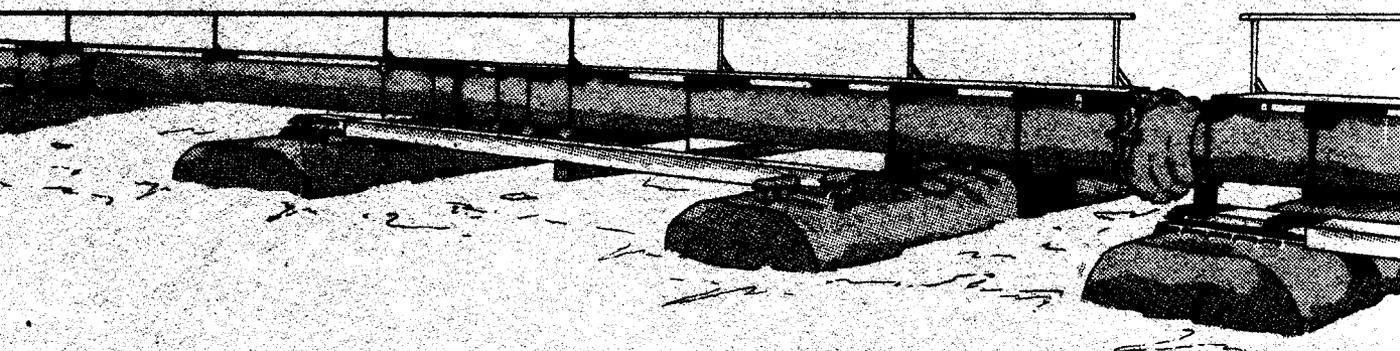
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May 1976

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Under Work Unit IC03

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SUBJECT: Transmittal of Contract Report D-76-7

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1. The contract report transmitted herewith represents the result 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 part of the Environmental Impacts and Criteria Development Project (EICDP) of the DMRP. Among other considerations, an objective of the EICDP is to determine, on a regional basis, the short- and long-term effects on water quality as a consequence of the disposal of dredged material containing a wide variety of chemical contaminants.
2. This research was conducted as Work Unit 1C03 to evaluate the direct and indirect effects of sediment organic fractions on the migration of various chemical constituents during the aquatic disposal of dredged material. This effort was undertaken because sediment organic matter, which is composed of various chemical groups such as humic acids, fulvic acids, carbohydrates, proteins, and petroleum hydrocarbons, is capable of complexing with heavy metals and nutrients. Thus, the aqueous phase concentrations, mobility, availability, and toxicity of heavy metals, nutrients, and other organic constituents may potentially be altered by the discharge of dredged material containing organic matter.
3. Results of this laboratory study with freshwater and marine sediments demonstrated the variability that can occur in the composition of sediment organic matter and that manganese, ammonia, and low levels of ortho-phosphate and cadmium may migrate into the water column. However, there is no evidence to suggest that either total sediment organic carbon or soluble organic carbon directly controls the release of either metals or nutrients even though labile organic ligands were indicated to be present in all samples.
4. The study indicated that sediment organic carbon and soluble organic matter would not be anticipated to have a demonstrable effect on water quality as a result of dredged material disposal unless high quantities of petroleum hydrocarbons were present in the sediments. Additionally, the numerical product of the sediment organic carbon content and the sediment organic nitrogen content (Sediment Organic Index) was useful in predicting the release of ammonia nitrogen from dredged material.

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However, the release of other metals and nutrients from sediments during leaching studies and elutriate tests was not related to any measured sediment parameter.

5. The study results are particularly important in evaluating the water-quality impacts of aquatic disposal of sediments containing high levels of organic matter. To assess these effects, regional information is needed on the quality of the dredged material, methods of disposal, and the nature of the aquatic media in which they are deposited. In addition, fundamental information is needed on the contaminant-to-sediment attachment mechanisms. Finally, methods need to be developed to predict, prior to the dredging and disposal operations, the nature and significance of the effect of the operation on water quality.



G. H. HILT

Colonel, Corps of Engineers
Director

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The disposal of both freshwater and saltwater sediments in open waters has been experimentally investigated in the laboratory. The emphasis of the experimental work was directed towards identifying the role that sediment organic carbon has in controlling various water-quality parameters at disposal sites. Long-term studies examined the possibility of transport of material from sediments into an overlying water column as well as monitoring the changes in the aqueous phase which initially contained large amounts of suspended matter. For the latter case, metal and nutrient concentrations were initially high but		

decreased significantly with time. Exceptions to this behavior were noted.

Specific components were identified which migrated from the sediment into the water column. They include ammonium-nitrogen, orthophosphate, cadmium, and manganese, the latter only in seawater media. Organic carbon and inorganic nitrogen underwent transformations with the systems investigated.

Both sediment organic carbon and soluble organic matter were generally found to have no demonstrable effect on water quality. Exceptions to this general conclusion were found in two sediments containing significant amounts of petroleum hydrocarbons.

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EXECUTIVE SUMMARY

The chemistry of dredged material (sediments) is quite complex and poorly understood. Preliminary laboratory studies simulating open-water disposal operations are necessary to give guidance to Corps personnel planning field experiments. One component requiring investigation is the organic matter associated with sediments. The concept that organic matter may potentially influence water quality at the disposal site is partially derived from the important role of soil organic matter in regulating concentrations of metal ions via chelation. Sediment organic matter may also play a significant role in the control of nutrients such as nitrogen and phosphorus.

A review of the literature has been conducted to determine what is known about sediment organic matter. Areas specifically addressed include the physical/chemical nature of sediment organic matter and metal-organic interactions. For the latter, the majority of experimental research has been conducted using organic material derived from soils. Some data is available on naturally occurring, water-soluble organic material.

Experiments were conducted to determine what would occur when sediments were initially mixed with deoxygenated water (a modification of the elutriate test), and whether sediments, placed in a new environment typical of what might be encountered in the field (10°C, 4-6 ppm dissolved oxygen, dark), would release materials into an overlying water column. The possibility of metals being complexed by solutes present

in the various aqueous phases was examined. Other experimental work was conducted to obtain additional information concerning the physical and chemical nature of the soluble organic matter found in sediment interstitial water.

Three different sediments from New York Harbor and three different sediments from the Great Lakes region were selected. In addition to evaluating the placement of the New York sediments in seawater and the Great Lakes sediments in fresh water, the latter sediments were also placed in seawater to simulate the effect of disposal site water salinity on less brackish sediments.

The results of the experiments indicate that the appearance of organic carbon in the water at the time of disposal or, with time, in the newly formed interstitial water is independent of total sediment organic-C. In general, nutrients and metals which are released into these same phases do not correlate with total soluble organic-C. An exception to this general finding may be in the case of lead and chromium in interstitial waters of freshwater systems. Nutrients and metals released may, however, be potentially related to specific soluble organic-C species. By selecting such diverse sampling locations, it had been anticipated that differences in the compositions of the sediment organic matter would be manifested in simulated disposal site water-quality parameters. For the majority of cases however, these measured parameters did not differ significantly from sediment to sediment and in no case was there a correlation with soluble organic-C. Two sediments

contained significant amounts of petroleum derived hydrocarbons. These same sediments also exhibited behavior with regards to soluble iron, phosphorus, rate of nitrification, and copper complexing capacity differing significantly from the other sediments. Lack of sufficient data precludes delineating a specific cause/effect relationship in the case of these two sediments, if one truly exists. Other sediments containing such hydrocarbons should be examined in order to determine if the observations are site specific or, if in fact, petroleum hydrocarbons can alter sediment behavior.

The fate of soluble organic-C released at the time of dredged material disposal is not entirely clear. Under the experimental constraints used (10°C, dark, open to atmosphere), conversion of organic-C to inorganic-C is suggested. Not all organic-C is transformed, however. This may be a result of the remaining organic-C being chemically resistant to further change, equilibrium considerations, or concentration dependent kinetic phenomena. Transport of organic-C from the sediment to the overlying water column (10°C, dark, 4-6 ppm dissolved oxygen) was not found but could easily have been masked by transformations from organic-C to inorganic-C.

Differences were found to exist between soluble organic species found in sediment interstitial waters. However, no conclusive evidence has been found to suggest that such differences are significant in their effect on disposal site water quality. It is concluded that sediment organic carbon, viewed as a distinct, homogeneous component of sediments,

has no discernible beneficial or detrimental effects on disposal area water quality. Hence, its absence or presence should not be of critical concern in formulating disposal criteria.

If receiving waters are oxygen deficient, or become so at the time of dredged material disposal, significant amounts of metals will be released into the water column. However, the actual concentrations of metals will remain below current water-quality criteria except potentially in the case of freshwater receiving locations. As the water becomes more oxidizing with time, the majority of these metal concentrations will fall off substantially except for manganese in seawater media. In the newly formed interstitial water, all metals will become enriched, sometimes quite substantially. Only with manganese in seawater media and, to a significantly lesser extent, cadmium in both freshwater and seawater media is transport from the sediment to the overlying water column suggested.

Ammonium nitrogen ($\text{NH}_4\text{-N}$) is released at substantial levels by all sediments in all receiving waters at the time of disposal. Nitrification will take place in freshwater sediments dispersed in freshwater but not in freshwater sediments dispersed in seawater. This is most likely due to osmotic damage to the nitrifying bacteria. Ammonium-N released by saltwater sediments dispersed in seawater will undergo nitrification although nitrification rates appear significantly affected by the nature of the original sediment. Ammonium-N is formed in the new interstitial water and is, in a number of cases, transported into the

overlying water column. Subsequent nitrification of this $\text{NH}_4\text{-N}$ is indicated. Nitrate-nitrogen can apparently be assimilated by bacteria in the sediment.

Only in the case of $\text{NH}_4\text{-N}$ released upon initial contact with the receiving water was a relationship found between the amount released and a sediment parameter. This sediment parameter was the Organic Sediment Index and is defined as the product of sediment organic carbon and sediment organic nitrogen. This is an empirical parameter with as yet no theoretical basis.

The release of ortho-phosphate at the time of disposal is generally low (except for the two petroleum-containing sediments) and these concentrations decrease with time. This is probably due to precipitation and/or sorption reactions and appears predominantly governed by iron. Ortho-phosphate increases in the interstitial water with time and is transported into the overlying water column.

The presence of metal complexing agents in the waters is indicated. Their nature (organic, inorganic, colloidal, soluble) as well as their importance could not be determined.

FOREWORD

The work described in this report was sponsored by the U. S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi, Dredged Material Research Program under Task 1C, "Effects of Dredging and Disposal on Water Quality," Work Unit 1C03, "The Effects of Sediment Organic Matter on the Migration of Various Chemical Constituents During Disposal of Dredged Material." The research was performed by the U. S. Army Cold Regions Research and Engineering Laboratory (USACRREL), Hanover, New Hampshire, during the period from February 1974 thru February 1976.

The report is the result of experimental work performed to assess the role soluble organic matter (associated with sediments) has in controlling metal and nutrients at disposal sites. A brief review of the literature on naturally occurring soluble organic matter and metal-organic interactions in aquatic environments is included.

The research was conducted under the supervision of Dr. B. E. Blom, Research Chemist, Earth Sciences Branch, USACRREL. Dr. R. P. Murrmann assisted in the planning and supervision of the project. Mr. T. F. Jenkins and Mr. D. C. Leggett assisted in the planning as well as in the experimental area. Mr. L. Gatto assisted in selecting sampling sites and was responsible for obtaining the sediments. Technical assistance was provided by Ms. L. Bos, Ms. V. Boyle, and Sp/4 W. Hannel. Mr. M. Hutton provided the X-ray analyses.

The research was monitored by Dr. C. R. Lee under the direct supervision of Dr. R. M. Engler, Project Manager, and the general supervision of Dr. J. Harrison, Chief, Environmental Effects Laboratory, WES.

The Director of WES during the study and preparation of this report was COL G. H. Hilt. Technical Director was Mr. F. R. Brown.

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

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

<u>Multiply</u>	<u>By</u>	<u>To Obtain</u>
feet	0.3048	metres
miles (U. S. statute)	1.609344	kilometres
cubic yards	0.7645549	cubic metres
pounds (force) per square inch	6.894757	kilopascals

EFFECT OF SEDIMENT ORGANIC MATTER ON
MIGRATION OF VARIOUS CHEMICAL CONSTITUENTS
DURING DISPOSAL OF DREDGED MATERIAL

I. INTRODUCTION

A. Need for Corps Research

In recent years the Corps of Engineers has dredged an average of 380,000,000 cu yd^{*} of sediment annually from the nation's waterways. Approximately 65% of this material is transferred to various streams, lakes, and coastal waters throughout the nation in a technique which has been commonly referred to as open-water disposal. The remainder of the material, due to economic considerations and/or legal restraints, is dispersed on land or in physically contained areas in or adjacent to waterways. It is generally acknowledged that in the majority of situations, placement in open water is an advantage for economic reasons. However, there have been objections to the open-water method (i.e., it has been banned by Michigan in the Great Lakes region) and the Corps has therefore had to store dredged materials by placing them in diked areas at considerable additional cost. Other locations are also faced with making decisions regarding selection of alternative techniques for handling dredged materials. The elutriate test, discussed in a later section, was developed by the Corps of Engineers and the Environmental Protection Agency (EPA) to determine the potential pollution status of

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

dredged materials from the standpoint of suitability for placement at open-water sites. The Corps Dredged Material Research Program is currently determining the chemical, physical, and biological effects of open-water placement of dredged materials. One goal is the refinement of the elutriate test to enable accurate prediction of the environmental consequences of open-water placement. The objective of this study is to determine if organic materials associated with sediments have a role in the control of potential pollutants disposed of in open waters.

B. Dredging Operations in Relationship to Problem

It is well recognized that sediments act as "sinks" for various chemicals soluble in water. Thus, for example, if a large dose of zinc is discharged into a waterway, a significant fraction would eventually associate with the sediment. Schroder (1) reported that the waters adjacent to a battery factory contained 2 ppm cadmium while the sediment contained 24% cadmium. During dredging, sediment is picked up and transported to a new location. There is some temporary disturbance in the water quality at a dredging site but because of dynamic equilibria the water probably returns to its original state. However, a different situation may develop if sediment is deposited at an open-water site where the water chemistry is far different from that of the overlying water at the original dredge site. The dredged material can be thought of as consisting of two phases, one liquid (interstitial water as well as some dredging site water) and the other solid. When the material is

placed in open water, the liquid phase in most cases rapidly mixes with the water at the site. The solid phase itself can be further divided into two classes based on particle size. The very small (colloidal) particles settle slowly, if at all, and may travel via diffusion and/or convection some distance from the site. Hence, chemicals associated with these particles may eventually become available for the biota. The larger particles settle to the bottom to form a new sediment interface. Here, chemicals may be released over a period of time as the new sediment interacts with the surrounding water by dissolution, ion exchange, desorption, and biological processes.

Whether any or all of these possibilities cause beneficial or detrimental effects on water quality and biota is dependent on many factors, some of which have not been completely assessed at this time.

C. Objectives of Study

One of the factors that is not well understood is the role of the sediment organic fraction. Scientists have long known that although both the inorganic and organic constituents of soils and sediments can bind metals, the naturally occurring organic fraction usually has several times the metal binding capacity of the inorganic constituents on a unit weight basis. In sediments this organic fraction is composed of various types of chemical compounds such as humic acids, fulvic acids, carbohydrates, proteins, petroleum hydrocarbons, etc., some of which are potentially capable of complexing (chelating) metallic ions. If the organic compounds are water soluble, then the net effect of soluble

complex formation may be to increase the apparent solubility of a metallic element. Chelation of metal ions can also reduce the free metal ion concentration which may then have an effect on the bioavailability of such contaminants. Metallic ions may also be associated in a similar way with insoluble organic materials. This could act to reduce free metal ion concentrations in solution with a concurrent increase in the metal concentration in the sediment. Alternatively, metallic ions can be bound to suspended colloidal matter which then acts as a carrier during dispersion of sediments at dredging and disposal sites. The chemical stability of the organic chelates varies widely depending on the strength of the specific organo-metallic bond. The equilibrium between the free ion and complexed forms depends on local factors such as metal ion and soluble organic concentrations, colloidal minerals, salt concentrations, pH, and temperature. The biodegradability of the complexes also varies with the nature of the organic matter and the stability of the complex. The biological effects of the free metals may differ considerably from those of complexed forms. In addition to complexing metals, organic substances may alter availability of nutrients such as phosphate and the various forms of nitrogen. Phosphorus and nitrogen are an integral part of the molecular structure of many forms of soluble organic substances which are energy sources for biological organisms. Thus, when solution/sediment and biological conditions are altered during dredging operations, release and/or uptake of soluble metals and nutrient chemicals can be expected to occur.

In order to plan further research, to develop first generation field studies, and to provide an interim guide for Corps of Engineers Environmental Impact Assessments relative to dredging operations, a thorough laboratory study and analytical characterization of the effects of sediment organic fractions on water quality is needed.

II. REVIEW OF LITERATURE

A. Introduction

Although insoluble organic matter plays a significant role in immobilizing metallic ions, soluble organic species could have the reverse effect of increasing solubility. Previously immobilized metal ions might thus become potentially bioavailable. Whether an equilibrium exists between the insoluble and soluble organic species or whether there is a net flux from one form to another is not known. All that can be said definitively is that organic compounds potentially capable of binding metals exist in soluble and/or colloidal form in most aquatic environments. They are not unique to dredged materials.

The types of soluble organic compounds identified in natural waters will be briefly reviewed. The role of metal-organic complexes will be discussed as will analytical techniques for their characterization.

B. Organics in Natural Water Systems

The organic material found in natural waters originates from both natural as well as synthetic sources. Vallentyne (2) and Croll (3) discuss various classes of compounds as well as certain species that have been identified in natural waters. One can reasonably conclude

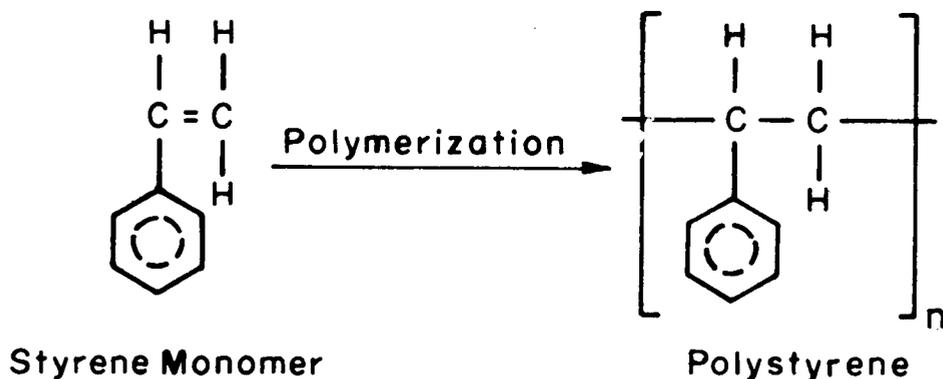
that given a sensitive and selective enough analytical procedure almost any specific organic compound might be found in a given water body.

Identification of specific compounds is necessary only for detection of potentially toxic chemicals (e.g. pesticides and carcinogens) or as an aid in identifying whether a particular industry is polluting a water body. As will be discussed later, it is a particular class of organic compounds that has more significance from the standpoint of organo-metallic interactions.

The stability of organics in water is discussed by Dayhoff (4). From a thermodynamic viewpoint very few of the soluble organic compounds found in natural waters are stable. The degradation of these compounds requires oxygen and would therefore be expected to deplete dissolved oxygen levels in water (5). However, Williams (6) states that dissolved organic carbon in the oceans is old, having a turnover time of approximately 3400 years, and is, in the practical sense, chemically and biologically inert. The chemical inertness to which he refers is no doubt the lack of further degradation of the molecule and not its ability to complex metals. The conclusion to be drawn from the available information is that chemical and biological degradation over a period of time seems to regulate the amount of organics found in waters. A true equilibrium does not exist in the thermodynamic sense of the word. Rather, a steady state may exist between the input of new organics and the removal of the "older" species. Thus, in a chemically and biologically active area, the organic components do not build up to intolerable levels. There

are, of course, areas where the lack of the proper chemical and biological requirements has resulted in concentrations of both natural and synthetic organics so high as to be a pollution problem in themselves. Typical aqueous organic carbon levels range from several parts per billion to perhaps several hundred parts per million in highly contaminated areas.

Historically, the first indication of the significance of organic material in water originated with studies done on lakes that were colored, generally yellow, and contained anomalously high amounts of iron (7-16). Such waters generally have an organic content of 10-30 parts per million (6,22). Much of the yellow color is due to a material, often referred to as fulvic acid, which is a group of naturally occurring polymeric molecules, containing carbonyl, hydroxyl, and carboxylic acid functional groups capable of interacting with metals. Synthetic polymers, such as polystyrene, consist of repeating monomer units:



where "n," the number of monomer units comprising the particular polystyrene molecule, is variable. Values of "n" can range from less than one hundred to several thousand depending on the conditions under which

the polymerization was carried out. With fulvic acids, and their parent humic acids, no identifiable monomer unit has yet been found due to the lack of information regarding their structures. It is unlikely that a repeating monomer unit in these natural polymers exists which is independent of the source of the original material.

The names humic and fulvic acid are commonly used by soil scientists but do not indicate well defined chemical structures. Figures 1 and 2 (17) show a fractionation scheme and possible origin of these types of materials respectively. Fulvic acid is considered by many investigators to be humic acid which has been degraded into smaller and more water soluble molecules. As indicated in Figure 2, oxidative degradation results in an increase in the number of oxygen functional groups which account for the increase in exchange acidity (and potential metal binding capacity) and the lower carbon content on a unit weight basis. Generally, the humic acids would be associated with the sediment phase and are removed from the sediment by extraction with base. Fulvic acids associated with the solid phase would also be removed in this process. The majority of soluble humic materials found naturally in water will generally be fulvic acids because of their higher solubility. Some humic acid can also be expected to be present. Non-humic substances, both natural and synthetic, can potentially appear in the humic acid or fulvic acid fractions solely on the basis of their particular chemical behavior. In general they would be expected to be less complex in structure and lower in molecular weight than the humic materials.

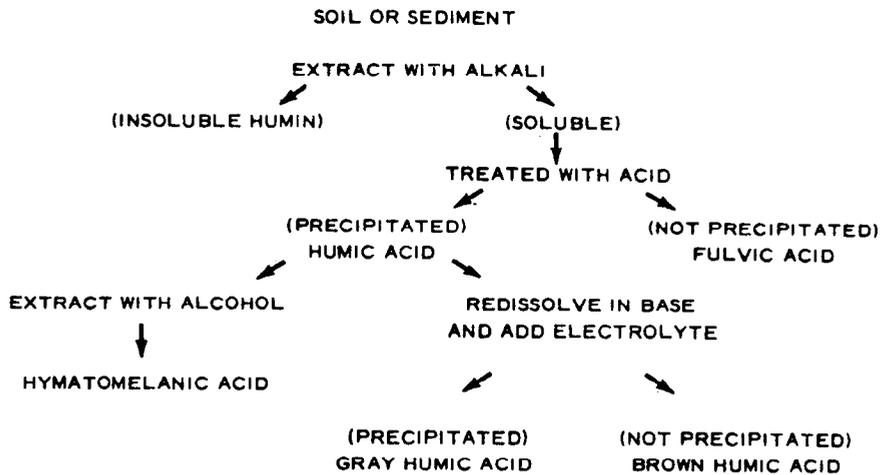


Figure 1. Fractionation of humic substances

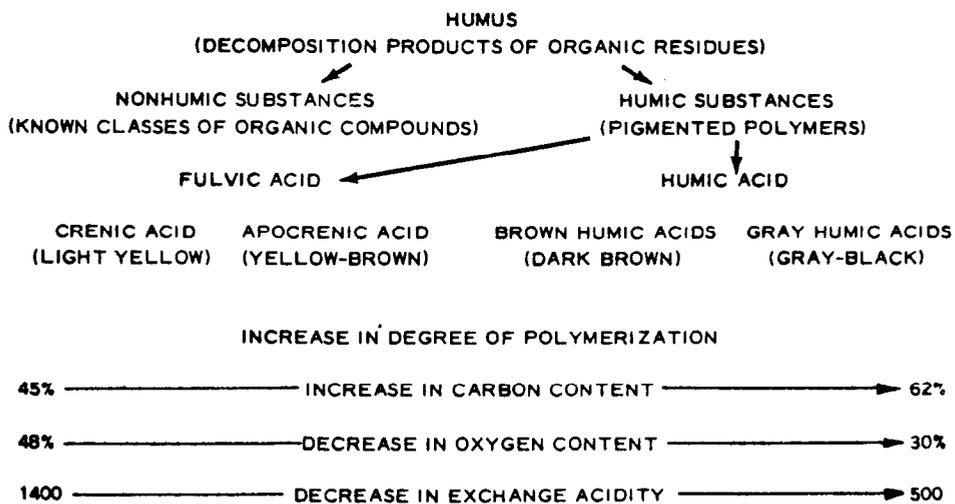


Figure 2. Classification of humic substances

Because humic materials are recognized chelating agents found in natural waters, and are generally the most abundant of the naturally occurring organics, the emphasis of the research has been directed towards these materials. Proteins, enzymes, and amino acids are examples of naturally occurring non-humic substances that are to be found in natural aqueous systems and are also capable of complexing metals. For example, leucine, an amino acid, if present in sufficient quantities, was able to reduce, apparently by forming soluble metal complexes, the adsorption of cobalt and zinc by sediments; however, it was concluded that at natural leucine concentrations in seawater, leucine by itself would not be significant in controlling the distribution of metals (23). The fact that there may be other organic compounds present in water during dredging operations, suggests that the total concentration of chelating agents may potentially be sufficient to have some regulatory effect on metal ion concentrations. Low molecular weight synthetic organic compounds that are introduced during dredging operations are generally thought to be rapidly degraded relative to the natural compounds. Some of the organic compounds may be chemically classified as surfactants because they have an affinity for the air-water interface and thus can become concentrated at the surface. Potential contaminants, such as metals associated with these surfactants, might therefore be concentrated at the air-water interface (24).

As indicated in Figure 2 humic materials are decomposition products of higher organic forms and can thus be found in almost any water source.

Some differences between humic materials from various environments have been noted. For example, Sieburth and Jensen (18) found that freshwater humic materials precipitated rapidly in a seawater environment. Whether this is due to ionic strength or solubility considerations, as contrasted with differences in humic structure due to origin, is not clear. Rashid and King (19) found marine organic matter to have a higher carbonyl content when compared to soil organic matter. Ishiwatari (20) on the other hand found little difference in the chemical composition and spectra of humic materials derived from marine and lake sediments. Further information on the nature of humic materials may be found in Schnitzer and Khan (21) and Jellinek (17).

C. Organo-Metallic Complexes in Natural Water Systems

(1) Introduction

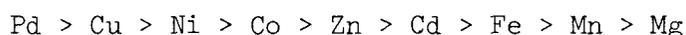
The existence of organo-metallic species and of organic chelating agents, both soluble and insoluble, in natural waters is often postulated. The possibility of such species existing may be highly dependent upon the quantity and type of inorganic species present. High levels of common cations can compete with trace metals for the organic chelating agents while the inorganic anions can serve to complex the metals. For systems in which heavy metal-organic interactions might be of significance, it is still not known whether these organic species are present as molecular entities in true solution or are primarily present as colloidal particles, or both. Regardless of the form or forms in which they may exist, their significance with regards to water quality is not well

understood. Rashid and Leonard (25) have shown that in the presence of humic substances, metal ions remain in solution in chemical environments which should cause them to precipitate. Thus, one might expect that the presence of soluble chelating agents might cause metals to remain in solution and thus be more biologically active and/or mobile in the environment. Shaw and Brown (26) demonstrated that the toxicity of copper to rainbow trout was reduced in the presence of NTA (nitrilotriacetic acid), a synthetic chelating agent. Chelating agents are often used to solubilize those metals whose inorganic salts would normally be considered insoluble while simultaneously maintaining low, free metal ion concentrations. Wood (27) has discussed the effect that some micro-organisms have on metals with special regard to the formation of alkyl-metals such as methylmercury. Based on the aqueous stability of methyl-metal compounds, he concludes that tin, palladium, platinum, gold, and thallium are potentially hazardous while cadmium, zinc, and lead are not, due to the instability of their alkyl forms in water. While a full discussion of the biological fates of metals is not within the scope of this study, it should be emphasized that biota can and will participate in the determination of the long-term fate of various heavy metals. One of the primary concerns in this study with regard to heavy metals is what role soluble organics have on complexation.

It was stated in the section on organics in natural waters that it is not so much small amounts of individual, identifiable organic compounds, such as leucine, that are of importance, rather, it is the

overall chemical class of compounds which is capable of complexing metals which is of primary concern. Because of their resistance to degradation, humic materials are often found to be the major constituent of both soluble and insoluble organics, and it is the metal-organic chemistry of these materials which is, therefore, of concern.

Irving and Williams (28) predicted that the stability of divalent metal ion complexes would follow the order:



Using soil fulvic acid Schnitzer and Skinner (29) found the stability series to be: (K_S = stability constant)

	$\text{Cu} > \text{Fe} > \text{Ni} > \text{Pb} > \text{Co} > \text{Ca} > \text{Zn} > \text{Mn} > \text{Mg}$	(0.1N KCl; pH=3.5)
log K_S	5.78 5.06 3.47 3.09 2.20 2.04 1.73 1.47 1.23	

and,

	$\text{Cu} > \text{Pb} > \text{Fe} > \text{Ni} > \text{Mn} \approx \text{Co} > \text{Ca} > \text{Zn} > \text{Mg}$	(0.1N KCl; pH=5.0)
log K_S	8.69 6.13 5.77 4.14 3.78 3.69 2.92 2.34 2.09	

As can be seen these are significant deviations from the predicted behavior. Schnitzer and Hansen (30) also demonstrated the effect of ionic strength on the stability constant, K_S :

	Log K_S (at pH = 3)	
	ionic strength	
	0.00	0.15
Cu	4.7	2.6
Ni	4.5	2.4
Co	4.3	2.2
Pb	3.6	2.1
Ca	3.6	2.1
Zn	3.2	2.0
Mn	2.9	1.7
Mg	2.7	1.6

Several inferences can be drawn from the data. Since the humic materials are polyelectrolytes of complex structure, increasing the pH results in the ionization of more acidic groups on the molecule, groups which can then complex with metal ions. Thus, at the pH values of natural waters, the stability constants can be expected to be somewhat higher than in their experiments (17). Second, increasing ionic strength has a substantial effect on the measured stability constants. Although divalent ions will be preferentially complexed in the presence of equivalent amounts of monovalent ions, the amounts of such monovalent ions, as well as the common divalent alkaline earth ions, found in natural waters suggest that in high ionic strength media lower stability constants can be anticipated. This may be quite important if freshwater sediments are placed in a high ionic strength (seawater) medium. Some evidence for the presence of complexed copper in seawater does exist (31) but the nature of the complex is unknown. Analytical techniques to detect metal complexes are discussed in the section on anodic stripping.

(2) Analytical Techniques

(a) General

It is desirable at this point to discuss analytical techniques potentially useful in characterizing soluble organic matter found in natural water systems as well as techniques for examining metal-organic complexes. Specifically, gel permeation chromatography and anodic stripping voltammetry will be discussed. Gel permeation has a relatively firm theoretical foundation when applied to known, relatively simple systems. Numerous difficulties, both with interpretation and experimental procedures, occur when aqueous systems of natural organics are

examined. Anodic stripping voltammetry is in its infancy, especially with regards to environmental applications. There are numerous experimental difficulties as well as difficulties in the interpretation of data.

It is not our intent to imply that such methods are without value. The nature of the problem regarding organic matter and metal-organic interactions in natural systems, however, requires the use of such state-of-the-art techniques despite their limitations.

(b) Gel Permeation Chromatography

Gel permeation chromatography (GPC) is a technique which has recently been utilized by a number of workers interested in characterizing naturally occurring organic compounds. GPC fractionation is based on molecular size in which the pore size of the packing, controlled during manufacturing of the gel, determines which molecules will be excluded from the interior of the gel particle. In operation a column is filled with particles of the desired packing material, the selection of the packing being dependent both on the solvent being used and the nature of the solute molecules. If a sample containing solute molecules of various sizes is passed through a given column, then those molecules which are too large to enter the gel pores will emerge from the column first. Smaller molecules have a higher probability of diffusing into the gel and are more efficiently retained. Thus smaller molecules emerge from the column after the larger ones, the time of their emergence ideally being a function of their molecular size or, as more commonly reported, their molecular weight. By proper choice of materials and techniques, it is possible to determine the molecular weight distribution of polymeric

organic materials. Reference materials (32-36) should be consulted for a more detailed theoretical treatment and additional practical applications of GPC.

The most important complication that can occur in GPC work is that separations take place that are not entirely based upon molecular size. This can be especially serious when dealing with aqueous systems where ionization of both solute molecules and the gel itself can take place. Even without ionization it is well known that organic materials can be adsorbed onto organic substrates. In general the solubility of polymeric molecules decreases with increasing molecular size, resulting in preferential adsorption of the larger molecules. In the presence of adsorption, retention characteristics are no longer a valid criterion for assigning molecular weights. Wershaw and Pinckney (37) reviewed these problems and took advantage of the adsorptive ability of Sephadex (a cross-linked dextran gel) to chemically fractionate humic acids. Swift and Posner (40) have also discussed the adsorptive properties of various gels.

In a series of papers (38-43), Posner and others have studied the fractionation of humic acids by gel filtration and ultracentrifuge techniques; adsorption was found to be negligible (40) on Sephadex gels studied when a buffer consisting of tris (2-amino-2-hydroxymethyl-1,3-propanediol) and HCl (pH=9) was used. Other large amino cations were also suitable. Subsequent work (41,42) demonstrated that calibration of GPC columns using dextran and protein standards was not entirely reliable due to the variations in the calibration from one gel type to

another. Nonetheless, calibration of Sephadex gels with dextran standards in tris buffer gave a calibration curve which reasonably described the elution behavior of humic acid fractions. Ultracentrifuge studies (41-43) showed that unfractionated and "mildly" fractionated humic acids were too polydisperse to be studied but that by extensive fractionation reasonable ultracentrifuge data could be obtained. Based on this ultracentrifuge data it was postulated that humic acid exists as a random coil, possibly with extensive branching, in solution. The original papers should be referred to for additional information on the physical properties of humic acids in solution. Whether humic materials in aqueous solution exist in true solution or as colloidal aggregates also influences their gel chromatographic behavior. As pointed out by Andrews (81) and discussed by Wershaw and Pinckney (37), "... Compounds which form molecular aggregates in solution will behave in at least three different ways on gel-permeation columns. Those compounds which form stable aggregates that do not dissociate under the physical and chemical conditions of the procedure will move through the column as though the aggregates were simply large molecules. If, however, the aggregates are in equilibrium with their dissociated constituent units, then the elution volume of the aggregated system will be concentration dependent. In addition, there will be some spreading of the solute on the column. If the aggregates are complexes of different molecular species, then in some instances gel-permeation chromatography will bring about dissociation of the otherwise stable aggregates." For the second case cited (equilibrium between

large and small particles), it can be anticipated that operating conditions such as concentration, flow rate, and column length will significantly affect the chromatogram. Papers by Wershaw et al. (37,44-46) are also of interest in this regard. Thus, the physical and chemical nature of humic materials in solution can be seen to be quite complex and only beginning to be understood. While gel permeation and other chromatographic techniques, in conjunction with other analytical techniques, can aid in the understanding of these abundant natural organic compounds, the application of these techniques is far from routine and, in fact, is itself in a research stage.

Studies that have been performed on naturally occurring organics are generally prefaced with a caution against assignment of strict molecular weight ranges to the fractions obtained. Because it has not been established that organic materials originating from widely diverse areas are chemically and/or physically similar, comparison of data between various workers is also difficult. It should also be noted that the work already discussed dealt with the humic acid fraction of humic materials. Whether the problems encountered with these materials can also be expected with the more soluble, lower molecular weight fulvic acid fraction is not known.

In the investigation of mercury-organic matter associations in sediment pore water using Sephadex gels, Lindberg and Harris (47) found highly enriched mercury concentrations in the pore water with the majority of the mercury associated with the <500 molecular weight

fraction for samples taken from the Florida Everglades while samples taken from Mobile Bay showed the bulk of the mercury to be associated with the >100,000 molecular weight fraction. Gjessing (48) studied the fractionation of organics in lake water on Sephadex and found only a large and a small molecular weight fraction with nothing in between. This may have resulted from an improper choice of gel packing. Ghassemi and Christman (49) studied the pH dependence of natural organics on Sephadex, noting an apparent size increase of the molecules with increasing pH. Hall and Lee (50) and Gjessing and Lee (51) found a number of ill-defined peaks with aqueous organics fractionated on Sephadex. Various parameters, such as COD, organic nitrogen, and color were measured for the various fractions. It was found that samples of organic matter from different sources gave different chromatograms. Thus this technique may be useful for the classification of water bodies. It should also be noted that large inorganic molecules, if present in natural waters, can also be fractionated by GPC (52).

(c) Methods for Analysis of Organo-Metallic Complexes

Several techniques are currently available for the determination of trace amounts of metals in aqueous systems, two of the more popular being atomic absorption and neutron activation analysis. Although both methods are very sensitive, they both lack the ability to discriminate between free metal ions and those that are complexed; only the total amount of metal is determined. Commercially available specific ion electrodes are available for some metals but their limit of sensitivity

is on the order of a part per million. In addition they sense changes in the activities of particular ions, which is of interest from a thermodynamic viewpoint but does not give concentrations directly. In a well-defined system it would be possible to use such electrodes if metal ion concentrations were sufficiently large. Sensitivities for these electrodes well below the values stated by the manufacturers have been reported by some workers (53-55). The electrodes discriminate between free metal ions and complexed forms, which is of advantage in certain applications. Determination of trace amounts of "free" metals by utilization of metal-catalyzed reactions has been reported (83), but this technique has not been developed to a practical stage. Polarographic stripping techniques offer the most promise for direct application in that reasonable sensitivity is possible in the determination of uncomplexed metal ions.

Classical polarography is historically related to the dropping mercury electrode. Simply stated, metal ions are electrically reduced at a mercury droplet at certain potentials. The electrical current involved in this process is measured and can be related back to the concentration of the metal ion in solution. Only those metals which can be reduced at the mercury anode can be analyzed, the lower sensitivity of the dropping mercury electrode being approximately one part per million.

Anodic stripping voltammetry (ASV) is a form of polarography which has undergone a rediscovery in recent times although it was first utilized many years ago. Recent developments permit analyses to be performed at the parts per trillion level. It, too, can differentiate between free

and complexed metal ions. Over the years numerous experimental techniques, involving both chemical and electronic manipulations, have been developed to aid the analyst using polarography in order that more interference-free determinations can be made, especially at the trace level.

ASV owes its current popularity to the fact that by using special, relatively inexpensive electrodes, conventional polarographic instruments can be utilized. The two most popular electrodes in trace metal analysis are the hanging mercury drop electrode (HMDE) and the mercury-covered graphite electrode (MCGE) (56-57). With the HMDE a stationary mercury droplet, as contrasted to the growing drop in the classical dropping mercury electrode, is the working electrode while with the MCGE a thin film (actually minute droplets) of mercury deposited on a graphite rod is the working electrode. The MCGE is the most sensitive of the two, being capable of determining concentrations on the order of 10^{-10} molar.

Both electrodes operate in an identical fashion. The first step involves plating the metals of interest into (or in some cases onto) the mercury. This is referred to as the concentration step because by increasing the plating time the concentration of the metals in the mercury can be increased; thus, very dilute solutions can be analyzed by using longer plating times. The second step is referred to as the stripping step. Here the reduced metals in the mercury are oxidized back into solution, the current produced generally being a function of the concentration of the metal in the mercury which in turn is a function

of the original concentration of metal ion in solution. Theoretical and practical discussions of the nature and problems of stripping techniques in general (58), the HMDE (59), and the MCGE (56,57) are found elsewhere.

Unfortunately, past applications of ASV to environmental samples are rather limited so the probability of success using this approach is unpredictable. Seawater has been investigated by Matson (56), Fitzgerald (60), and Seitz (61) and the existence of complexes, including organo-metallic, was noted. Information regarding the ASV technique, including photodegradation of organic complexes, can be found in these references. Cadmium (62,63) and zinc (64) in seawater have been studied using polarographic techniques other than ASV. It was concluded that cadmium exists primarily as the monochloro complex, $CdCl^+$, and that zinc is found primarily as Zn^{+2} and $Zn(OH)_2^0$. Determining the complexation of metals in natural waters is discussed by Mancy (65), Allen et al. (66) and Matson et al. (67). Techniques for increasing the sensitivity of analyses using a HMDE while at the same time decreasing the analysis time are discussed by Bond (68) and Zirino and Healy (69). The latter paper also discusses the importance of pH in relation to ASV data. ASV can also be used to determine the complexing capacity of water (70, 82). The use of ASV in conjunction with GPC has also been investigated (56,67, 71). However, as has been stated previously, assignment of molecular weights to the fractions obtained in these papers should be avoided.

Under suitable conditions ASV can successfully distinguish between free and tightly bound metal ions in solution. Separation of the metal

complexes into organic and inorganic complexes is potentially possible only if the organic matter can be completely destroyed without altering other aspects of the system. In this regard peroxide oxidation or ultraviolet irradiation can be used, the latter being preferable with regard to potential contamination but less desirable from the standpoint of efficiency and time. In Figure 3 (65) is shown an experimental procedure for characterizing a water sample for the various forms of heavy metals present.

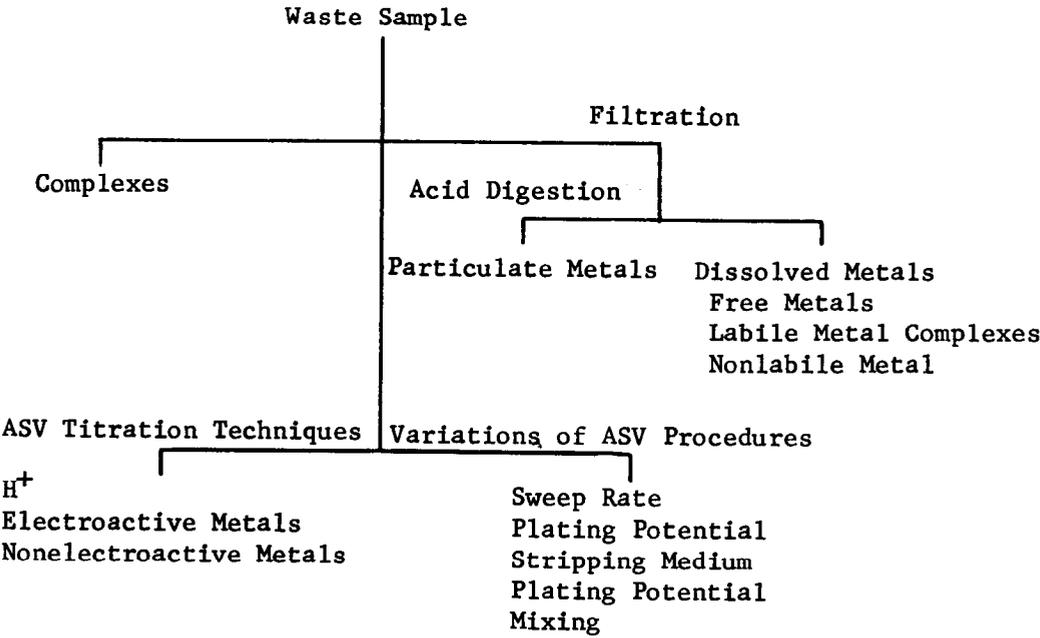


Figure 3. Suggested Anodic Stripping Procedure for the Examination of Metal Complexation. After Mancy (65)

III. EXPERIMENTAL

A. General Experimental Approach

A diagram of the experimental approach used in this study is shown in Figure 4. The interstitial (pore) water as well as the colloidal phase were identified as being potentially the most significant contributors to the appearance of a soluble organic fraction when dredged materials are deposited in open water. In the long-term experiments the possibility that sediments from an essentially freshwater environment might potentially be placed in a seawater environment was also considered.

B. Sediment and Water Samples

(1) Site Selection - Sites for sediment sampling were selected with the assistance of the New York and Detroit Districts. The selection criteria included the requirements that the sediments be expected to contain a reasonable amount of soluble organic matter, that a range of conditions from light to heavy pollution be sampled, but that areas with known, highly localized pollutant problems be avoided. In order to meet these requirements, areas with fine-grained sediments were selected and each location was further divided into five sublocations. Fifty sediment samples were collected from each of the three sites within each District location. Each site had five sublocations (A-E), from each of which ten cores were collected. The sampling areas are shown in Figures 5 and 6. Descriptions of the cores collected from the various sublocations are given in Tables 1, 2, and 3.

Results for E_h measurements on the sediments are shown in Table 1. The data indicate that the sediments are in general in a transitory

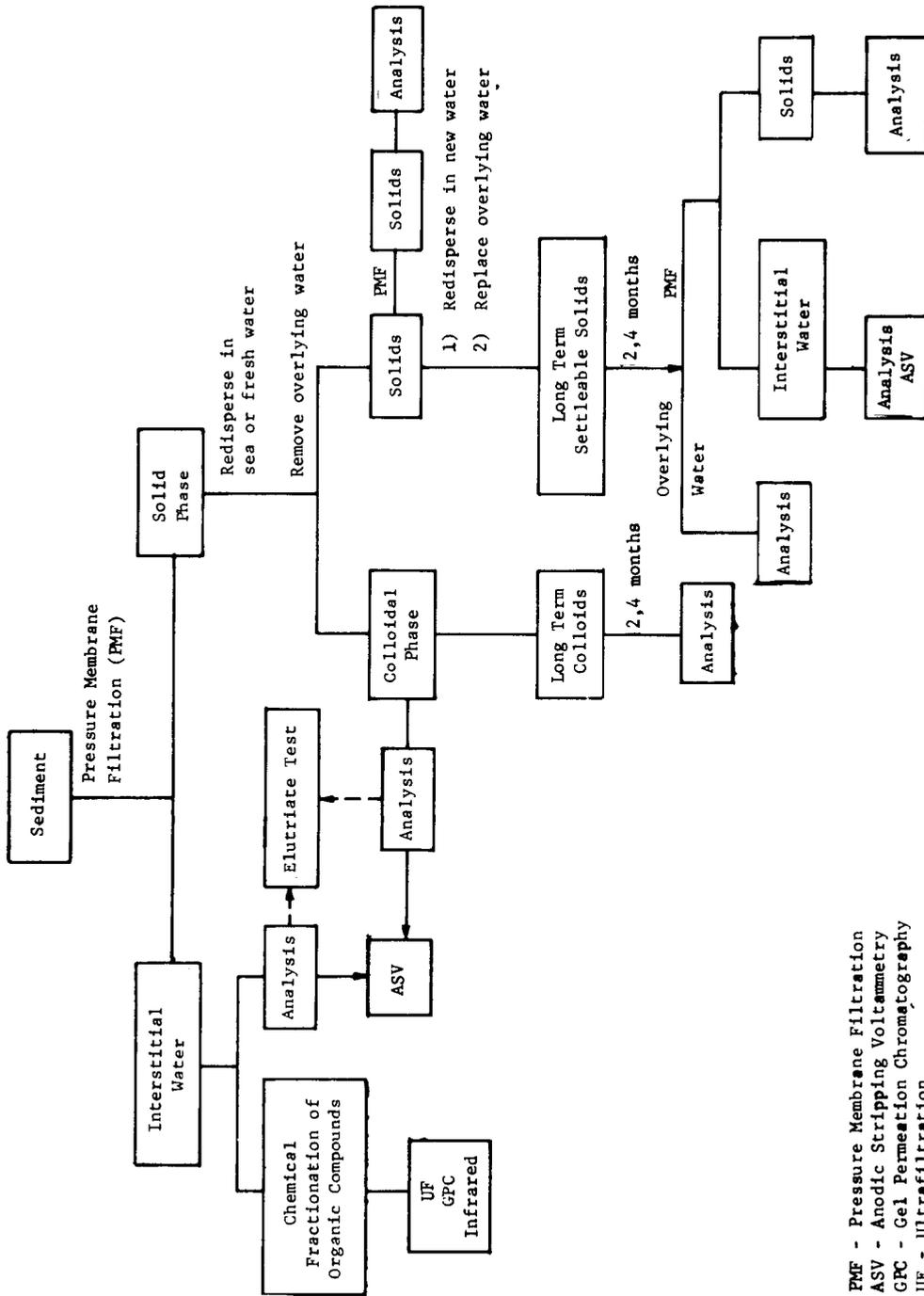
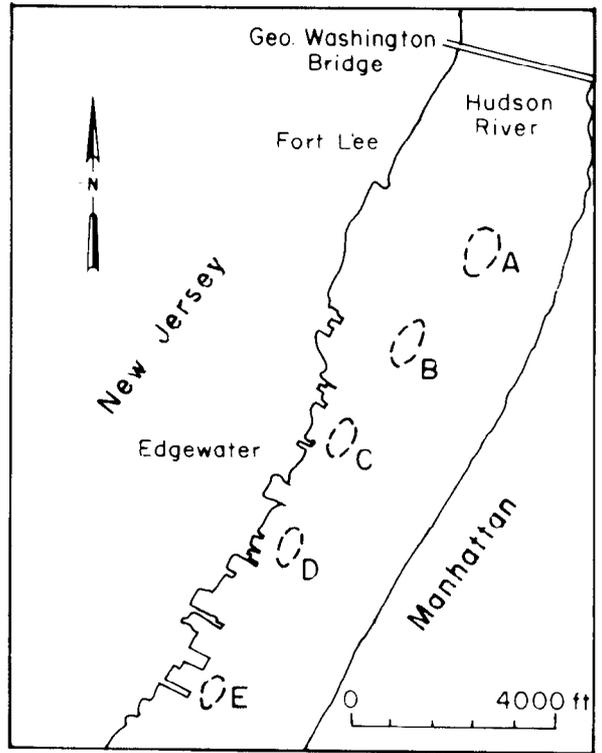
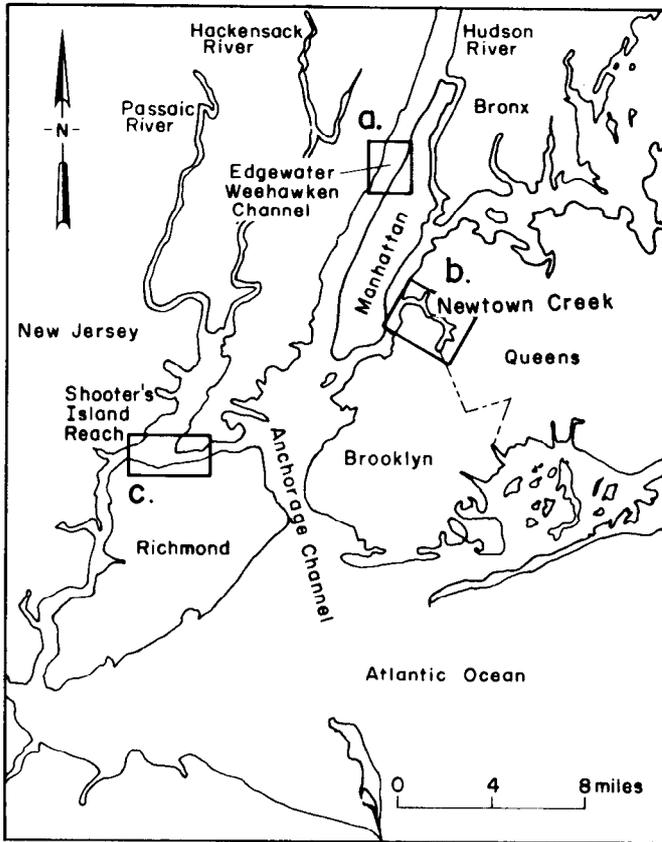
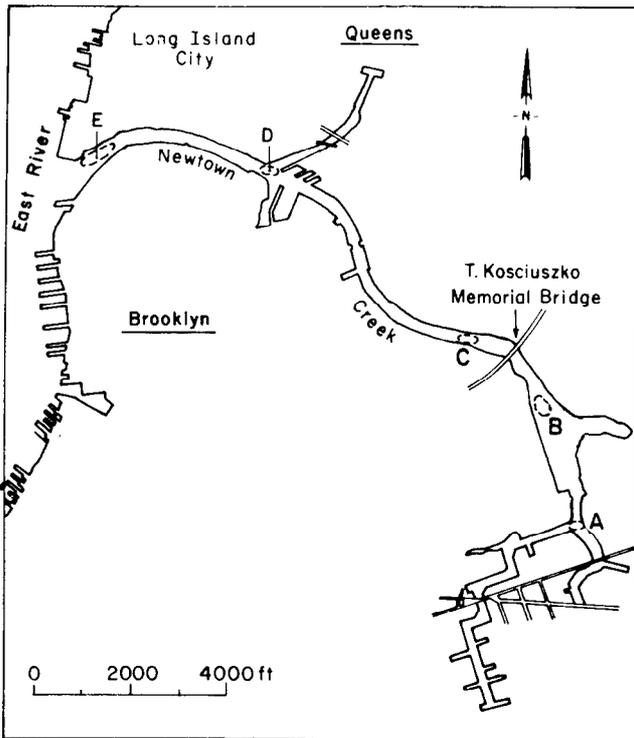


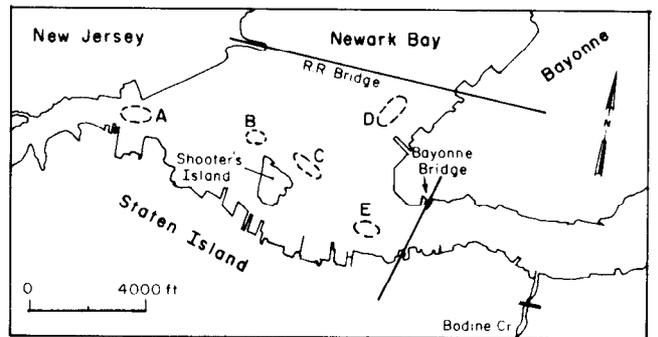
Figure 4. Experimental Procedure Used in Current Study



a.



b.



c.

Figure 5. Sampling Areas, New York District

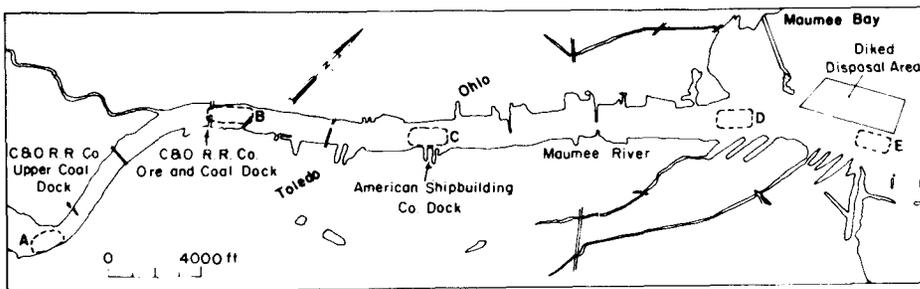
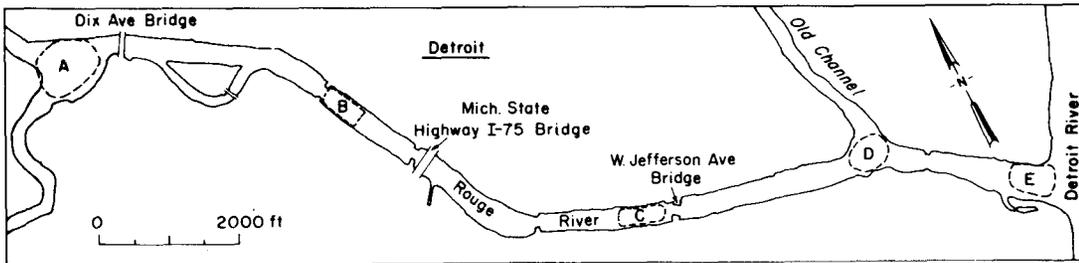
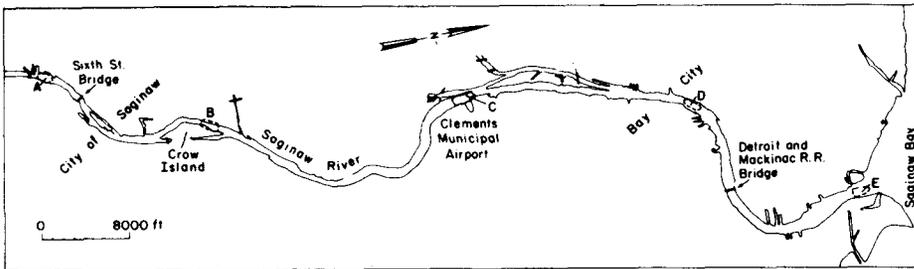
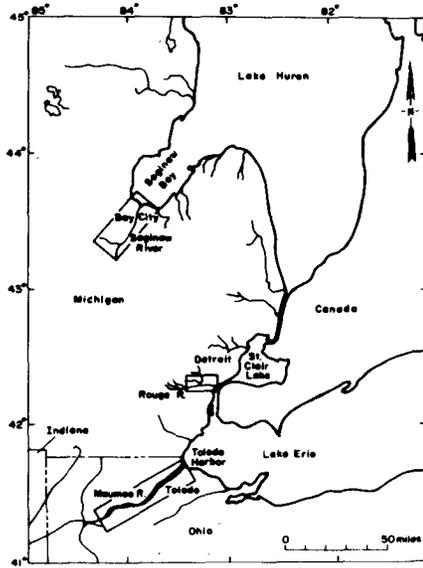


Figure 6. Sampling Areas, Detroit District

Table 1. Variations of E_h in Sediments

Site/Sublocation	E_h (+standard deviation)					Average
	A	B	C	D	E	
Hudson	217(36)	214(53)	128(33)	201(42)	205(37)	193(37)
Shooter's	109(64)	125(51)	174(70)	172(38)	214(59)	159(66)
Newtown	-80(36)	-33(63)	--	-60(105)	-74(94)	-62(77)
Rouge	91(87)	82(125)	75(119)	94(107)	97(123)	88(103)
Saginaw	266(71)	166(95)	185(87)	154(74)	79(79)	170(98)
Maumee	197(92)	111(107)	189(94)	169(170)	190(160)	171(125)

range between oxidation and reduction; the more positive the E_h , the more oxidizing the system. Newtown Creek is obviously in a much more reducing condition which confirms the visual observations. Because of the large standard deviations in the Detroit samples, it is not possible to conclude that the Rouge River average is statistically different from Maumee and Saginaw. Average pH values for all sediments were in the range of 6.8-7.1.

(2) Sediment Sampling and Storage - Cores were collected with a 5 cm diameter x 75 cm long gravity coring device (Wildlife Supply Co., Saginaw, Michigan). In cores taken from the Newtown Creek location in New York Harbor, it was evident that the coring device was entirely in the sediment as the upper closing mechanism was being jammed by grit. However, full coring tubes could not be obtained. Density variations probably exist within the sediment such that the corer rapidly moves through the upper, "diluted" sediment before stopping at the denser, underlying region. The core-catching portion of the corer was subsequently modified so that for samples taken in the Detroit District, the coring tubes were generally full.

Table 2.

New York Sediments (Marine)

Site	Texture	Sedimentary Structure	Color	Odor	Remarks
Hudson River					
A	Clay; minor silt	Layering at top	brown-grey	none	
B	Silty Clay	Layering at top	brown-grey	faint H ₂ S?	
C	Silty Clay	Layering at top	brown-grey	none	
D	Silty Clay	Layering at top	tan-brown	none	
E	Upper-silty sand Lower-silty clay	Layers	upper-tan-grey lower-black	none none	
Shooter's Reach					
A	Clay, Sandy clay	Some layering	black	hydrocarbon	
B	Clay	Some layering	black	hydrocarbon	
C	Sandy clay-minor grav.	None	black	hydrocarbon	
D	Clay-sand	None	black	hydrocarbon	Red clay sand on bottom of some cores
E	Sandy Clay	None	black	hydrocarbon	
Newtown Creek					
A	Clay, Sandy silt	None	black	heavy hydrocarbon	
B	Silty clay	None	black	heavy hydrocarbon	
C	Silty clay	None	black	heavy hydrocarbon & H ₂ S	
D	Sandy clay	None	black	heavy hydrocarbon & H ₂ S	
E	Sandy silt	None	black	heavy hydrocarbon	Some shells

Table 3.

Detroit Sediments (Fresh Water)

Site	Texture	Sedimentary Structure	Color	Odor	Remarks
Saginaw River					
A	Sandy clay	None	grey-brown	None	minor vegetation
B	Sandy clay	Upper layer sand	grey-brown	None	shells in sand layer
C	Silty clay	None	tan-grey	None	
D	Silty clay	None	tan-grey	None	
E	Silty clay	None	grey-black	None	
Maumee River					
A	Silty Clay & Sandy Silt	None	grey-tan	None	bark, wood, shells, plant fibers
B	Silty clay	None	grey-tan	None	
C	Silty clay	Upper-tan clay Lower-grey-tan	grey-tan	None	upper layer appeared recently deposited
D	Silty clay	Upper-tan clay Lower-grey-tan	grey-tan	Slight sewage	upper layer appeared recently deposited
E	Silty clay	Upper-tan clay Lower-grey-tan	grey-tan	Lower half sewage	upper layer appeared recently deposited
Rouge River					
A	Silty clay	None	grey black, grey tan	Sewage	slight hydrocarbon odor
B	Silty clay	None	tan-black	Sewage	slight hydrocarbon odor
C	Silty clay	None	grey-black	Sewage	slight hydrocarbon odor
D	Silty clay	None	grey-tan	Sewage	
E	Silty clay	top had lighter brown layer	grey-tan	Sewage	hydrocarbon odor

After collection, the core tubes were placed in an insulated box and at the end of the day were packed in ice (in New York, dry ice was used) and returned by air freight to the laboratory. Samples were kept cold if immediate transportation could not be arranged. For dry-ice packed cores, the tubes themselves were surrounded by insulation and were not in contact with the dry ice. Nevertheless, a number of the cores arrived at the laboratory in a frozen state and had to be thawed. The ice-packed samples arrived with ice still present but with no evidence of freezing within the tubes themselves. Upon arrival at the laboratory, the samples were placed in a +5°C room and the shipping crates attached to nitrogen lines and continuously purged. Generally, there was a 3-day delay between the time the cores were collected and the time they arrived at the laboratory.

The sediments from a given site were removed from the coring tubes and composited in acid-washed, nitrogen-purged plastic cans in the +5°C storage room. One core from each of the five sublocations within an area was emptied into the can and this process repeated until all the tubes from an area were emptied into a single can. The cans were then covered and a nitrogen purge tube placed inside, purging being maintained until the sediments could be dewatered. Measured oxygen levels were 1% or less in the vapor space above the sediments. Approximately one month elapsed between the time the New York samples were collected and the dewatering of the sediments began. During this period there was no visual oxidation of the sediments and the odor had apparently remained

unchanged (i.e. volatile hydrocarbons and sulfides, if detected at the time of collection, were still much in evidence a month later). This suggests that the storage interval and procedure were, on a qualitative basis, sufficient in preventing gross chemical and biological changes from occurring. Although it would have been desirable to work with fresh sediment, this was not possible due to the large amount of sediment required for this study.

(3) Water Samples - Weather and sea conditions in the New York Bight and Great Lakes precluded collection of samples of water from current or future disposal sites for utilization in the experiments.

It was therefore necessary to collect fresh water from Mallet's Bay in Lake Champlain (44°34'N, 73°13'W) and seawater from outside the breakwater at Rye, New Hampshire (44°0'N, 70°44'W). Subsurface water (3 meters) was collected using a submersible pump and stored in polyethylene containers previously rinsed with sample water. The containers were stored in the +10°C room until needed.

C. Sample Preparation

(1) Extraction of Interstitial Water - Sediments were dewatered using three acrylic pressure membrane filtration units, each with a filtration area of 79 cm²; 0.45 μm membranes were used. The sample compartment was filled with sediment and pressurized to 6.9 x 10⁵ pascals (N/m²) with nitrogen and the water collected in acid-washed, nitrogen-purged polyethylene bottles. It was found necessary to purge

the area below the membrane with nitrogen in order to prevent oxidation of iron in the interstitial water. Forty milliliters of sample were used to rinse each sample bottle. Pressure was maintained for three hours, at which time the sediment was removed and placed in nitrogen purged containers for storage. With all samples, several liters of water had collected on the sediment surface during the storage period. This water was removed prior to membrane filtration of the sediments and was saved for use in the organic fractionation work. The extracted water was stored at +5°C until needed. The nitrogen-purged interstitial water samples were stored in polyethylene bottles under water to prevent oxidation. This procedure was satisfactory with the first two sediments dewatered (Newtown and Shooter's), but oxidation of the Hudson River samples occurred under these conditions. Because the process is irreversible, it was decided to allow all the samples to oxidize completely. (For the Detroit samples acidified, aliquots were taken prior to oxidation so that ferrous and ferric iron could be determined.) It was verified by organic carbon determinations that oxidation did not result in a detectable change in the organic carbon concentrations. Further, there is no reason to expect that air oxidation would significantly alter the chemical nature of the organic carbon. Other parameters, such as nitrogen, phosphorus, etc., were found to be unaffected when pre-oxidation samples were compared with acidified and filtered oxidized samples. For analysis of total heavy metals, the suspensions were acidified with nitric acid (Ultrex) to redissolve the precipitate. For the soluble metal complex

studies, the suspension was filtered (0.45 μm) to remove the precipitate and then stored at +5°C. For the organic fractionation work, the filtered waters were acidified with HCl to pH=2 in order to prevent bacterial growth. Interstitial waters derived from sediments in the long-term experiments were acidified upon collection with HCl (Ultrex) to pH<2.

(2) Long-Term Experiments -

Because of the bulk of sediment involved (approximately 20 kilograms for each site), it proved difficult to mix the samples well enough in their dewatered condition so that representative samples could be taken. Some mixing had already taken place during the transfer of sediment from coring tubes to storage container and also during the dewatering phase. In order that homogeneous samples be available for the long-term studies, the following procedure was adopted. Using a small, plastic-coated coring device, a number of random cores were taken from each of the dewatered sediments and mixed with nitrogen-purged water (fresh or marine) in the 4:1 ratio specified in the elutriate test (72). The suspension was stirred for 1/2 hour both manually and by bubbling with nitrogen, following which it was allowed to settle for 24 hours. The overlying water was then removed for use in what will be referred to as the long-term colloidal studies. Samples of this water, both neutral and acidified, were retained for analysis (Colloidal, t=0 months). For the long-term colloidal studies, approximately 1-liter duplicate aliquots of this water were placed in 1-liter TPX jars (polymethyl pentene, #6758-04, Cole-Parmer, Chicago, Ill.) and stored at +10°C. Only the

freshwater sediment dispersed in fresh water contained appreciable amounts of suspended solids after the 24-hour settling period. On a weight/weight basis this amounted to: Saginaw - 0.33%; Rouge - 0.09%; and Maumee - 0.17%.

After removal of the overlying water, the solids were dispersed into 9 liters of nitrogen-purged water contained in 91 cm high by 17 cm diameter acid-washed polyethylene pipet jars (#1392F, Dynalab Corp., Rochester, NY). Sediment not utilized was dewatered as previously described and retained under nitrogen for analysis (Sediment, t=0 months). After the suspension was stirred manually and with nitrogen bubbling for 1/2 hour, it was again allowed to settle for 24 hours. At the end of this period the overlying water was discarded and replaced carefully with fresh, deoxygenated 15 liter aliquots of either fresh water or seawater. As indicated previously, the Detroit District sediments were suspended in both fresh and salt water while the New York District sediments were resuspended in salt water only. Two samples were prepared, one for analysis after two months, the other after four months. Sediment depths (after two months) were 5-8 cm. The cylinders were stored in a water bath at 10°C and the water column dissolved oxygen (DO) concentration was measured periodically with a DO probe (model 85, Delta Scientific, Lindenhurst, N.Y.). DO levels were kept at approximately 4-6 ppm by purging the upper 2/3 of the water column in each cylinder with an oxygen-nitrogen (4% oxygen) mixture. This was done to maintain an environment (DO and temperature) for the sediment which might reasonably

be expected at a site where dredged materials are redistributed. All long-term samples were stored in the dark except that they received approximately two hours of illumination per week during periods when personnel were working in the storage room. After the initial oxygen-nitrogen purge, aliquots were taken for analysis and establishment of the base line (Overlying water, t=0 months).

(3) Preparation of Organic Fractions -

The scheme used to isolate and fractionate the soluble organics obtained from the interstitial water (and the surface water which appeared during storage) is shown in Figure 7. In this procedure acetone is used as the extractant, a separate organic phase being formed by "salting out" the acetone and the organic materials with ammonium sulfate. Ammonium sulfate was chosen because of its high solubility in water and low solubility in acetone. Other salts are also suitable and their salting-out properties have been discussed by Christian (73).

Another fractionation procedure utilizing n-butanol in place of acetone was also examined. Visual observations indicated that changes were occurring when the n-butanol extraction procedure was utilized; solutions which had previously been extracted with chloroform contained chloroform-soluble materials after the butanol extraction. Acetone appeared to be a slightly better extractant based on visual observation of color removal, the aqueous phase being virtually colorless after the acetone extraction. Also, the presence of a large amount of salt in the aqueous phase probably enhances the fractionation (73). Concern over

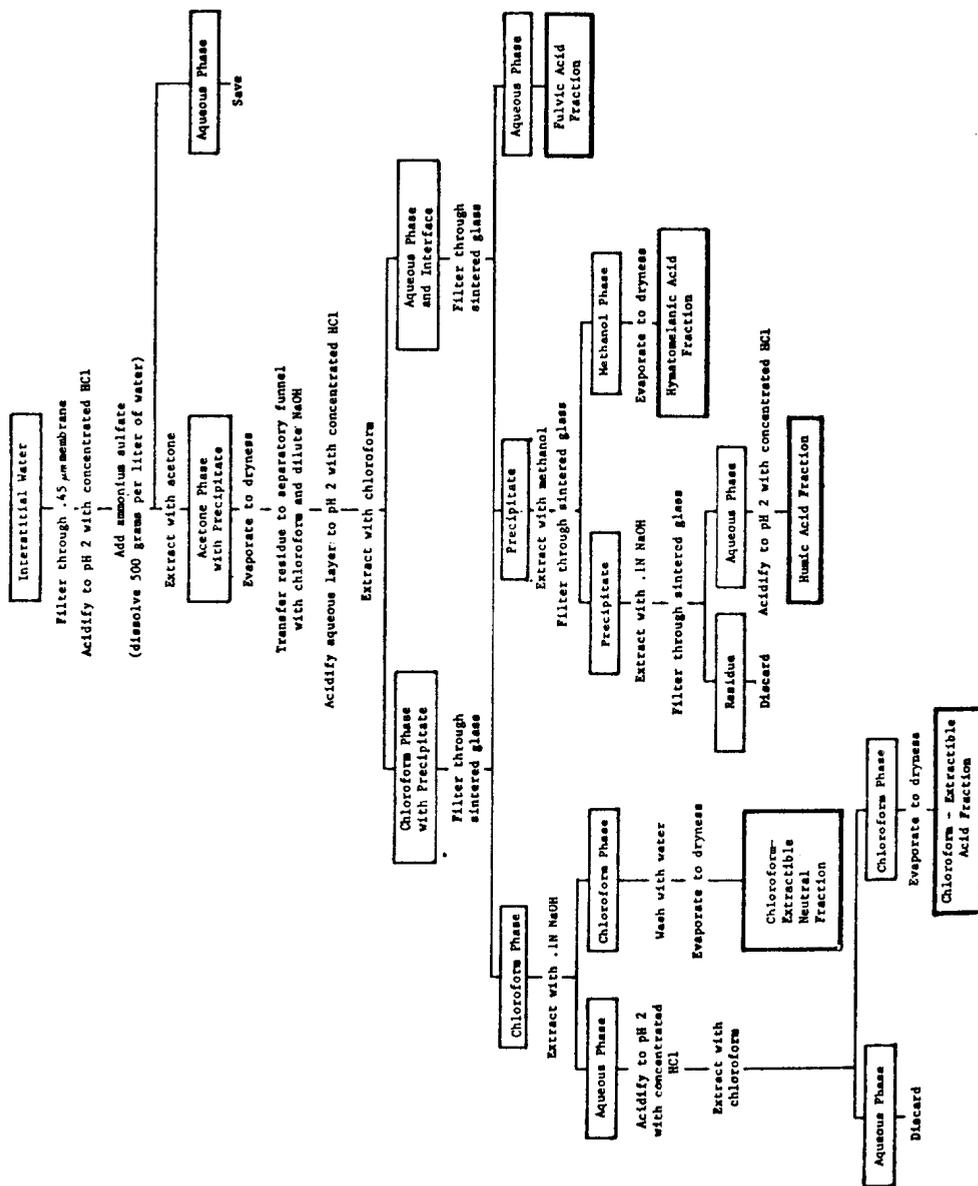


Figure 7. Isolation of Organic Fractions from Interstitial Water

the possible esterification of the carboxylic acid groups of the organic matter by butanol led to the decision to use the acetone procedure.

Other workers (74) have used acetone to remove the fulvic acid fraction from total organic matter extracts. However, Schnitzer (75) indicates that fulvic acid is only moderately soluble in acetone. Therefore, the classical definitions (see Figure 1) have been utilized in the fractionation procedure of the aqueous phase. The humic acid fractions were purified by dialysis (12,000 MW cut-off tubing) in HCl (pH=2) followed by filtration through the acid-washed ultrafiltration membrane (Millipore PSAL, nominal molecular weight cut-off = 500) and subsequent washing with distilled water. Fulvic acid fractions were purified by passage through a strong acid cation exchange resin (AG 50W-X8, Bio-Rad, Richmond, California) in the H⁺ form. Samples were eluted with distilled water and the resin was regenerated with hydrochloric acid. Purification was initially attempted with the PSAL membrane but proved unsuccessful with several, but not all, samples as a result of large amounts of low molecular weight species in some samples.

D. Analytical Techniques

(1) Characterization of Aqueous Samples -

Measurements of pH in the field were made using a portable Orion Ionalyzer (Model 407-Orion Research, Cambridge, Mass.), silver/silver chloride electrode (#90-02-00), and a Beckman #41263 glass electrode (Beckman Instruments, Fullerton, Calif.). Laboratory pH measurements were made using a Corning Model 10 pH meter (Corning Instruments, Corning,

NY) and a Markson #1808 combination electrode (Markson Science Inc., Del Mar, Calif.). Measurements of E_h were made using seven platinum micro-electrodes (80), the Orion meter, and reference electrode. The electrodes were calibrated in Zobell's Solution (77). "In situ" measurements on the sediment were made by placing the electrodes in a container filled with fresh sediment and waiting until the meter drift had apparently ceased (5-10 minutes). Calibration solutions were at approximately the same temperature as the sediment. E_h results are the average of 35 readings (7 electrodes \times 5 sediment samples, one sample from each sub-location).

Chemical oxygen demand (COD) was performed according to standard procedures (78) utilizing Hach reagents (Hach Chemical Co., Ames, Iowa). Below COD = 20 the relative error was approximately 30%. The higher COD levels generally had relative errors of approximately 14%.

Initially ammonium and nitrate nitrogen in the various aqueous solutions were determined by steam distillation of ammonia (79) followed by reduction of nitrate to ammonia using Devarda's alloy. Aqueous ammonia concentrations were determined using an Orion Ammonia electrode (#95-10). Subsequently, it was found that ammonia could be determined directly using the ammonia electrode and the method of standard additions with a relative error of 6%. The effect of dissolved salts was negligible. Total Kjeldahl nitrogen (TKN) determined with Technicon instrumentation gave nitrogen values similar to the ammonia probe method with the latter being the more sensitive. Some ammonia nitrogen levels were also

determined using the TKN equipment but bypassing the digester. Invariably nitrogen levels determined in this fashion were higher than the TKN levels. The reason for this is not clear. For standards prepared in seawater, TKN levels were approximately 7% low and ammonia nitrogen levels 5% high. The reported ammonia nitrogen values are those determined using the probe method or, if these were not available, corrected TKN values have been utilized. The latter was accomplished after comparison of TKN results with probe data, all obtained using the same standard solutions. Nitrates were determined using Technicon equipment with dissolved salts having no apparent effect. Precision was approximately 7%.

Total phosphate was also determined with the Auto-Analyzer and was compared to results obtained using prepackaged chemistry (Hach) and a Coleman Model 6/20 Colorimeter (Coleman Instruments, Maywood, IL) with 1-cm cells ($\lambda=700$ nm) calibrated with phosphate standards. The correlation was excellent ($R=0.99$) between the two methods at higher levels with the manual method again showing increased sensitivity and precision (6%) at low levels. Orthophosphate and polyphosphate were determined using Hach reagents, the latter only if a discrepancy between ortho and total phosphate was observed.

Ferrous and total iron were determined using Standard Methods (78), Hach chemistry, and the described colorimeter ($\lambda=510$ nm). Alkalinity was measured by potentiometric titration with standard HCl (78). Conductivities were measured with a YSI Model 31 Bridge (YSI, Yellow Springs, Ohio) and a cell with a 1-cm^{-1} cell constant.

Organic carbon was determined using a Beckman Model 915 Total Organic Carbon Analyzer. Precision was ± 1 ppm organic-C. Inorganic carbon was eliminated by acidifying solutions with phosphoric acid and shaking.

Infrared spectra of the organic fractions were obtained using a Perkin-Elmer Model 167 grating spectrophotometer (Perkin-Elmer Norwalk, Connecticut). Samples were prepared either as KBr pellets or chloroform smears on NaCl plates.

Ultraviolet spectra were obtained with a Beckman Model DB spectrophotometer (Beckman Instruments, Fullerton, California) using 1-cm cells.

Gel permeation was carried out using two grades of Sephadex (Pharmacia Fine Chemical, Piscataway, New Jersey). The first column (1.5 cm x 65 cm) contained G-25 (fractionation range = 100-5000 MW); while the second column (1.5 cm x 90 cm) contained G-75 (fractionation range = 1000-50,000 MW). Fractionation ranges are based upon dextran standards. The dead volume (complete exclusion of solute from gel) was determined with Blue Dextran 2000 (MW= 2×10^6 , Pharmacia). A flow rate of approximately 0.5 ml/min was utilized. Eluant buffer was prepared by dissolving 24.2 g of tris (2-amino-2-hydroxymethyl-1,3-propanediol) in 2 liters of distilled water and adding this to 960 ml of 1% (v/v) hydrochloric acid. The pH of the final solution was 8. Chromatograms were monitored at $\lambda = 220$ nm using a 1-mm path length flow cell with a tris-filled 1-mm cell as reference. Output from the spectrophotometer

was amplified and fed to a 10-inch strip chart recorder. The samples themselves were initially in solid form and were brought into solution with dilute sodium hydroxide to pH=8. One-half milliliter of this solution was then taken as the sample.

Ultrafiltration was carried out with a Millipore ultrafiltration cell (XX4204710) and Pellicon (Millipore) membranes with molecular weight cut-offs of 1000, 25,000, and 100,000 (manufacturer's values based on enzyme standards). Starting solutions were pH=8 in sodium hydroxide and were approximately 40 ml. Pressure was applied (30 psi nitrogen) and the sample volume was reduced to approximately 5 ml. Three 10-ml aliquots of pH=8 sodium hydroxide were then used to rinse the remaining material through the membrane. The final 5-ml fraction on top of the membrane was diluted to 40 ml and organic carbon levels determined on both the material retained by the membrane and that which passed through. One membrane of each series was used for the humic fractions. Leak detection and membrane performance were tested with Blue Dextran 2000 and other dextran standards, respectively. Fulvic fractions were handled identically but with another set of membranes. All samples were filtered through 0.45 μ m membranes prior to ultrafiltration.

Anodic stripping voltammetry (ASV) determinations for cadmium, lead, and copper were carried out using a Model-SSP-5A polarograph (Chemtrix, Beaverton, Oregon) fitted with a storage oscilloscope. A PAR (Princeton Applied Research, Princeton, NJ) polarographic cell (#'s 9300,9301), salt

bridge (9332), outgassing tube (9330), and saturated calomel electrode (9331) were used. The polarograph was operated in a three-electrode configuration utilizing a platinum wire counter electrode. Both a hanging mercury drop electrode (HMDE; PAR #9323) and a mercury-covered graphite electrode (MCGE; PAR #9319) were used, the specific electrode utilized being dependent upon the concentration of the ion being analyzed. Oxygen removal and stirring were controlled using either pre-purified nitrogen or carbon dioxide in conjunction with a vanadium (II) oxygen scrubber. pH was controlled with either ultra-pure HCl or redistilled ammonium hydroxide. Unless otherwise indicated the following experimental conditions were maintained:

Plating potential - 1.0 V

Sample volume - 10 ml

Plating time - 2 minutes

Rest period - 30 seconds

Stripping velocity - 1 volt/second

Mercury utilized in the HMDE was of triple-distilled quality and was further purified by a technique described elsewhere (83). The graphite electrode was plated with mercury from a 10% potassium nitrate solution (20 ml, pH \approx 4.2 with carbon dioxide purging) containing 5 ppm mercury. Plating was carried out at 0.0 V for one hour. The useful life of the MCGE was generally about two days after which it was necessary to clean and replate the graphite rod.

In practice the stripping peak for copper is usually sufficiently well-defined for analytical purposes when the MCGE is used but is often obscured by the mercury dissolution peak especially when using the HMDE. It was therefore necessary to add pyridine (1% by volume) to some solutions in order to separate the two peaks. Pyridine had no appreciable effect on the stripping currents for cadmium and lead. All solutions were initially acidic ($\text{pH} < 2$) and because determinations were carried out at pH 5 it was necessary to add hydroxylamine hydrochloride ($2 \times 10^{-3} \text{ M/L}$) in order to reduce any ferric iron to the ferrous state (82). Colloidal and precipitated iron species are formed at these higher pH values and can subsequently entrap and/or adsorb metal ions of interest. Hydroxylamine hydrochloride had no effect on cadmium and lead peaks but the sensitivity was increased slightly for copper.

All metal concentrations were determined using the method of standard additions and were corrected for blank values. Diluent distilled water and 0.2M KCl were treated with Chelex-100 chelating resin to reduce heavy metal impurities to insignificant levels. The polarographic cell was washed with nitric acid between determinations. In order to ascertain the potential chelating ability of the organic matter present, the samples were oxidized with hydrogen peroxide. To an acidic 10-cc sample was added 100 μl of 30% hydrogen peroxide and 250 μl of concentrated ammonium hydroxide. The samples were then heated at 80°C for seven hours. At the end of the first and second hours, 100 μl spikes of hydrogen peroxide were added to each sample. At the end of five hours,

250 μ l of hydrochloric acid was added and heating continued for an additional two hours. The following day the samples were quantitatively transferred to 25-ml volumetrics, diluted to volume with purified distilled water, and a 10-ml aliquot taken for analysis. On some seawater samples the hydrogen peroxide had not been completely destroyed during the procedure and it was therefore necessary to reheat the basic solutions for approximately two hours and again add acid followed by an additional one hour of heating. Oxidations were carried out in duplicate. The average precision for all metals in the unoxidized solutions was approximately 7% and 13% for the oxidized solutions.

Metals in solution were determined using a Perkin-Elmer 403 Atomic Absorption Spectrometer and an HGA 2100 Graphite Furnace. All freshwater samples were analyzed by direct injection of a 20- μ l aliquot into the furnace and compared with aqueous standards. Seawater samples were run in a similar fashion except that lead and cadmium injections were followed by a 50- μ l aliquot of 50% ammonium nitrate solution (103). A technique termed "ramping" was used during the drying cycle. Instead of drying at a constant temperature, the temperature was gradually increased manually in increments until the sample was completely dried. This "ramping" procedure is necessary in order to prevent spattering. Standard solutions were treated in a similar manner. The ammonium nitrate solution was passed through a column containing Chelex 100 exchange resin to remove heavy metal contaminants.

Analyses for cadmium in seawater samples show strong optical absorptions during drying and charring if ammonium nitrate is absent; in its presence base lines are flat during these two heating stages. In spite of this procedure erratic results were sometimes obtained for cadmium and lead. Analysis of spiked seawater solutions indicated reasonable agreement between experimental and expected concentrations for Zn, Fe, Mn, Cu, Cr, Ni. Below 50 ppb the relative error for each metal, determined with standards prepared in seawater, was found to be: Zn (11%), Fe (9%), Mn (11%), Cr (17%), Ni (29%), Cu (32%), Cd (35%), and Pb (50%). Colorimetric iron determinations compared favorably with the atomic absorption method for all but a few samples (Figure 8). It is not clear why five of the samples differ significantly from the atomic absorption results. Interferences such as phosphate, chromium, zinc, copper, nickel, and cadmium are not present in sufficient quantities to be significant. Other species can also interfere but were not measured.

In order to emphasize the trends that are occurring, the total metal data are presented as relative values compared to original seawater and lake water. These base values, determined by atomic absorption, are:

	ppb							
	<u>Zn</u>	<u>Fe</u>	<u>Mn</u>	<u>Cu</u>	<u>Cr</u>	<u>Ni</u>	<u>Pb</u>	<u>Cd</u>
Seawater	30	100	50	5	5	10	5	2.9
Lake Water	10	30	10	3	1	6	2	2.2

The levels are somewhat high compared to published data for open waters. This is probably a result to some extent of the sites from which they

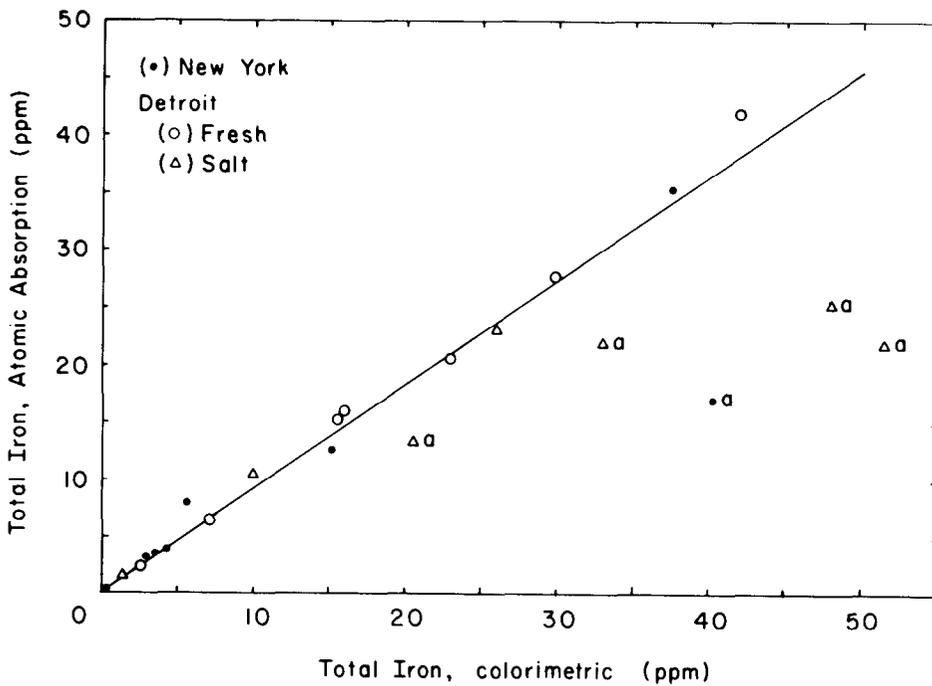


Figure 8. Comparison of Atomic Absorption versus Colorimetric Determination of Iron, Interstitial, and Colloidal (t=0) Solutions ("a" is for reference purposes for Table 11)

were selected and to a greater degree the storage and extensive manipulation involved. Of importance, however, is that these concentrations were determined just prior to contacting of the sediment with the waters. Hence, subsequent changes in metal concentrations are meaningful.

(2) Characterization of Sediments -

Sediment samples, if not properly handled, can undergo chemical transformations which can cast doubt on the interpretation of chemical analyses subsequently performed upon them. In order to minimize any potential changes, the following handling techniques were adopted. After the sediments had been dewatered, the moist filter cake was

transferred to a glove bag where it was broken up, composited, and transferred to a Pyrex Mason-type jar, all under a nitrogen atmosphere. The jars were then stored at +3°C until the samples could be analyzed. Prior to removing a subsample for analysis, the samples were again placed in a nitrogen-purged glove bag. The top 3-5 cm of sample, most susceptible to oxidation, was discarded and the remainder of the material thoroughly mixed. Concretions or any other large particles were discarded. Before any analyses were performed, the moisture content of each sediment sample was determined to establish the approximate amount of moist sample required to obtain the desired sample size on a dry weight basis. All samples were weighed in the glove bag under nitrogen. Solutions and reagents which were used in the analyses were purged with nitrogen for ten minutes and then mixed with the sediment samples in the glove bag. They were then capped and mixed. For the following procedures only, the weighing step was carried out under nitrogen: total nitrogen, free iron oxides, total phosphorus, and total heavy metals. All other procedures were carried out totally under a nitrogen atmosphere. All solutions were filtered using a Millipore filtration apparatus (#1104700 and 1104710). The upper unit was purged with nitrogen during this step. All filtered extracts were adjusted to pH=1.0 with HCl. All values are expressed on a dry weight basis.

(i) Cation exchange capacity - One hundred milliliters of 1N NH_4OAc , pH 7, were added to approximately 20 grams of sediment. The mixture was shaken for one hour and allowed to settle overnight. The

mixture was then filtered using the Millipore filtration apparatus. The sample was leached incrementally with additional NH_4OAc solution to obtain a total volume of 200-225 ml of filtrate. The filtrate was transferred to a 250-ml volumetric flask, acidified with HCl to pH 1.0, and made up to a volume with NH_4OAc . This solution was set aside for determination of individual exchangeable cations as described below. The sediment in the Millipore funnel was then leached incrementally with 200-250 ml of isopropyl alcohol to remove excess NH_4OAc . The sample was then transferred using distilled water to a Kjeldahl flask (800 ml). Boiling stones, a total volume of about 450-500 ml of distilled water, and 25 ml of 1N NaOH were added to the flask. The sample was distilled into 50 ml of 4 percent boric acid, a total of about 200 ml of distillate being collected. The final distillate was titrated with 0.1 N HCl using a standard indicator solution. The meq of NH_3 collected is equivalent to the exchange capacity when expressed in meq/100 g sediment.

(ii) Exchangeable cations - The NH_4OAc extract from the exchange capacity determination was analyzed for individual exchangeable cations (Na, K, Ca, Mg, Fe, Mn) with a Perkin-Elmer Model 403 atomic absorption spectrometer using an air/acetylene flame. Instrument settings were established using procedures recommended by the manufacturer. Results were expressed as parts per million of cations on a dry weight basis.

(iii) Total nitrogen - Approximately ten grams of sediment was mixed with 20 ml of water in a 800-ml Kjeldahl flask and allowed to

stand for 30 minutes. Then 10 grams K_2SO_4 , 1.0 g $CuSO_4 \cdot 5H_2O$, 0.1 g HgO (red), and 30 ml concentrated H_2SO_4 containing 2 g salicylic acid per 40 ml were added. The mixture was digested according to the standard procedure (79) for 5 hours. The sample was cooled, 500 ml distilled water added, and recooled. To the same flask, 25 ml of 16 percent $Na_2S_2O_3$ solution, several granules of mossy zinc, and 50 ml of 50 percent NaOH were added. The flask was immediately connected to a distillation column. About 200-250 ml of distillate was collected in 50 ml of 4 percent boric acid. The distillate was titrated with 0.1N HCl using the standard indicator solution. The results were expressed in terms of ppm NH_4-N on a dry weight basis.

(iv) Ammonium nitrogen - Approximately twenty-five grams of sediment was added to 400 ml of water, shaken vigorously, and allowed to stand overnight. Boiling stones and 5 ml of 1 N NaOH were added and 200 ml of the liquid were distilled into 50 ml of 4% boric acid solution. The distillate was titrated with 0.1 N HCl and the results expressed as ppm NH_4-N on a dry weight basis.

(v) Nitrate and nitrite-nitrogen - Fifty grams of sediment, 0.5 grams $CaSO_4$, and 250 ml of water were shaken for 10 minutes on a mechanical shaker, allowed to settle a few minutes, and filtered through a Millipore filter under N_2 . Nitrate-nitrogen was determined by the phenoldisulfonic acid method (79) and nitrite-nitrogen was determined by the diazonium method (79). Results were reported in ppm NO_3-N and NO_2-N on a dry weight basis.

(vi) Organic nitrogen - Organic nitrogen was calculated by subtracting $\text{NH}_4\text{-N} + \text{NO}_3\text{-N} + \text{NO}_2\text{-N}$ from total nitrogen.

(vii) Free iron oxides - The procedure followed was that given elsewhere (79).

(viii) Organic phosphorus - The method used for determination of organic phosphorus was adapted from those recommended in Methods of Soil Analysis (79) and Saunders (108). Two grams of sediment was ignited in a silica crucible for one hour at 550°C . The ignited sample and a duplicate 2-gram unignited sample were then extracted for 2 hours with 100 ml of 0.2N H_2SO_4 on a mechanical shaker. Inorganic phosphorus in the extracts was determined using a standard molybdate method (109). An aliquot of sample 3-10 ml in volume, depending on the phosphate concentration, was mixed with 2 ml of ammonium molybdate-HCl reagent and 2 ml of Elon reagent. The solution was diluted to a volume of 25 ml, mixed and allowed to stand for 15 minutes for color development. Color intensity of the sample, blanks, and standards carried through the extraction procedure was determined using a colorimeter. The increased phosphorus resulting from ignition in comparison to unignited samples was taken to represent organic phosphorus. Results were expressed as parts per million on a dry weight basis.

(ix) Total phosphorus - Total phosphorus was determined using two methods. The first employed was an acid-digestion technique. Two grams of sediment were mixed with 30 ml of 60% perchloric acid in a 250-ml volumetric flask. The mixture was digested on a hot plate until white fumes appeared (3-4 hours) and was then cooled and diluted to

volume with distilled water. The resulting solution was filtered and phosphorus determined using the molybdate method employed for analysis of organic phosphorus. Results were reported as parts per million phosphorus on a dry weight basis. Later, in determining organic phosphorus, it was found that total phosphorus as determined by ignition was often different than by digestion. Consequently, the average values were reported.

(x) Organic carbon - Organic carbon was determined by a Walkley-Black method similar to that outlined in Methods of Soil Analysis (79). Ten ml of water was mixed with approximately 2 g of sediment in a 250-ml Erlenmeyer flask and bubbled with air for approximately 10 minutes. Ten ml of 1N $K_2Cr_2O_7$ was added and mixed. Twenty ml of concentrated H_2SO_4 containing silver sulfate was added to the flask, the mixture swirled for one minute, and then refluxed for approximately 2 hours. Water (150 ml) and several drops of o-phenanthroline indicator were added, and the resulting mixture allowed to cool. The suspension was titrated with 0.5 N $Fe (NH_4)_2(SO_4)_2$. The $Fe (NH_4)_2(SO_4)_2$ was standardized repeating the procedure without sediment. The percent organic carbon was calculated using the following equation:

$$\% \text{ Organic-C} = \frac{\text{meq } K_2Cr_2O_7 - \text{meq } Fe (NH_4)_2(SO_4)_2}{\text{g, dry sediment}} \times .3$$

(xi) Total heavy metals - To determine total metals present in the sediments, two grams of sediment were digested with 20 ml of concentrated

HNO_3 in a 100-ml Erlenmeyer flask for 30 minutes on a hot plate. The mixture was cooled, after which 10 ml of concentrated HClO_4 and 5 ml of concentrated H_2SO_4 were added. The sample was further digested for 5 hours or until the volume of remaining acid was reduced to about 5 ml. The sample was then made up to 100 ml with distilled water and filtered. The concentrations of heavy metals other than mercury were determined directly on the extract using the atomic absorption spectrometer. An air/acetylene flame was used when the concentration of a given element was sufficiently high. For low concentrations, the graphite furnace was employed. Instrument settings were established using procedures recommended by the manufacturer. Results are reported in parts per million or billion on a dry weight basis.

For mercury, one gram of sediment was predigested with 5 ml of concentrated HNO_3 in a 300 ml BOD bottle by heating on a hot plate for 30 minutes at 60°C . A second stage of digestion was achieved by adding 15 ml of aqua regia (1 part nitric to 3 parts hydrochloric acid) with further heating for 60 minutes at the same temperature. The above digestion procedure has been reported in detail by Hamm and Stewart (102). The determination of mercury in the digest was performed with a Coleman Mercury Analyzer MAS-50 using the manufacturer's suggested procedure. The digested sample was diluted to 100 ml with distilled water. Five ml of 5-percent KMnO_4 was added and mixed. Other oxidizing reagents added next in sequence were 5 ml 5.6N HNO_3 (swirl and wait 15 sec); 5 ml 18N H_2SO_4 (swirl and wait 45 sec). Reducing agents were then

added in the order: 5 ml 1.5 percent hydroxylamine hydrochloride; 5 ml 10 percent stannous chloride. At this point the solution was analyzed using the Coleman MAS-50. Results were reported in parts per billion on a dry weight basis.

(xii) Dilute acid extractable heavy metals - For the determination of all extractable metals except mercury, ten grams of sediment was shaken with 50 ml of 0.1N HCl for one hour and filtered under N₂ using a Millipore filtration apparatus. The concentrations of extractable heavy metals in solution were determined by atomic absorption spectroscopy as described above for total heavy metals.

For mercury, five grams of sediment was shaken with 50 ml of 0.1N HCl for one hour. The suspension was filtered, and the soil leached with an additional amount of 0.1N HCl until a total filtrate volume of 100 ml was obtained. The extractable mercury was then determined using the Coleman Mercury Analyzer procedure described above in determining total mercury.

IV. RESULTS AND DISCUSSION

A. Long-Term Experiments

The long-term experiments consisted of the colloidal phase and cylinder (water overlying sediment) experiments in duplicate. One set of samples was analyzed after two months and the remaining set after four months. Data were also compared to initial (t=0) conditions. The conditions under which these initial samples were collected were described in Section III C(2). Because these experiments are simulating the

deposition of sediment matter in a new environment, values for initial interstitial waters in the column experiments are those of either the original freshwater or seawater. The experimental controls utilized were temperature (10°C) and, in the case of the cylinders, a dissolved oxygen level of approximately 4-6 ppm. Controls (i.e. cylinders and jars containing fresh water or seawater but no sediments) were maintained under identical conditions. As stated previously the samples received about two hours of indirect incandescent illumination per week. All samples were filtered through a 0.45- μ m membrane, acidified (pH=2, HCl), and stored in the dark at approximately 8°C until analyses could be performed. Using this preservation technique, no significant changes in phosphorus and nitrogen data were found even after four months of storage. Over the course of the long-term experiments, the sediment phase in the cylinders tended to increase in density. Table 4 shows the approximate weight of dry sediment in each cylinder and the percentage decrease in the volume compared to the initial volume.

Table 4. Sediment Dry Weights and Volume Changes
(± Standard Deviation) in Cylinders

	2 months		4 months	
	Weight <u>g</u>	% Decrease Volume	Weight <u>g</u>	% Decrease Volume
Hudson	940	23+7	810	18+4
Newtown	660	22+6	610	17+6
Shooter's	1020	19+4	840	19+5
Saginaw-Salt	1010	23+6	1010	18+6
Fresh	710	12+10	870	21+8
Rouge-Salt	850	22+7	800	27+7
Fresh	1070	27+6	1140	23+6
Maumee-Salt	610	29+5	610	28+8
Fresh	530	17+9	700	29+6

It must be emphasized that the colloidal and cylinder experimental systems are not necessarily at equilibrium or even in a quasi-steady state. By measuring a number of parameters at only three time intervals, we can only show apparent trends that may be of significance in the field. It should also be emphasized that the term "colloidal", as used to describe certain experiments in this report, is used only in a descriptive sense. True colloidal-size species can exist in all the various solution phases examined. However, the "colloidal phase" in these experiments, because of the method of preparation, can be expected to potentially contain more colloidal-size particles, at least initially, than the other solution phases.

To simplify the discussion, the results of these experiments will be discussed under the particular parameter that was measured. All concentrations reported are for soluble species, soluble being arbitrarily defined as that which passes through a 0.45- μm membrane. Data which are presented graphically are also presented numerically in the Appendix.

In the discussions that follow, reference is made to data measured at intervals of two and four months. The two-month samples were actually terminated after approximately 82 days and the four-month experiments after approximately 155 days. Pressure membrane filtration, as described previously, was utilized to obtain interstitial water from the sediments in the cylinders. All sediment in a cylinder was utilized to obtain interstitial water samples at the two- and four-month intervals.

(1) Organic Carbon

(a) Colloidal Phase

The changes in organic-C as a function of time are shown in Figure 9. Only the Rouge-Fresh and Newtown samples do not level off but instead show small increases after two months.

Sorption of soluble organic compounds by clay (94) and coprecipitation with iron (95) have been suggested as possible mechanisms for organic-C removal. Significant quantities of iron did precipitate in all samples except Newtown and Shooter's. Our experience with the original interstitial solutions indicated that soluble organic-C levels were unchanged by the precipitation of iron itself. The following data indicate that the decrease in soluble organic-C after two months is fairly constant:

<u>Sample</u>	<u>% Decrease, Organic-C</u>
Hudson	33
Newtown	33
Shooter's	32
Saginaw-Salt	37
Fresh	29
Rouge-Salt	50
Fresh	31
Maumee-Salt	39
Fresh	30

Further, the iron data shown in Figure 23b indicate that the amount of iron originally present has little effect on the carbon levels two months later. This suggests that sorption and/or coprecipitation are either not significant or are not terminal reactions in themselves. Coating of carbonate particles by organic-C has also been suggested (94).

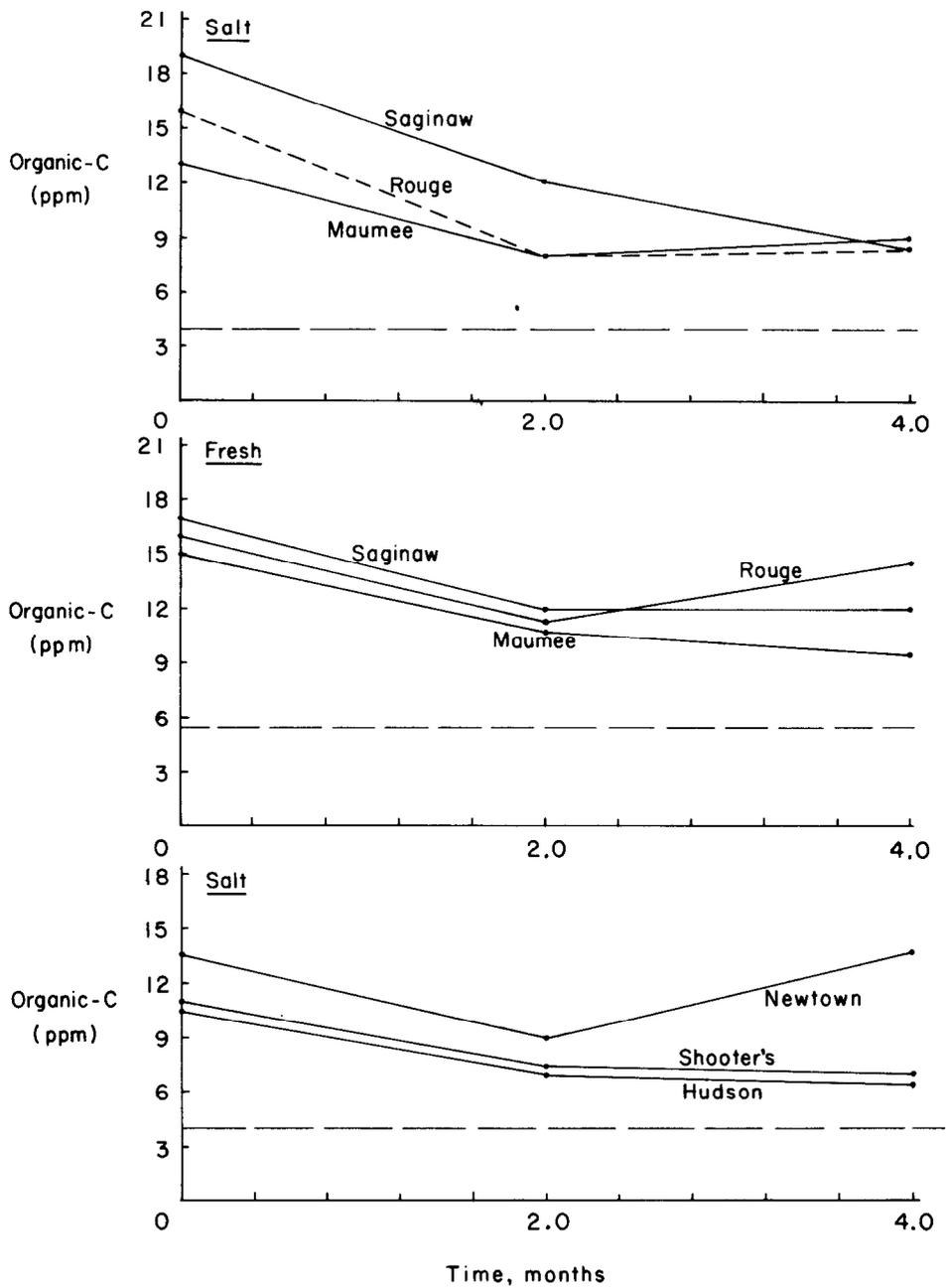


Figure 9. Changes in Organic-C Levels (Colloidal) with Time. (Horizontal lines represent levels in controls)

As will be discussed later (Section IV-B(2)), significant amounts of inorganic-C may be present in all samples except Detroit-Salt. Although solubilization of carbonate minerals is certainly a possibility, biological conversion of organic-C to inorganic-C is a more likely source (94).

Figure 10 is a schematic representation of the carbon cycle in natural waters (94). In our experiments the possibility of photosynthetic conversion of inorganic-C to organic-C has been eliminated. Heterotrophic activity (respiration), however, can still occur, and it is this mechanism which may partially be responsible for the conversion of organic-C to inorganic-C to inorganic-C. The anomalous behavior of the Detroit-Salt samples suggests that either heterotrophs have been severely inhibited by the drastic change in environment or that inorganic-C is being removed from the system. Under these circumstances it is not clear by which mechanism organic-C is depleted.

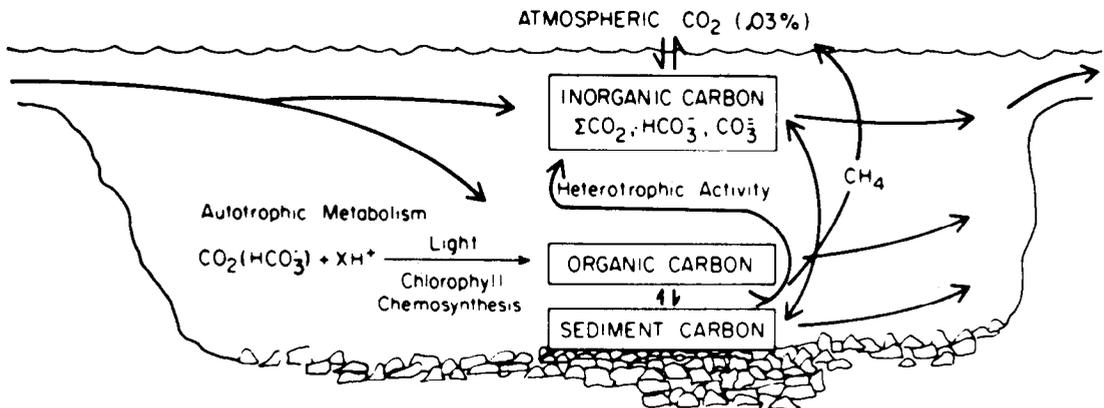


Figure 10. A Schematic Representation of the Carbon Cycle. After Kerr et al. (94)

It is not possible for us to draw any definitive conclusions regarding the fate of the organic carbon. Interactions of organic carbon with iron (sorption and/or coprecipitation) are not indicated. Transformation of soluble organic carbon into other forms of carbon seems to be the most likely possibility.

The fact that organic-C levels do not change significantly between two and four months indicates that either what remains is resistant to further transformations and/or interactions or that the system has reached a stage where for some reason the heterotrophs are no longer capable of continuing the conversion process. It is possible that the system is at equilibrium with respect to the two forms of carbon. Such an equilibrium cannot be dynamic, however, due to the lack of a suitable energy source (light) capable of converting inorganic-C to organic-C.

(b) Cylinders

Organic-C levels for the overlying water and interstitial water are shown in Figures 11 and 12. Sediment organic-C levels are listed in Table 5.

Table 5. Sediment Organic Carbon Levels

Sample	Elapsed Time, months-		
	0	2	4
Hudson	3.1	3.5	3.3
Newtown	8.0	8.7	8.8
Shooter's	7.1	6.9	6.4
Saginaw-Salt	3.7	3.8	3.2
Fresh	4.5	4.5	3.9
Rouge-Salt	10.9	8.8	8.9
Fresh	10.0	8.9	9.1
Maumee-Salt	3.6	4.4	4.1
Fresh	3.7	3.3	3.6

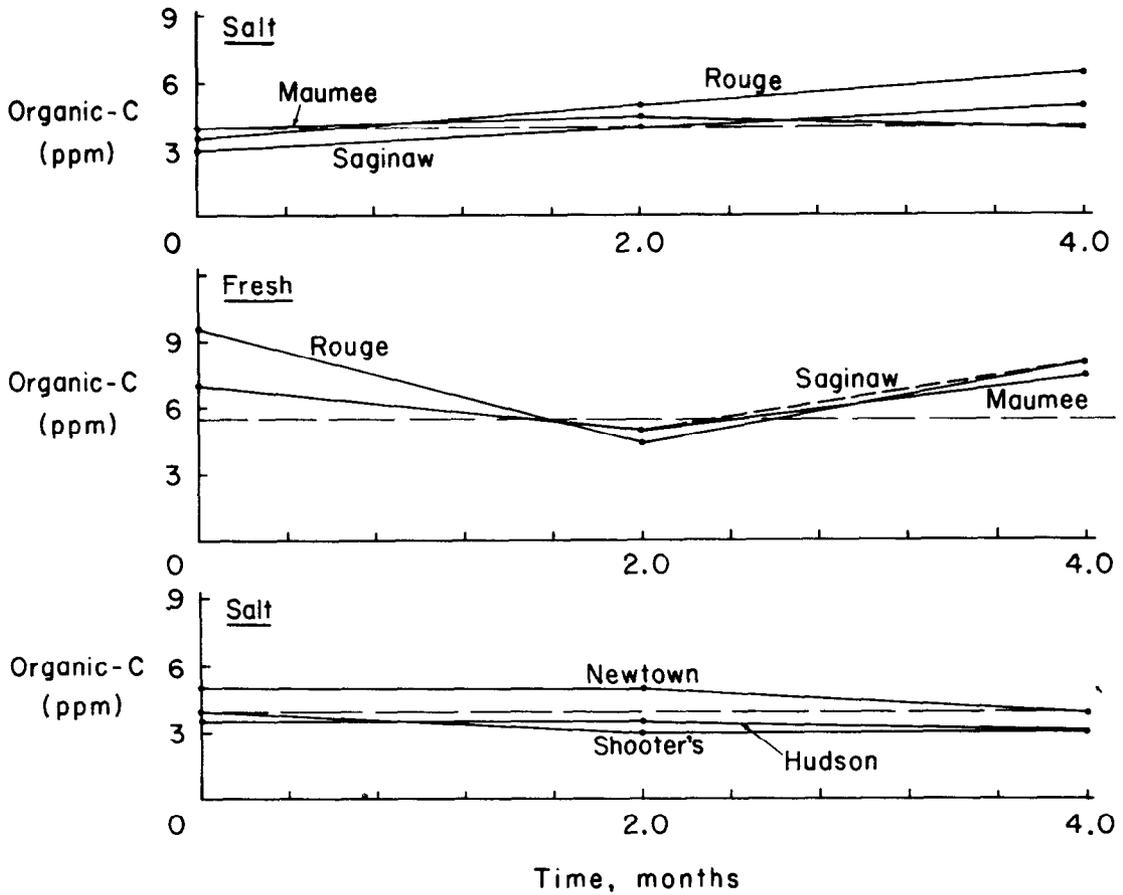


Figure 11. Changes in Organic-C Levels in Water Column with Time

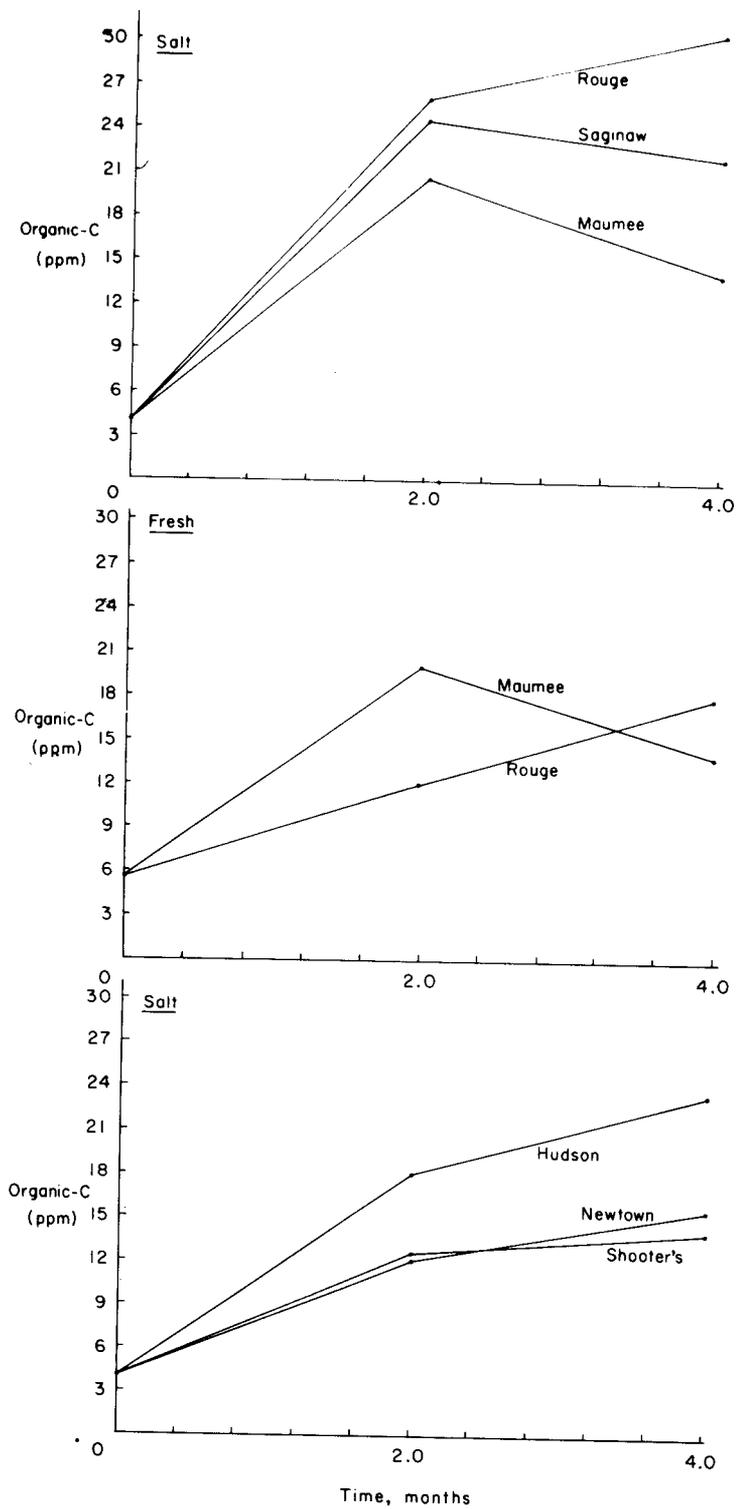


Figure 12. Changes in Interstitial Organic-C with Time

The initial high value for the Rouge-Fresh carbon in the overlying water may reflect to some degree partial mixing of the sediment and water when the water was added to the cylinder. During the four-month duration of the experiment, it was evident by the odor that something was being stripped out of the Rouge-Fresh cylinders during the N_2-O_2 purge. Whether organic materials were being removed is not known. Organic carbon seemed to be entering the water column from the sediments for the Detroit samples but not for the New York sediments. The precision of the organic-C measurements at these low levels precludes a definite verification of this, however.

Interstitial organic-C levels increase with time due to chemical and/or biological processes. Interstitial organic-C levels for Saginaw-Fresh went from 5.5 ppm to 27 ppm after four months. Both the Maumee-Fresh and Maumee-Salt samples show a significant decrease in organic-C between two and four months (Figure 12). The reason for this is not known. Rouge-Fresh and Rouge-Salt behave in a significantly different fashion. This may be due to the nature of the organic matter associated with this sediment. No correlation was found between overlying water organic-C and interstitial organic-C, suggesting that simple diffusion is not controlling the movement of organic-C into the water column. Purging of the system and possible resultant losses of volatile carbon might possibly be masking any relationship between the interstitial and overlying water.

The data on sediment organic carbon show there is essentially no change in this parameter over the time frame of the experiments. The concentration of organic carbon in the interstitial waters does not correlate with the sediment organic carbon and has not reached the levels found in the original interstitial waters (Appendix Table A5). This indicates that the solubilization of organic carbon is complex, probably both biologically and chemically controlled, these in turn being highly dependent upon the environment in which the sediment is located and the sediment itself. The transformations of carbon in natural systems are complex and only tracer studies can determine the particular fate of the inorganic and organic species.

(2) Nitrogen

(a) Colloidal Phase

Forms of nitrogen in colloidal phase as a function of time are shown in Figure 13. $\text{NO}_3\text{-N}$ values are actually the sum of nitrate and nitrite nitrogen.

The $\text{NH}_4\text{-N}$ results shown were all determined using the ammonia probe except for the Maumee-Salt sample at $t=0$. This particular sample turned green upon the addition of base (possibly due to the presence of nickel) and gave $\text{NH}_4\text{-N}$ levels of approximately 270 ppm. The TKN result for this one sample is being utilized as it is more consistent with the values at $t=2$ and $t=4$ determined with the probe.

Nitrification took place rapidly in the Detroit-Fresh and Hudson samples, slowly in the Newtown and Shooter's samples, and was insignificant

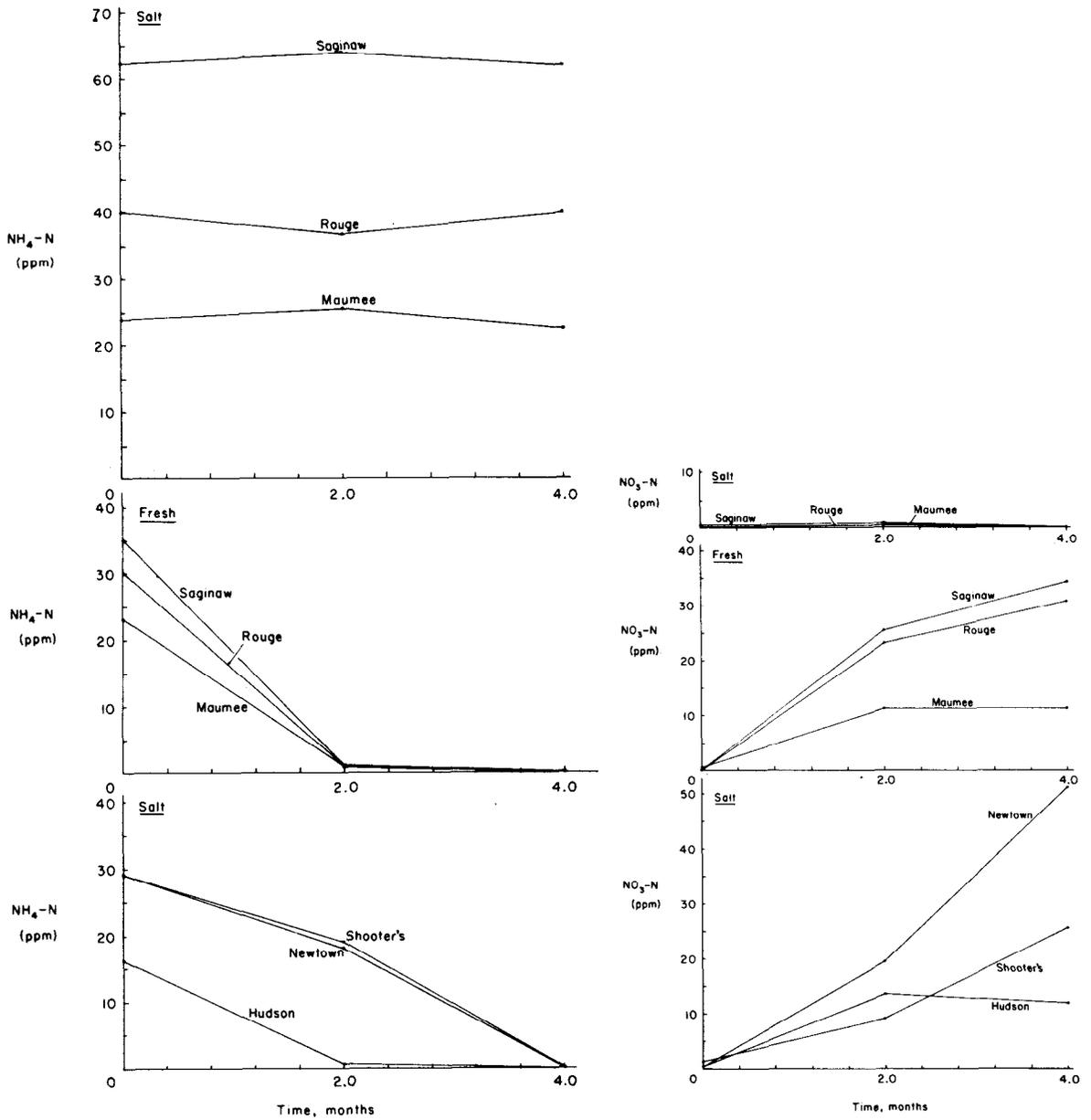


Figure 13. Changes in Nitrogen Levels (Colloidal) with Time

in the Detroit-Salt samples. For the Detroit samples there are several possible explanations. If the nitrifying species are associated with the sediment itself, then they would be species which had adapted to a freshwater environment. By placing them in a seawater environment, they are very likely to undergo irreversible damage due to osmotic effects as water migrates out of the cells. Secondly, the high salt level could displace, by exchange reactions, potential inhibitors associated with sediment. If such inhibitors were released, their effect would probably be manifested regardless of the source of the nitrifiers (i.e. sediment and/or seawater). With Shooter's and Newtown, osmotic damage is not likely due to the saline environment from which these sediments originated (see Table 12). Because these two sediments contained relatively high amounts of potentially toxic metals, it is possible that inhibitors were released which slowed, but did not prevent, the nitrification process. In a recent study Chen et al. (107) found that nitrification was dependent both on salinity and as yet other unidentified species. The sum of the nitrogen species is shown in Table 6.

Table 6. Sum of Nitrogen Series ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$)
in Colloidal Samples (+9%)

Sample	Elapsed Time, months-		
	$\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$, mg/l		
	0	2	4
Hudson	16.9	16.1	11.8
Newtown	29.1	37.4	51
Shooter's	30.1	27	26
Saginaw-Salt	62.2	64.8	62
Fresh	35	26.5	34.3
Rouge-Salt	40.1	37.5	40
Fresh	30	24.2	30.8
Maumee-Salt	24	26.7	22
Fresh	23.5	12.3	11.2

Chen et al. (93), using lake sediments, found that under aerobic conditions nitrate is assimilated by microorganisms in sediments into forms of organic-N. Using diatoms as a source of particulate organic-N and seawater, it has been shown (94) that such a system, when stored in the dark, undergoes decomposition of particulate-N to $\text{NH}_4\text{-N}$, which is subsequently followed by nitrification. Illumination causes $\text{NH}_4\text{-N}$ to decrease with a consequent rise in particulate-N. It is possible that all of these events are occurring in our colloidal systems. What is observed at any particular time is a consequence of the concentrations of specific components and the kinetics of the reactions involving the various forms of nitrogen. The steps of the nitrogen cycle are illustrated in Figure 14. A possible explanation for what was observed in our experiments is that $\text{NH}_4\text{-N}$, liberated during the formation of the colloidal phase undergoes nitrification in the absence of any inhibitors.

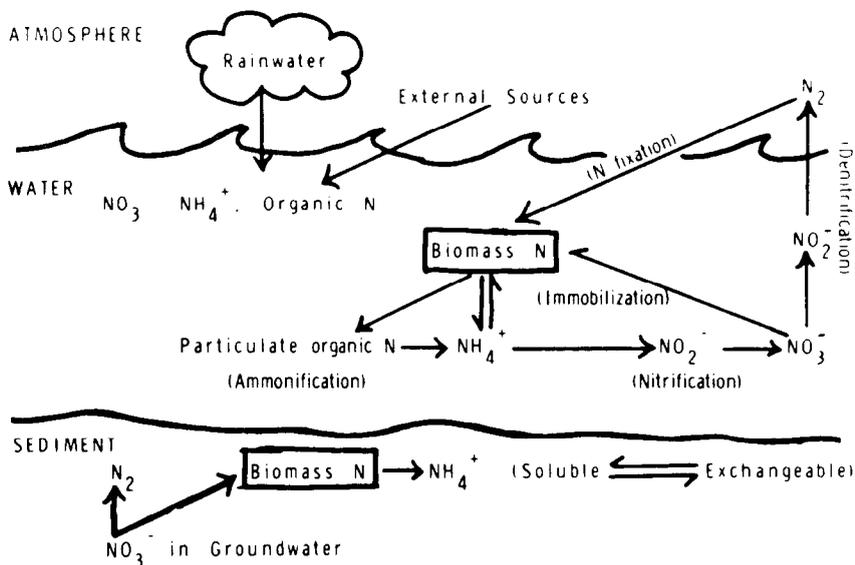


Figure 14. The N-Cycle in Sediments and Waters.
After Keeney (91)

Some $\text{NH}_4\text{-N}$ may also be removed by some form of interaction with the solid phase. Nitrate levels increase as nitrification proceeds even when there is no detectable $\text{NH}_4\text{-N}$, due to the decomposition of particulate-N to $\text{NH}_4\text{-N}$ and subsequent rapid conversion to $\text{NO}_3\text{-N}$. Nitrate levels do not necessarily reach previous $\text{NH}_4\text{-N}$ levels as $\text{NO}_3\text{-N}$ is lost by assimilation with the particulate phase. Only the Newtown sample shows a significant increase in the total amount of soluble nitrogen forms, suggesting that there is considerable particulate-N available and/or that removal mechanisms are inefficient. Nitrogen fixation may also be a possibility (91).

It is quite obvious that the complexity of these systems makes it difficult to delineate specific cause-effect relationships. If the colloidal phases were prepared under different experimental conditions (i.e. perhaps with oxygen-containing water) then the observations might be totally different. If, however, the conditions were reasonably representative of actual field situations, then some general conclusions might be made. Transfer of sediments originating from a freshwater environment into a saline environment will probably result in the lack of nitrification taking place unless sufficient nitrifying bacteria are available at the dispersal site. The rate of nitrification of ammonium-N for saline sediments which are placed in a saline environment and for freshwater sediments placed in freshwater environments will be high but dependent both upon characteristics of the sediments as well as the receiving waters.

(b) Cylinders

Figure 15 shows the amounts of ammonium and nitrate nitrogen in the overlying water as a function of time. For all cases except Hudson, Shooter's, and Maumee-Fresh there is a significant increase in ammonia-N after two months. Decreases in ammonia-N are generally coincident with increases in nitrate-N, suggesting that nitrification is taking place. Decreases in nitrate-N levels may be due to either denitrification in the water column or, more likely, diffusion of nitrate to the sediment and its subsequent assimilation and possible denitrification (91). Controls (cylinders containing no sediments) showed constant nitrate-N and ammonia-N levels over the four-month period, indicating

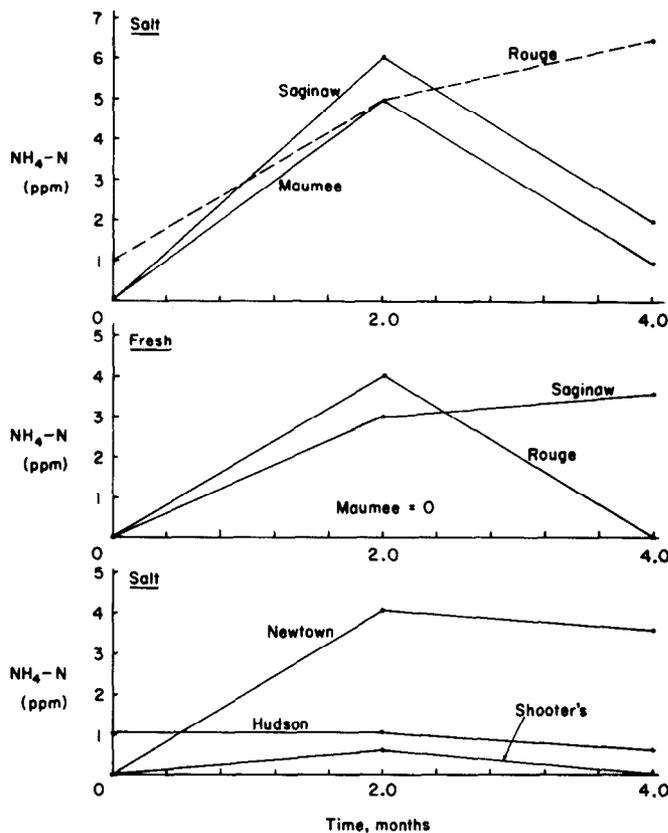


Figure 15. Changes in Nitrogen Levels in Water Column with Time

that processes in the sediment are responsible for the observed transformations. The data in Table 7 show that the sum of ammonia-N and nitrate-N is not constant and that some exchange is taking place between the sediment and water column. The behavior of the Detroit-Salt samples

Table 7. Sum of ammonia-N and nitrate-N in cylinders ($\pm 9\%$)

Sample	Elapsed Time, months-		
	NH ₄ -N + NO ₃ -N, mg/l		
	0	2	4
Hudson	0.2	3.2	1.4
Newtown	0.2	4.2	4.4
Shooter's	0.2	3.1	0.4
Saginaw-Salt	0.2	6.2	6.7
-Fresh	1.2	4.0	3.9
Rouge-Salt	0.2	5.1	7.3
-Fresh	1.2	4.9	4.2
Maumee-Salt	0.2	5.7	6.3
-Fresh	1.2	2.0	1.5

is different from that of the corresponding freshwater samples. Higher nitrogen values are found in the Detroit saltwater systems, which may indicate that dissolved salts are tying up potential exchange sites. Nitrogen fixation within the water column itself cannot be ruled out. Dugdale and Dugdale (92) found that fixation of molecular nitrogen occurred even in samples stored in the dark although at a rate much slower than in those samples which were stored in the light. Keeney (91) has briefly reviewed the literature on nitrogen fixation and finds that nitrogen fixation apparently occurs under a variety of conditions although the responsible species may be quite different. In our own experiments the water column remains in a saturated to supersaturated condition with

respect to nitrogen. The general lack of knowledge with regards to nitrogen fixation mechanisms precludes the possibility of determining if such reactions were operational and of significance.

Figure 16 shows the ammonia-N and nitrate-N levels in the interstitial waters as a function of time. For Saginaw-Fresh, $\text{NH}_4\text{-N}$ increased from approximately 0 to 9 ppm over four months and NO_3 from 1.2 to 14 ppm over the same period (Appendix Table A6). All samples show an initial increase in the ammonia-N levels with all but Rouge-Salt and Hudson decreasing after four months. Nitrification of the ammonium is probably taking place but no discernable trends are evident. The sum of ammonium-N and nitrate-N is again variable (Table 8). The relatively

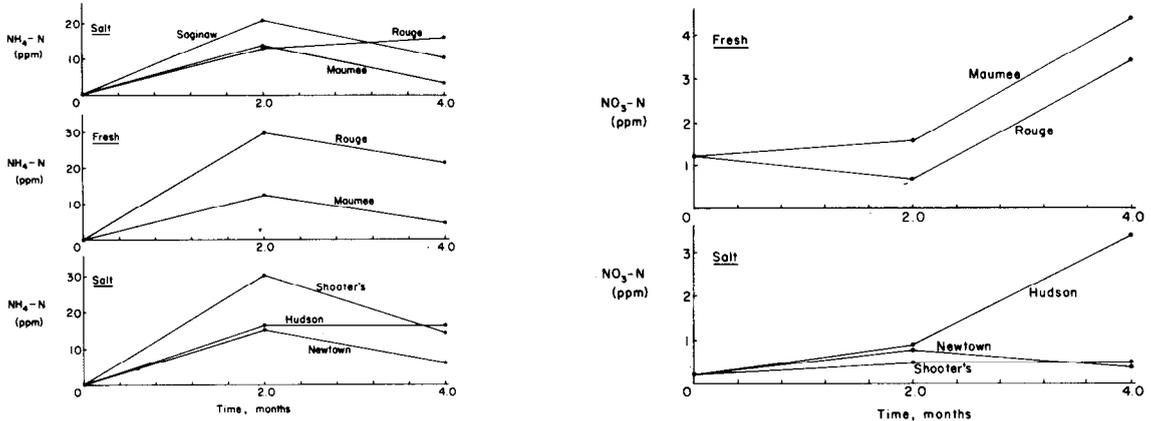


Figure 16. Changes in Interstitial Nitrogen Levels with Time

Table 8. Sum of Ammonium-N and Nitrate-N in Interstitial Waters (\pm 9%)

Sample	$\text{NH}_4\text{-N} + \text{NO}_3\text{-N, mg/l}$			
	2 Months		4 Months	
	Sum	% $\text{NO}_3\text{-N}$	Sum	% $\text{NO}_3\text{-N}$
Hudson	17.4	5.2	20	17.0
Newtown	16.1	5.0	6.7	6.0
Shooter's	31.4	1.6	15.1	3.3
Saginaw-Salt	21.9	4.1	10.4	2.9
Fresh	--	--	23	61.7
Rouge-Salt	14.4	9.7	18.4	13.0
Fresh	30.7	2.3	24.5	13.9
Maumee-Salt	52.2	69.	4.2*	19
Fresh	14.1	11.3	48.5	9.1

*Skewed peak observed for nitrate

low amounts of $\text{NO}_3\text{-N}$ for the majority of interstitial samples indicate that the sediments are essentially anoxic with only minor amounts of oxygen permeating from the water column past the sediment-water interface. A number of samples show an increasing percentage of $\text{NO}_3\text{-N}$ (Table 8), which may indicate slow diffusion of oxygen into the interstitial water. There are insufficient data to offer an explanation of the Saginaw-Fresh sample and the problems encountered with the Maumee-Salt have been discussed previously.

The distribution of nitrogen in the sediments is shown in Table 9. The only parameter showing significant variation is $\text{NH}_4\text{-N}$. The difference between $t=0$ and $t=2,4$ may reflect some change in the redox potential of the sediment.

Table 9. Forms of Nitrogen in Sediments (0, 2, and 4 Months)

	Total-N, %			Organic-N, %			NO ₃ -N, μm/g			NH ₄ -N, μg/g		
	0	2	4	0	2	4	0	2	4	0	2	4
Hudson	0.17	0.14	0.13	0.15	0.13	0.11	0.8	1.2	0.2	220	60	157
Newton	0.24	0.25	0.26	0.20	0.24	0.24	0.2	0.4	0.1	415	58	196
Shooter's	0.21	0.18	0.14	0.18	0.12	0.13	0.2	0.1	0.1	322	44	122
Saginaw-Salt	0.17	0.18	0.18	0.14	0.18	0.17	0.5	0.3	0.7	258	52	76
Fresh	0.21	0.20	0.21	0.17	(.18)0.19		0.2	0.1	0.5	347	--	173
Rouge-Salt	0.20	0.14	0.14	0.17	0.13	0.13	0.2	0.9	0.1	333	89	101
Fresh	0.17	0.16	0.15	0.13	0.14	0.13	0.2	0.1	0.1	322	242	173
Maumee-Salt	0.16	0.18	0.20	0.13	0.17	0.19	1.0	2.1	0.1	347	133	130
Fresh	0.19	0.16	0.15	0.15	0.14	0.12	0.2	0.1	0.8	449	225	257

Figure 17 shows that a correlation exists between overlying water NH₄-N and interstitial water NH₄-N where no surface film was evident.

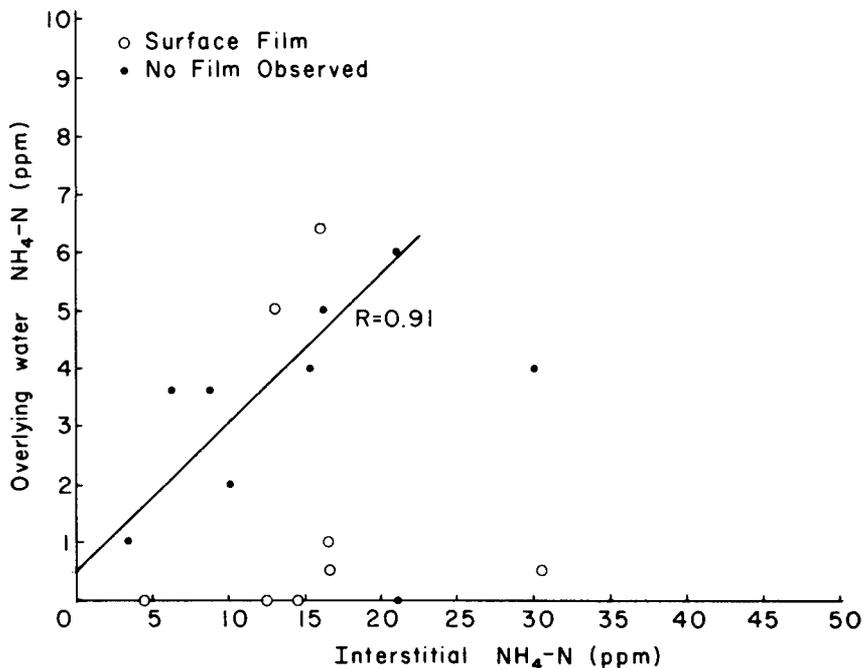


Figure 17. Relationship Between Overlying and Interstitial NH₄-N

The concept of an often visible oxidized microzone at the sediment-water interface has been discussed by Keeney (91), and it has been suggested that such a zone might interfere with sediment-water interchanges. Definite surface films were observed for Hudson, Shooter's, Maumee-Fresh, and Rouge-Salt. The appearance of a surface film coincides with low overlying water $\text{NH}_4\text{-N}$ levels in all cases except for the Rouge samples where the situation is reversed.

It should be further noted that $\text{NO}_3\text{-N}$ levels were found to have substantially increased over the four-month period in most of the interstitial samples where a visible oxidized layer was evident. The exceptions were Shooter's, where no increase was noted, and Rouge-Fresh, where there was an increase in interstitial $\text{NO}_3\text{-N}$ but no visible oxidized surface layer. This latter fact may indicate that some type of surface film existed. If $\text{NO}_3\text{-N}$ were present only in a surface film, then it would have to be present at an enormously high concentration as the entire volume of sediment in the cylinder was utilized to obtain the interstitial water sample.

(3) Phosphorus

Transformations and movement of phosphorus in lake sediments have been discussed by Syers et al. (96), and the dynamics of this system are shown in Figure 18 (96).

Although a number of mechanisms have been suggested that would be capable of controlling P-levels in interstitial waters, the single most important parameters are Fe(III), Al(III) clays, and Ca^{+2} (97) because of their abundance and ability to precipitate and/or sorb phosphate.

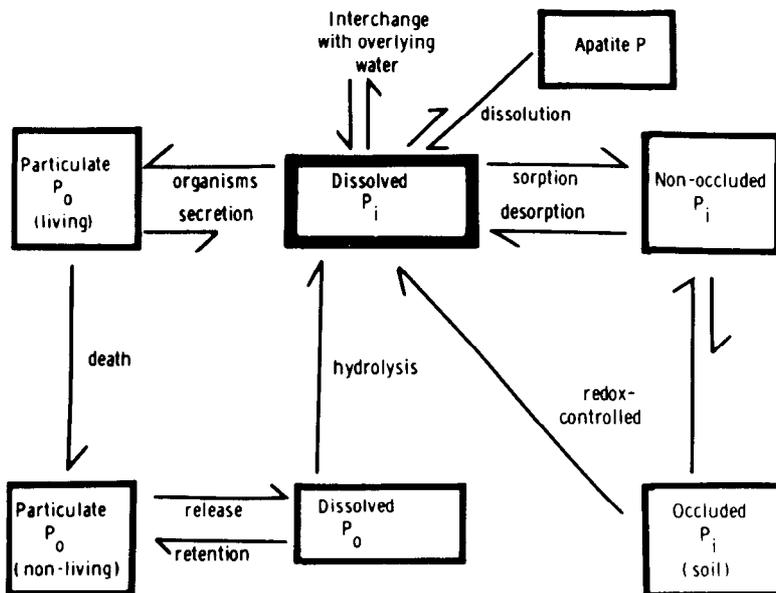


Figure 18. Dynamics of Sediment P (P_i = inorganic P; P_o = Organic P). After Syers et al. (96)

(a) Colloidal Phase

Variations in soluble ortho-P as a function of time are shown in Figure 19. Only in those samples which contain small amounts of iron

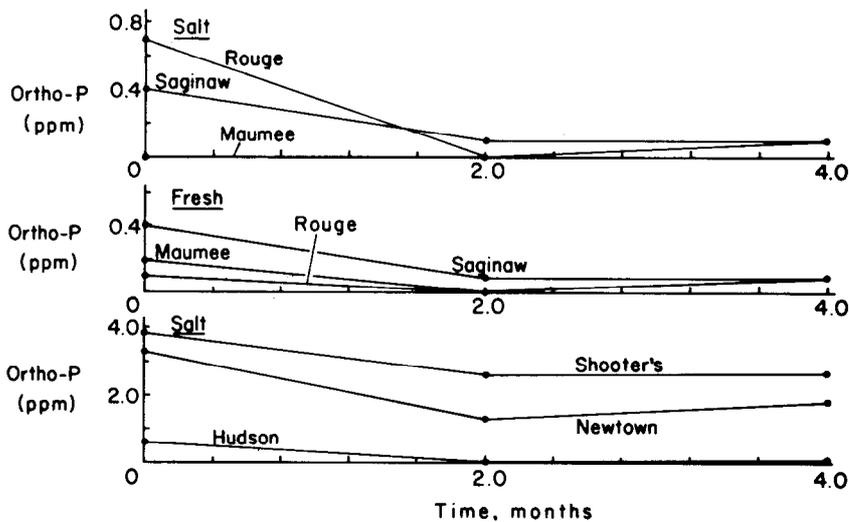


Figure 19. Changes in Ortho-P Levels (Colloidal) With Time

(Newtown and Shooter's) do large amounts of soluble P appear. In all cases there is a decrease of both iron and P with time. The Detroit-Salt samples and the Hudson sample were initially clear at the time of collection with ferrous iron subsequently oxidizing to form a visible reddish floc. Newtown and Shooter's were slightly turbid and the Detroit-Fresh samples were all highly turbid. Formation of a visible iron floc could not be observed in any of these five samples. The amount of P lost in the Newtown and Shooter's samples agrees quite well with the measured iron decreases (Figure 23b); for Newtown the calculated ortho-P remaining in solution is 1.6 mg/l versus 1.3-1.8 mg/l measured and for Shooter's, 2.2 mg/l calculated versus 2.6 mg/l measured. This is based on simple FePO_4 precipitation. Various hydroxy phosphates might also be formed. Although the Detroit samples contain significant amounts of carbonates (Section IV-B(2)), it has been suggested that carbonates are not the most important P-controlling component of calcareous sediments (96,98).

(b) Cylinders

Figures 20 and 21 show the variations in ortho-P in the overlying waters and interstitial waters as a function of time. Interstitial ortho-P rose from approximately 0 to 2 ppm in Saginaw-Fresh over four months. For several of the samples, there is definite indication that phosphorus is moving out of the sediment and into the water column. Interstitial ortho-P increases in Newtown and Shooter's probably by desorption from the sediment (96). The appearance of ferrous iron in

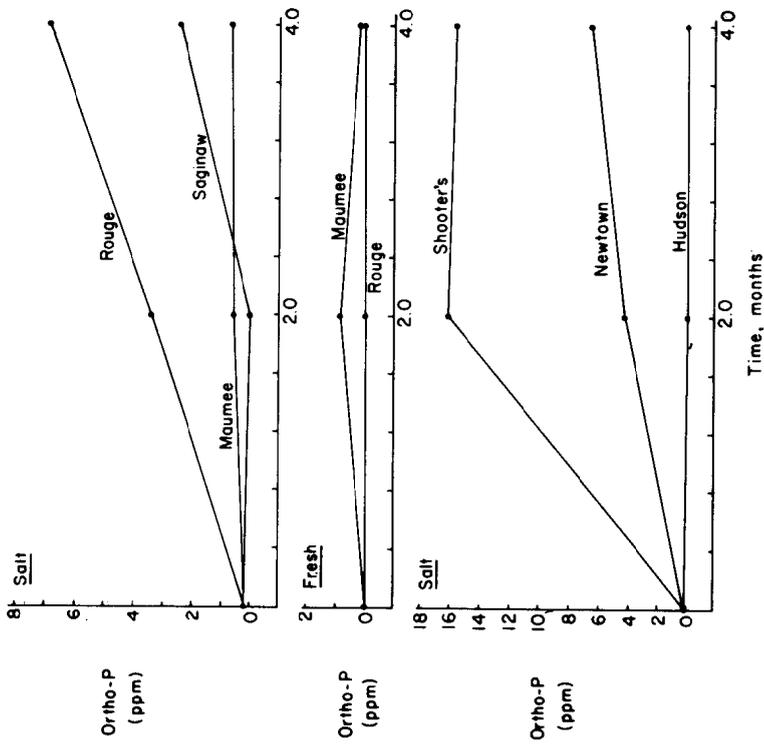


Figure 21. Changes in Ortho-P Levels in Interstitial Waters with Time

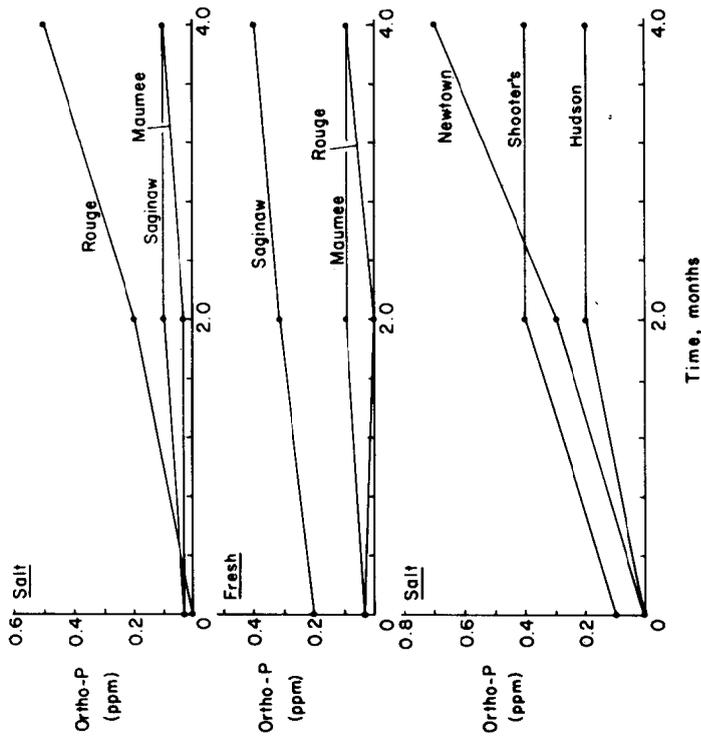


Figure 20. Changes in Ortho-P Levels in Overlying Waters with Time

the interstitial waters does not necessarily coincide with solubilization of ortho-P for the Detroit-Salt samples; Maumee and Saginaw contain relatively large amounts of ferrous iron, while Rouge is still quite low. The same observation can be made for the New York samples. Ortho-P can be solubilized under aerobic conditions although at a much slower rate than if the system is anaerobic.

It is clear that in these experiments indicators of anoxic conditions (Fe^{+2} , NH_4^+) cannot be used to ascertain whether ortho-P will be solubilized. The form in which P is associated with the sediment would seem to be the controlling factor in determining its dissolution.

Figure 22 suggests that there is a relationship between interstitial-P

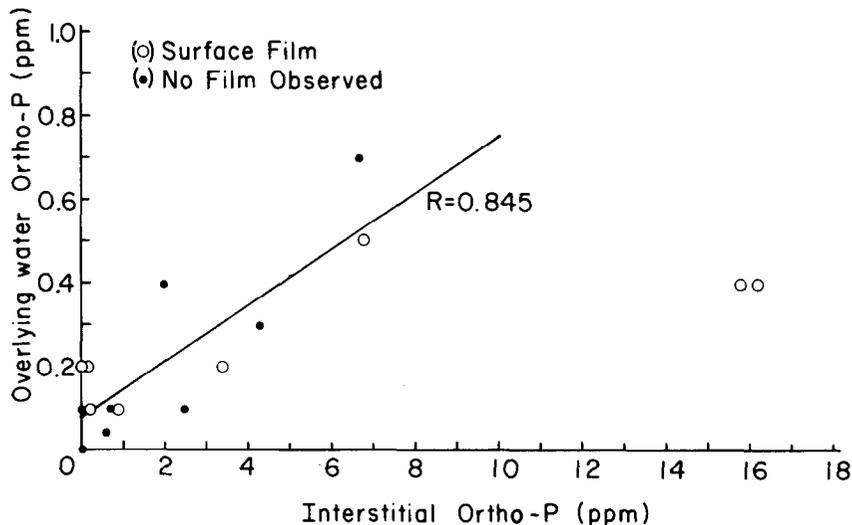


Figure 22. Comparison of Overlying Water P Values with Interstitial P Levels

and overlying water-P except in the case of the Shooter's samples. The concept of a physical barrier, as discussed in the nitrogen section, does not seem to be operative under these experimental conditions. Table 10 shows the distribution of P within the sediments. Total-P is taken as the average of the total-P values determined by ignition and acid extraction.

Table 10. Phosphorus in Sediments

<u>Sample</u>	<u>Elapsed Time, months-</u> <u>Total-P, $\mu\text{g/g}$</u>			<u>Elapsed Time, months-</u> <u>Organic-P, $\mu\text{g/g}$</u>		
	<u>0</u>	<u>2</u>	<u>4</u>	<u>0</u>	<u>2</u>	<u>4</u>
Hudson	1400	1290	1210	78	49	73
Newtown	(2520)	4620	5760	294	291	396
Shooter's	1560	1360	1490	69	97	136
Saginaw-Salt	1020	1000	940	92	53	74
Fresh	890	960	1070	63	88	83
Rouge-Salt	1540	2080	1900	166	183	211
Fresh	1310	1830	1780	61	134	149
Maumee-Salt	1110	1150	1290	103	167	193
Fresh	1046	1110	1270	57	68	50

It is not clear exactly what is happening with the Newtown samples. Ferric iron is known to interfere with the molybdate method but addition of stannous chloride to some of the samples to reduce ferric iron had no effect on the measured optical absorbances. The total amount of iron should not vary between samples since they all had a common, well-mixed origin.

Concretions had been noted in the original sediment and were avoided when subsamples were taken for analysis. Possibly over the

course of the experiments breakdown of these concretions caused an increase in iron and/or phosphorus. This, however, cannot be verified.

Exchangeable iron was determined on the original sediment (t=0) and correlates well with total-P. This is not surprising in light of iron-P interactions but the data could also be indicating interference by iron in total-P determined by the molybdate method. Unfortunately, we do not have data on the total amount of iron present in the extracts utilized in the total-P determinations.

The values for total-P obtained are quite reasonable and the absolute magnitudes are consistent with the nature of the sampling areas. Variations are thought to be a result of analytical difficulties. The result for Newtown (t=0) reflects an analytical problem that was not detected until the two- and four-month values were obtained. Organic-P values seem somewhat low and probably reflect the difficulties in the determination of this particular component. For these reasons and because the cycling of phosphorous through inorganic and organic forms is poorly understood, we will forego any discussion on potential transformations.

Baturin (99), analyzing deep-sea sediments, found that sediment P was closely related to sediment organic carbon. Except for Newtown the sediments in this study show a similar relationship - $\% \text{ Total-P} = 0.011 (\% \text{ Organic-C}) + 0.073$; (R = 0.90). However, as with Baturin's findings, the relationship is not sensitive enough to be useful as a predictive tool. He also reported that interstitial ortho-P correlated

more closely with sediment organic-C than with sediment total-P. No such correlations were found in the sediments utilized in this work.

(4) Metals

The relative changes in metal concentrations in solution for all samples are shown in Figure 23 a through h and in Table A-6. In general, the trends observed for the cylinders are identical to those observed in the colloidal phase. The initial sampling of the cylinder waters was performed while they were still in an anoxic state (p.34); metal levels are initially high and fall off as the system is transformed to a moderately oxidizing environment. Cadmium behaves exactly opposite to the other metals and such behavior may be due to the insolubility of the sulfide with subsequent transformation to more soluble forms.

For all seawater samples, manganese levels remain essentially constant with time. As discussed by Morgan (106), divalent manganese is thermodynamically unstable in the presence of oxygen at pH levels normally encountered in natural waters. However, the presence of large amounts of chloride ion, such as in seawater, leads to the formation of significant amounts of chloro-manganese complexes, the net result being to greatly reduce the rate of oxidation of divalent manganese.

Iron follows a predictable trend as concentration decreases as oxidation proceeds. The interaction in solution between iron and organic matter has been widely investigated and a schematic model of potential reaction pathways is shown in Figure 24 (76). The data in Table 11 show the distribution of forms of iron in selected samples.

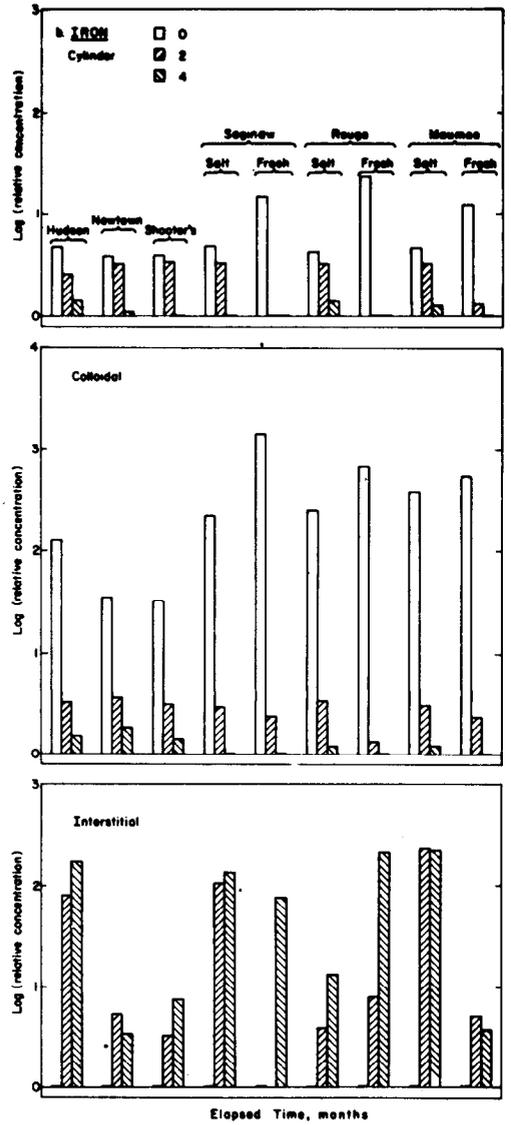
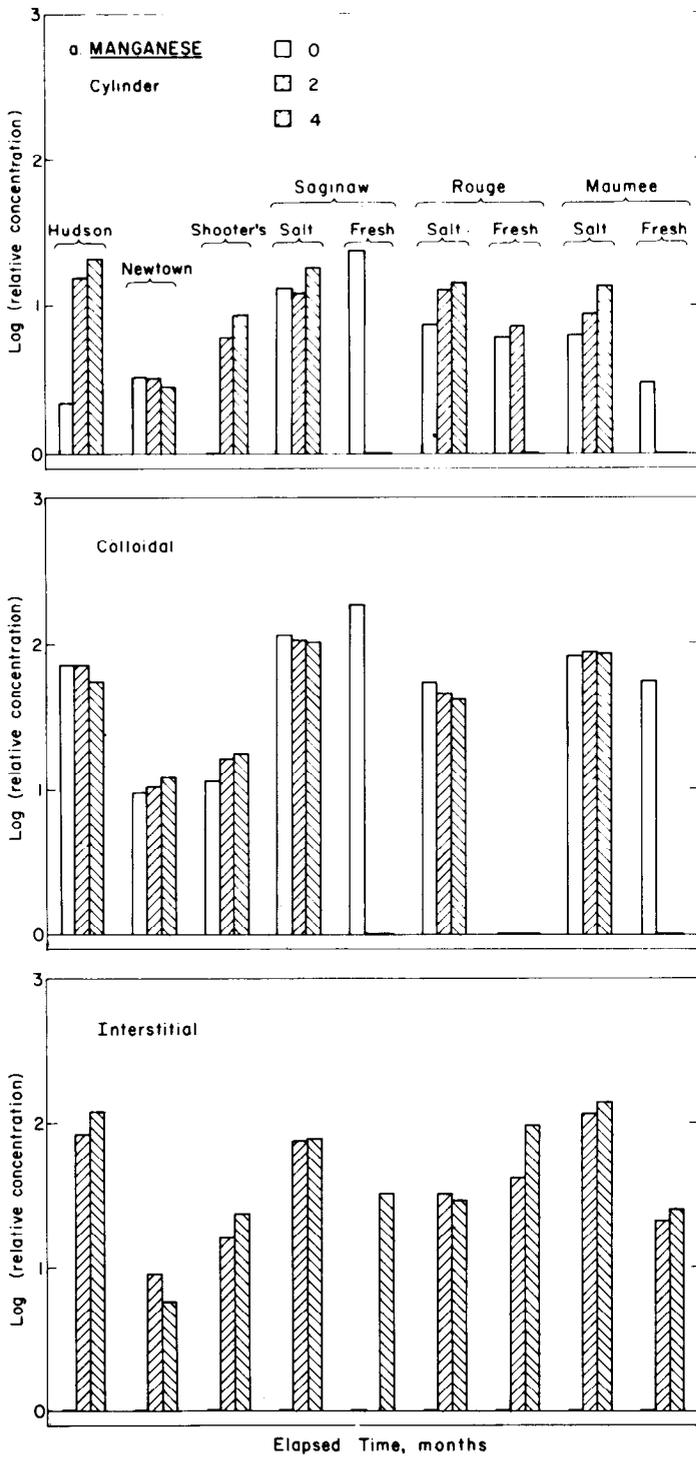
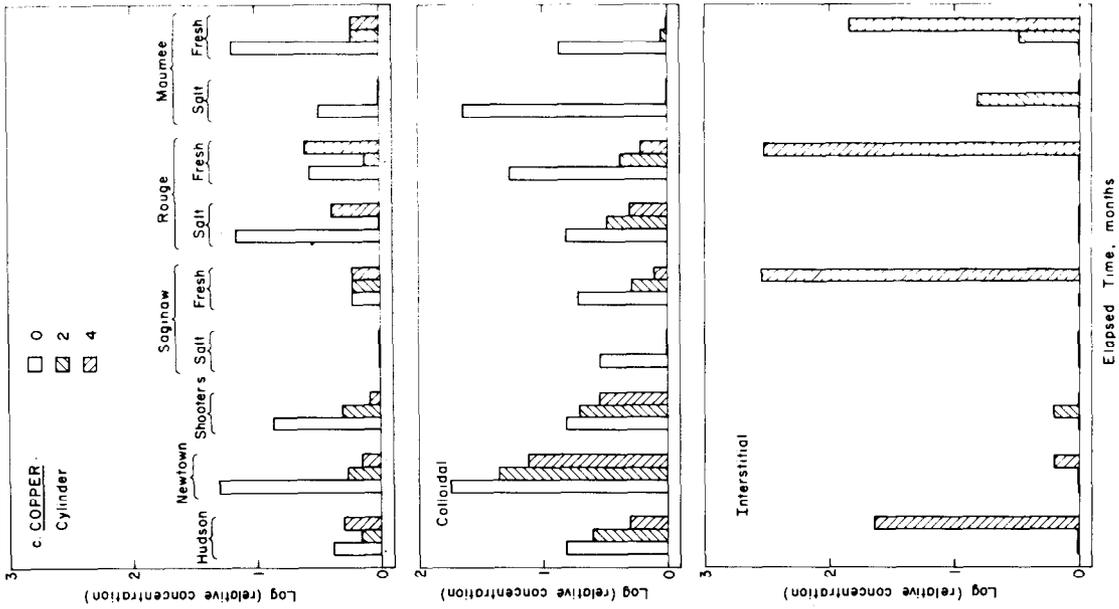
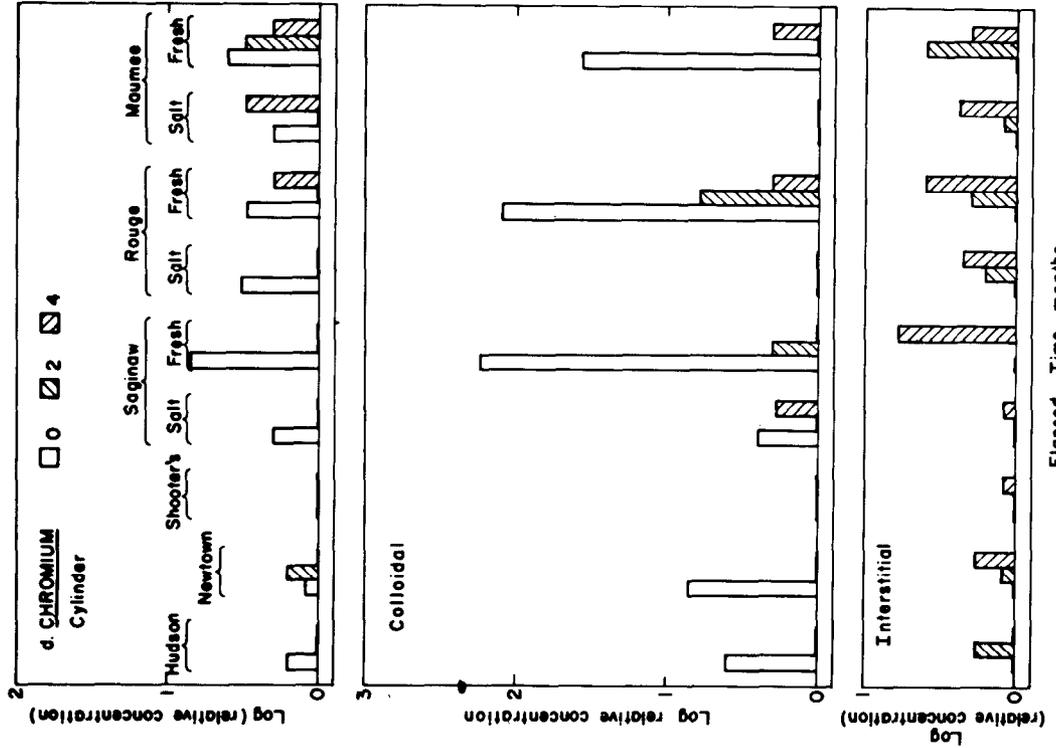


Figure 23a. Changes in Total Metal Concentration with Time. (The Ordinate is the Logarithm of the Concentration Relative to Either the $\log (C/C_{\text{control}})$ Seawater or Lake Water Control.)

Figure 23b. $\log (C/C_{\text{control}})$ (cont'd)

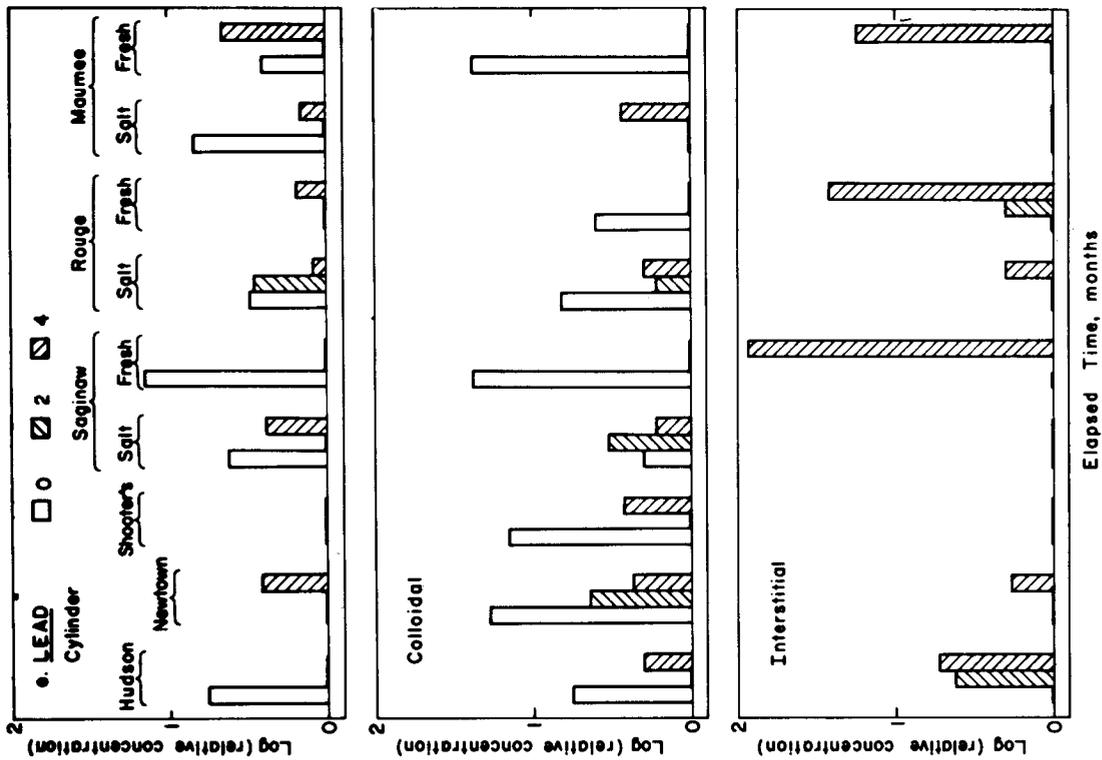


c

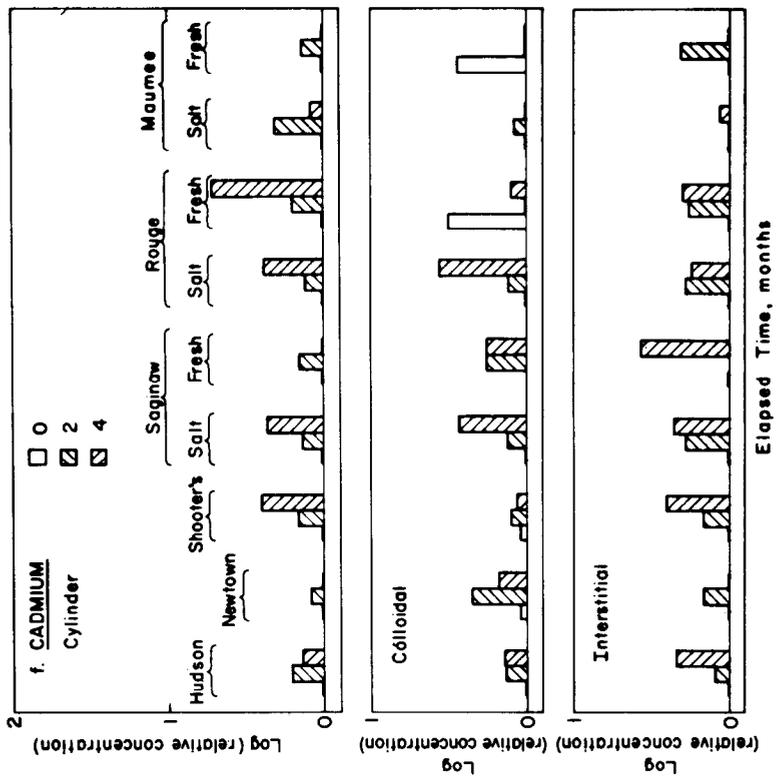


d

Figure 23. Log (C/C₀) Cont'd



e



f

Figure 23. $\log (C/C_{control})$ Cont'd

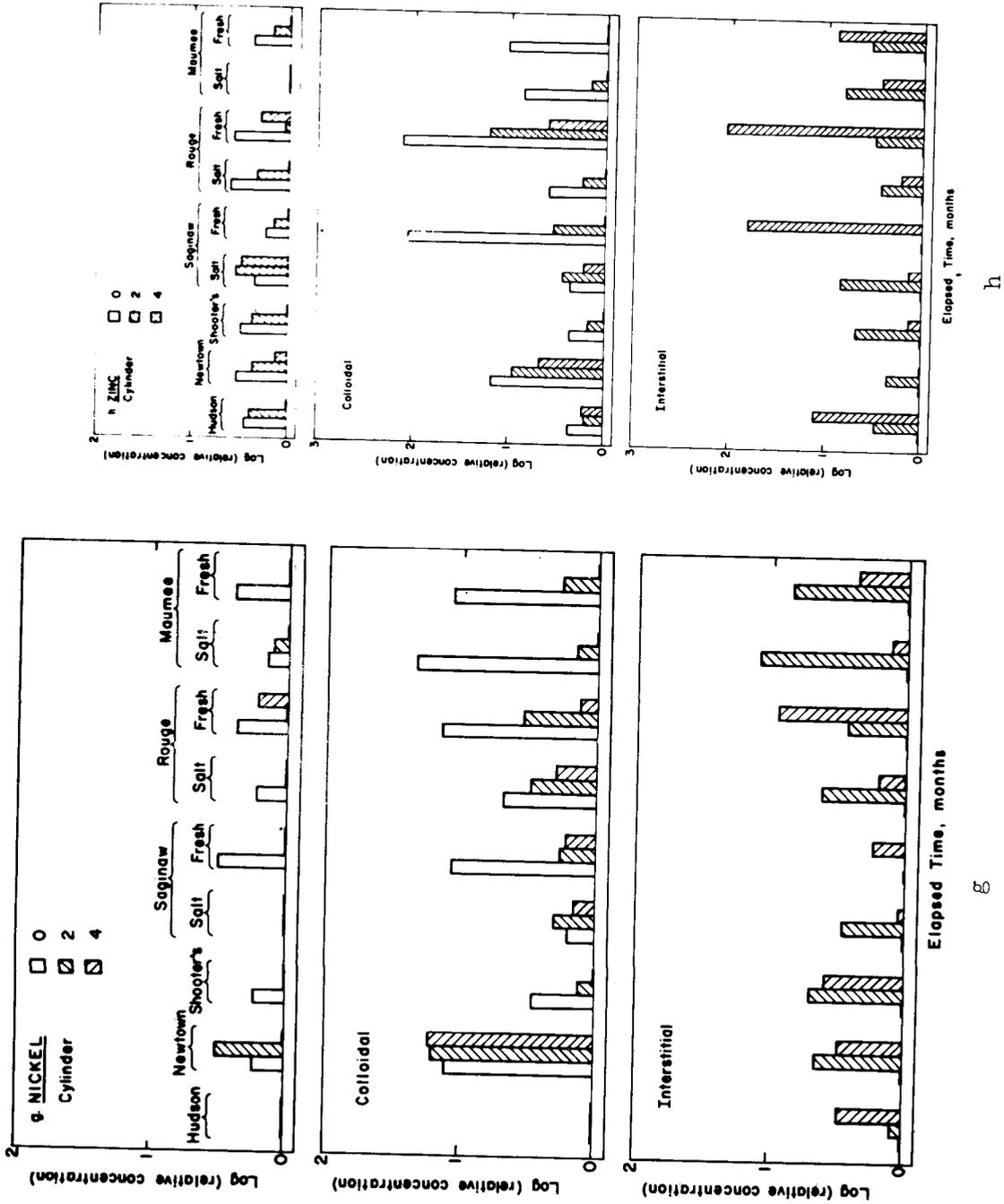


Figure 23. log (C/C control) Concluded

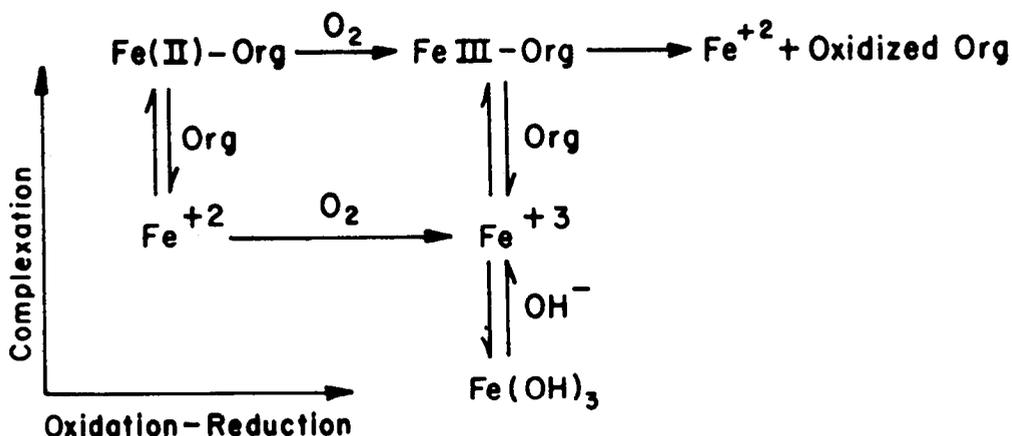


Figure 24. Schematic Diagram of Iron-Organic Cycle.
After Theis and Singer (76)

Table 11. Forms of Iron in Selected Samples (mg/l.)
(Relative Error = 3%)

	Colloidal		Interstitial			
	t=0 months		t=2 months		t=4 months	
	Fe ⁺²	Fe ⁺³	Fe ⁺²	Fe ⁺³	Fe ⁺²	Fe ⁺³
Hudson	11.8	3.4	3.4	2.2	20 ^a	20 ^a
Newtown	3.5	0	0.2	0	0.7	0
Shooter's	2.3	0.6	0	0.4	0.5	0
Saginaw-Salt	26 ^a	7 ^a	8.8	1.2	13.7	6.9
Fresh	41	1.0	---	---	2.0	0.6
Rouge-Salt	40 ^a	8 ^a	0	0.3	1.2	0.2
Fresh	14.	9	0	0.1	0.9	6.2
Maumee-Salt	390 ^a	-	17.3	8.7	52 ^a	0 ^a
Fresh	16	0	0.2	0.2	0.2	0

a - Samples differing significantly from atomic absorption results (Figure 8).

The presence of large amounts of iron is due to the reducing environment of these systems. The presence of ferric iron suggests that either this species is present in colloidal or chelated form and passes through the 0.45- μm membrane or that, as indicated in Figure 24, both ferrous and ferric iron are present under the particular complexation-redox conditions of these particular systems.

The colloidal samples rapidly oxidized and no ferrous iron was detected in these samples after two months. Certain types of organic compounds can prevent or retard ferrous oxidation (76) but such compounds are apparently not present in sufficient quantities to influence these systems. No correlation was found between soluble iron and organic carbon in the colloidal samples.

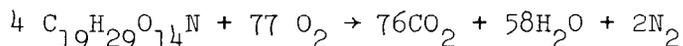
Interstitial waters show expected behavior with generally increasing amounts of metals being solubilized (Figure 23). In examining the Detroit-Salt and Detroit-Fresh systems, it is seen that, with the notable exception of manganese, metal levels are generally higher in the fresh-water interstitial solutions than in the corresponding saltwater solutions. Increasing ionic strength will have two major effects on metal solubility. First, the solubility of metal salts will be increased, due to activity coefficient considerations, if the increase in ionic strength is the result of an inert electrolyte. If the electrolyte is not inert and the electrolyte anion is capable of forming soluble complexes with the metals, this will also result in increased metal concentrations. Second, as mentioned previously, stability constants of

metal-organic complexes decrease with increasing ionic strength. The appearance of increased amounts of metals in the freshwater systems thus suggests that metal-organic complexes (of unknown strength) might be responsible for the observed trends. The iron data in Table 11 suggest that iron coming into solution exists in various ferric/ferrous ratios. As indicated in Figure 24 organic matter can have a significant effect on this process. Soluble iron is not related to soluble organic carbon. Hydrated iron oxides may initially be solubilized and stabilized by the organic carbon and then, depending upon the redox potential, undergo some of the transformations shown in Figure 23. Only with chromium and to a lesser extent lead is a trend observed between soluble metal and soluble organic carbon. This is only true for the freshwater samples (Figure 25).

B. Other Experimental Approaches

(1) Chemical Oxygen Demand (COD)

COD data for a number of freshwater samples are shown in Figure 26. The precision of the organic carbon determinations at lower levels for the colloidal and cylinder waters is far greater than the comparable COD determinations thus giving rise to considerable scatter in the data. The solid line represents the theoretical COD of a fulvic acid derived from river water (21) with the composition C - 46.2%, H - 5.9%, N - 2.6%, O - 45.3%. The theoretical COD was calculated using the equation:



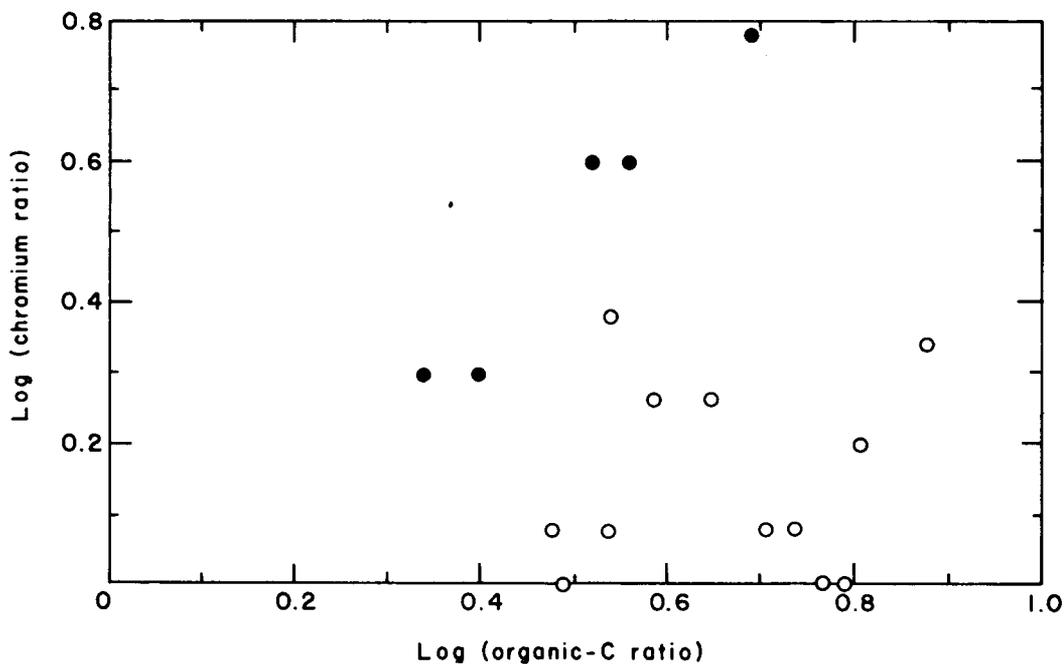
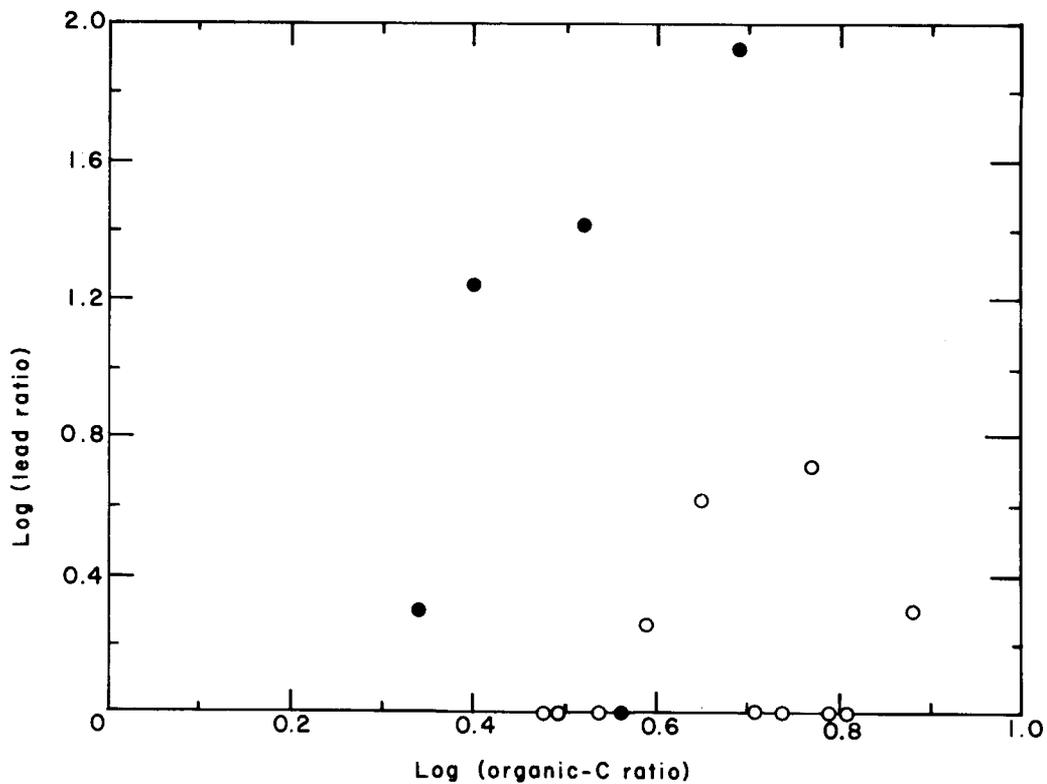


Figure 25. Comparison of Lead and Chromium Concentrations with Soluble Organic-C, Interstitial Waters. (Concentrations Relative to Background Levels. Closed Circles are Freshwater Samples, Open are Seawater)

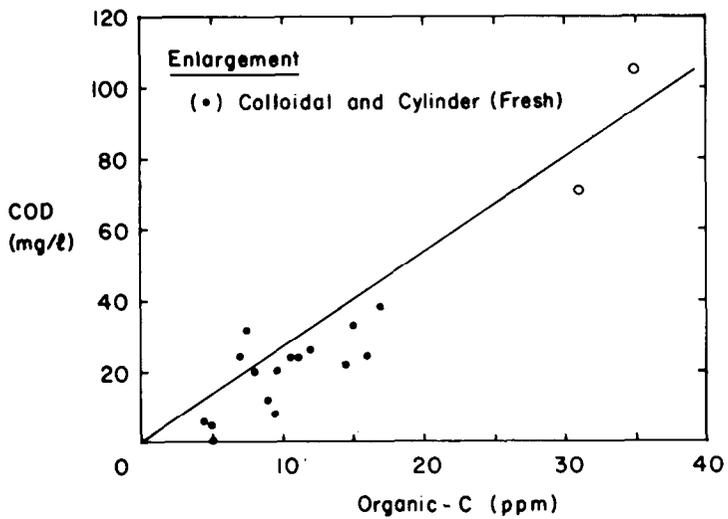
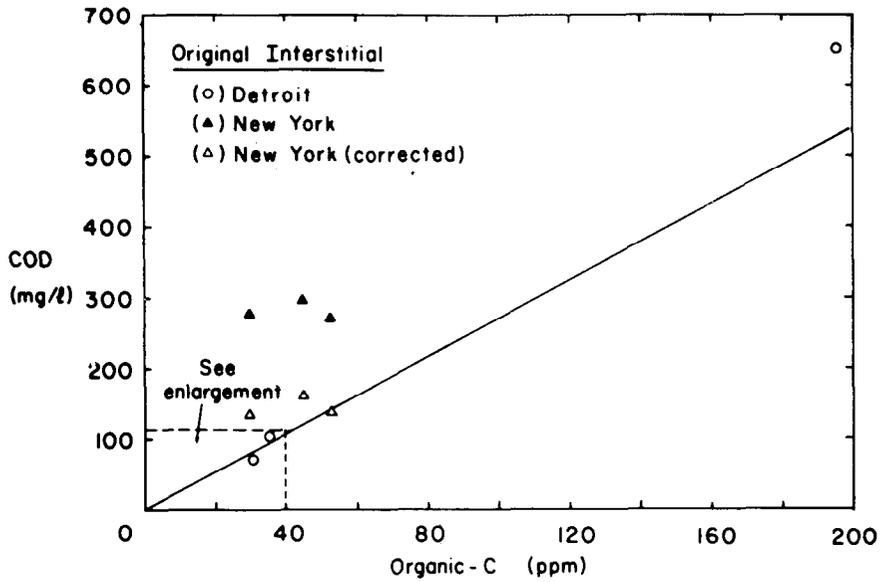


Figure 26. COD Versus Organic-C, Various Solutions

As can be seen the COD values of the colloidal and cylinder waters closely follow the theoretical line and this may be indicative of the possible humic nature of the organic material in these systems. The interfering effect of chloride ion on COD determinations is well known and is the probable explanation for the positive deviation of the COD values of the New York area interstitial waters. Chloride ion was not determined in any of the samples but an indication of how much is potentially present can be seen from the conductivity data (Table 12):

Table 12. Specific Conductance of Original Interstitial Waters

<u>Sample</u>	<u>Specific Conductance</u> ($\mu\text{mho/cm} \times 10^{-3}$)
Hudson	24.7
Newtown	30.1
Shooter's	30.7
Saginaw	2.47
Rouge	2.79
Maumee	1.83
Seawater	45.2

Without specific knowledge of the chloride ion concentrations in the Detroit interstitial waters, this potential source of error cannot be entirely excluded. However, the rather large positive deviation of the Rouge River interstitial water might also be due to the presence of large amounts of nonhumic organics. It was observed at the time of collection that the Rouge sediment had a definite odor that could best be described as sewage-like in nature. Other natural and man-made

organics have higher theoretical COD's and in addition, compared to humic materials, may be more easily oxidized. This possibility, along with some contribution from chloride, may explain the high COD of the Rouge sample.

Attempts to determine COD values for seawater samples using varying amounts of mercuric sulfate to bind the chloride ion were unsuccessful. One approach that was tried was to use seawater instead of the distilled water blank normally utilized in the determinations. The effect of this was to lower the calculated COD values (Figure 26) but it only proved satisfactory at higher COD values. In general, COD data on saline samples were unreliable. Examination of the "corrected" COD values for the New York samples shows that the Newtown and Shooter's samples have significant positive deviations from the theoretical line. Both these samples contained considerable amounts of hydrocarbons. Although the data are limited, it appears that a combination of COD and organic carbon determinations may prove useful as a screening technique in differentiating between "natural" background organics and artificially introduced materials.

(2) Ultraviolet Measurements

Ultraviolet (UV) spectrophotometry for the analysis of water for various components has been utilized by a number of workers. Monselise (84) found that nitrates in drinking water could be measured at 220 nm with the only interference being sodium carbonate. Ogura and Hanya (85), in examining the UV spectrum of seawater, found that nitrate,

bromide, and organic matter all contributed to strong absorbances in the 210-230 nm wavelength range. Bromide ion was found to be the most strongly absorbing species in seawater. Armstrong and Boalch (86) used UV measurements at 220 nm and 250 nm to follow seasonal variations in seawater at various locations. Of importance is their conclusion that an absorbance maximum observed at 210 nm is spurious and due to losses within the instrument they were using. Urkva (87), in examining the nature of organic materials in surface fresh waters, also finds a maximum at 220 nm which he concludes is real. Ogura and Hanya (89) report no maximum in their spectra of seawater. In our work we observed maxima and it seems unlikely that these are due to scattering losses within the sample. Spectra (89) are also presented for waters which have known organic contaminants such as ligno-sulfonates. Wilson (88) studied the absorption of fulvic acids in water at slightly higher wavelengths and found that both ferrous and ferric iron interfered. Fulvic acids from different sources behaved similarly in their UV spectra with the notable exception of a fulvic extracted from peat. This may be due to the presence of lignin. In general it appears that organics in waters can be quantitatively analyzed using UV absorbances. Because natural organic matter usually shows no maxima and increases in absorbance with decreasing wavelength, any suitable wavelength can be selected using concentration, path length, and expected interferences as selection criteria. For the sake of consistency our data are reported with maxima included and treated as being of significance.

Results

Figure 27 shows typical UV spectra for both the colloidal and cylinder phases of the Rouge sediment. The initial colloid sample ($t=0$) was acidified and therefore contains a large amount of ferrous and ferric iron. In addition acidification would lead to removal of carbonates thereby suppressing the maximum at 210 nm. The spectra of a number of different interfering substances are shown in Figure 28 for comparison. As can be seen, carbonate, nitrate, and ferric iron all show a maximum in the same wavelength region. Data for the other samples are given in Table 13.

A multiple linear regression analysis of these data using organic carbon, total iron, and nitrate as independent variables gave the following:

	<u>Correlation Coefficients, R</u>			
	<u>Org.-C</u>	<u>Fe</u>	<u>NO₃-N</u>	<u>Combined</u>
Fresh	0.362	-0.255	0.952	0.954
Salt	0.220	-0.032	0.933	0.943
(Fresh & Salt)	0.300	-0.150	0.861	0.863

The results are not surprising in light of the fact that insofar as the initial colloids are concerned, ferrous iron predominates and absorbs only very weakly. With time the ferrous iron is oxidized and precipitates apparently leaving only nitrate nitrogen as the main absorbing species. Inorganic carbon measurements were not included within this study and therefore the exact contribution of carbonate

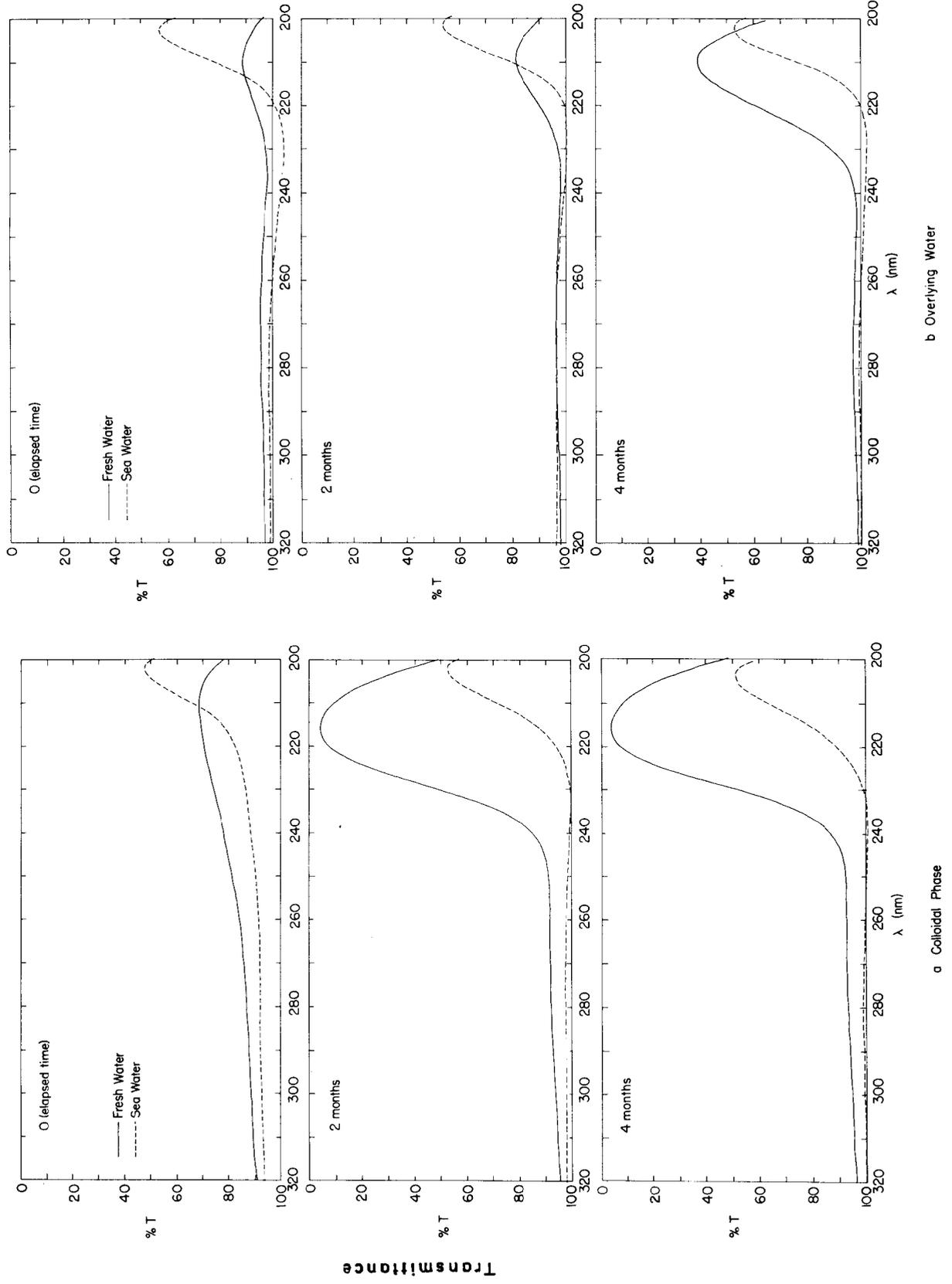


Figure 27. Ultraviolet Spectra of Rouge Colloidal and Overlying Waters

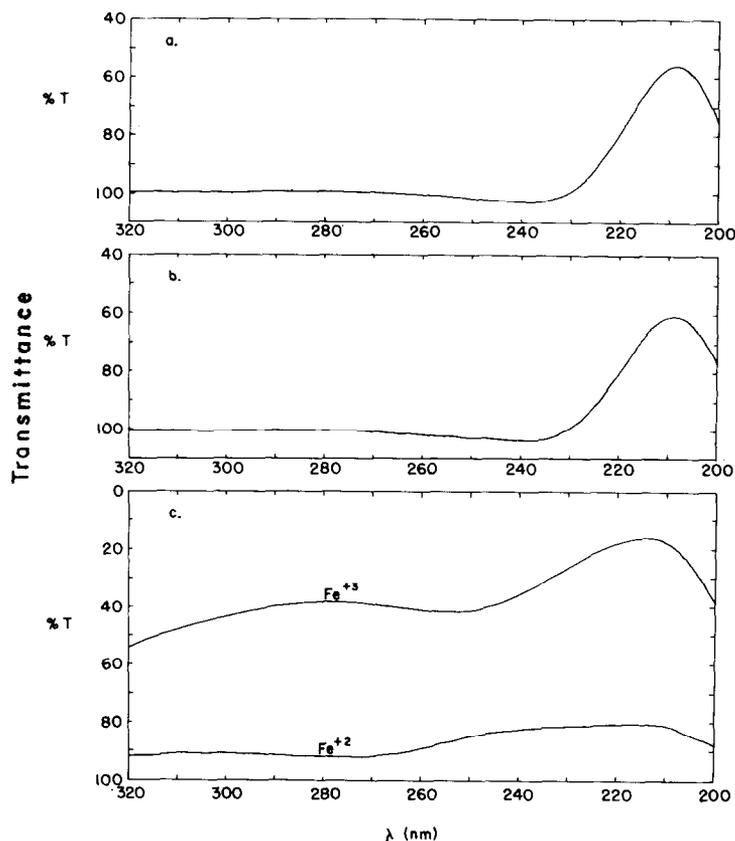


Figure 28. Interfering Substances in UV Region. (a) 6ppm NO_3^- -N. (b) pH = 9.85 carbonate-bicarbonate buffer (10 ppm inorganic-C, (c) Fe^{+3} (10 ppm) and Fe^{+2} (39 ppm)

species to the measured absorbance is not known. However, it should be noted that for the Rouge-Fresh (cylinder) samples, although nitrate-nitrogen is increasing, inorganic carbon was also found to be increasing with relatively high amounts of inorganic carbon being present. An

Table 13. A_{\max} and λ_{\max} for Samples

(Freshwater samples diluted 1:5; seawater samples 1:11)

	Elapsed Time months		
	<u>0</u>	<u>2</u>	<u>4</u>
<u>Cylinders</u>			
Hudson	0.284 AU(202nm)	0.310(204)	0.323(204)
Newtown	0.244(202)	0.301(202)	0.301(202)
Shooter's	0.308(202)	0.314(204)	0.288(203)
Saginaw-Salt	0.300(202)	0.297(202)	0.352(205)
Fresh	0.089(210)	0.155(209)	0.092(209)
Rouge-Salt	0.268(202)	0.288(202)	0.297(202)
Fresh	0.081(210)	0.119(210)	0.420(210)
Maumee-Salt	0.335(205)	0.301(203)	0.382(206)
Fresh	0.114(210)	0.237(210)	0.201(210)
Seawater			0.229(202)
Lake Water			0.056(210)
<u>Colloidal</u>			
Hudson	0.310(203)*	0.426(209)	0.585(209)
Newtown	0.314(202)*	0.469(209)	0.939(214)
Shooter's	0.319(204)*	0.393(206)	0.854(212)
Saginaw-Salt	0.328(202)*	0.284(202)	0.252(202)
Fresh	0.222(210)*	1.19(215)	1.15(216)
Rouge-Salt	0.337(202)*	0.297(202)	0.310(202)
Fresh	0.187(210)*	1.16(216)	1.19(216)
Maumee-Salt	0.377(204)*	0.342(204)	0.260(202)
Fresh	0.180(210)*	0.848(212)	0.824(213)
Seawater			0.252(202)
Lake Water			0.125(209)

*Acidified Solutions

estimate of the amount of inorganic carbon can be made by taking the nitrate-nitrogen data from Figures 13, 15, 16 and subtracting its contribution from the total absorbance with the aid of Figure 29. Results are shown in Table 14.

The seawater samples also contain a significant contribution from bromide ion, which accounts for their generally higher levels than the freshwater samples. The colloidal samples were exposed to the atmosphere and could be expected to pick up CO_2 . However, the wide range in calculated values suggests that dissolution of carbonate minerals and/or

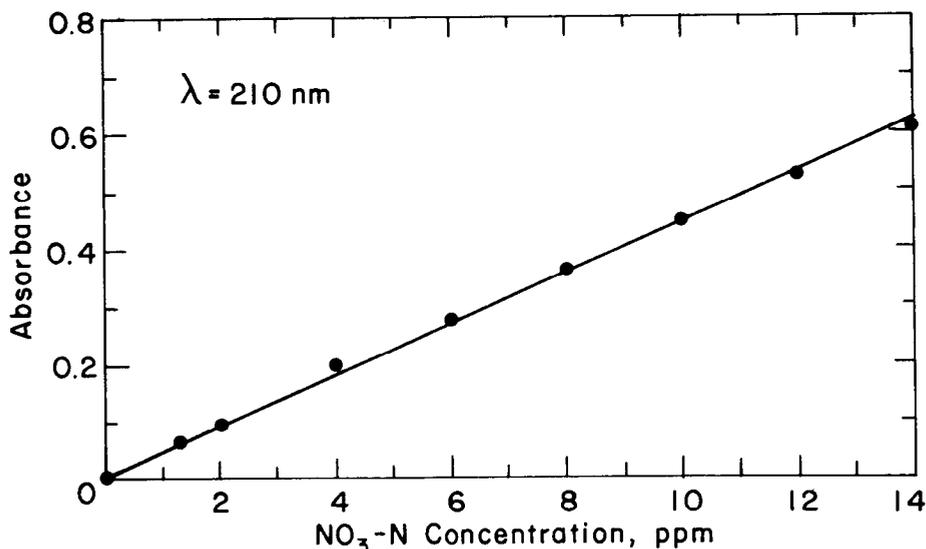


Figure 29. Calibration Curve for $\text{NO}_3\text{-N}$

Table 14. Absorbance at λ_{\max} less contribution from nitrates.

	Months					
	<u>0</u>	<u>2</u>	<u>4</u>	<u>0</u>	<u>2</u>	<u>4</u>
	Cylinders			Colloidal		
Hudson	0.26	0.29	0.30	0.29*	0.36	0.45
Newtown	0.22	0.28	0.28	0.30*	0.38	0.73
Shooter's	0.29	0.29	0.27	0.30*	0.34	0.74
Saginaw-Salt	0.28	0.28	0.32	0.31*	0.26	0.25
Fresh	0.07	0.14	0.07	0.22*	0.96	0.85
Rouge-Salt	0.25	0.28	0.28	0.33*	0.28	0.31
Fresh	0.06	0.10	0.39	0.19*	0.95	0.91
Maumee-Salt	0.32	0.28	0.34	--	0.32	0.26
Fresh	0.09	0.21	0.17	0.16*	0.74	0.71
Seawater			0.21			0.24
Lake Water			0.03			0.10

*Acidified Samples

conversion of organic-C may also be occurring. The original colloidal solutions were prepared under nitrogen atmosphere. Purging systems such as these with nitrogen lead to the precipitation of various carbonate species which upon re-equilibration with the atmosphere can be expected to redissolve.

The data in Table 14 suggest that for the New York and Detroit-Fresh samples other absorbing species are present. Carbonate is the most likely species and it is of interest that the Detroit-Salt samples show no apparent increase in absorbance. The pH of all samples was approximately 7.7 - 8.2. At a given pH the mole fraction of $\text{CO}_3^{=}$ is higher in seawater than in fresh water so ultraviolet measurements

should detect any carbonate present. In addition, the solubility of calcium carbonate (based upon solubility product and carbonate equilibria considerations) is several times greater in seawater than in fresh water. The absence of increasing carbonate may be due to inhibition of microbial activity (107) due to the high saline environment. All the Detroit samples were qualitatively found to contain carbonates. The presence of carbonate does have a desirable consequence in that it is potentially available for metal ion precipitation. Proposed EPA water-quality criteria permit up to 30 ppb cadmium in hard waters (>100 mg/l as CaCO_3) but only 4 ppb in soft waters (100).

Measurements at Longer Wavelengths

Above a wavelength of approximately 240-250-nm, the various interferences previously discussed no longer absorb. Only ferrous and ferric iron interfere in this region (Figure 28) with the ferric species having a significantly greater influence on the measured absorbance. Figure 30 shows the iron-corrected absorbances at 254 nm as a function of measured organic carbon. In general the values fall into two groups: those solutions below the line were generally low in iron (Cylinders $t=0,2,4$; Colloidal $t=2,4$), while the solutions above the line generally required a significant correction for iron. The absorbance is quite sensitive to ferric iron ($d(\text{Abs})/d(C_{\text{Fe}}) = .043$) so that any underestimation of the amount present leads to substantial errors. Wilson (88) overcame this problem by oxidizing his solutions to completely eliminate ferrous iron and then carefully correcting for the total amount of

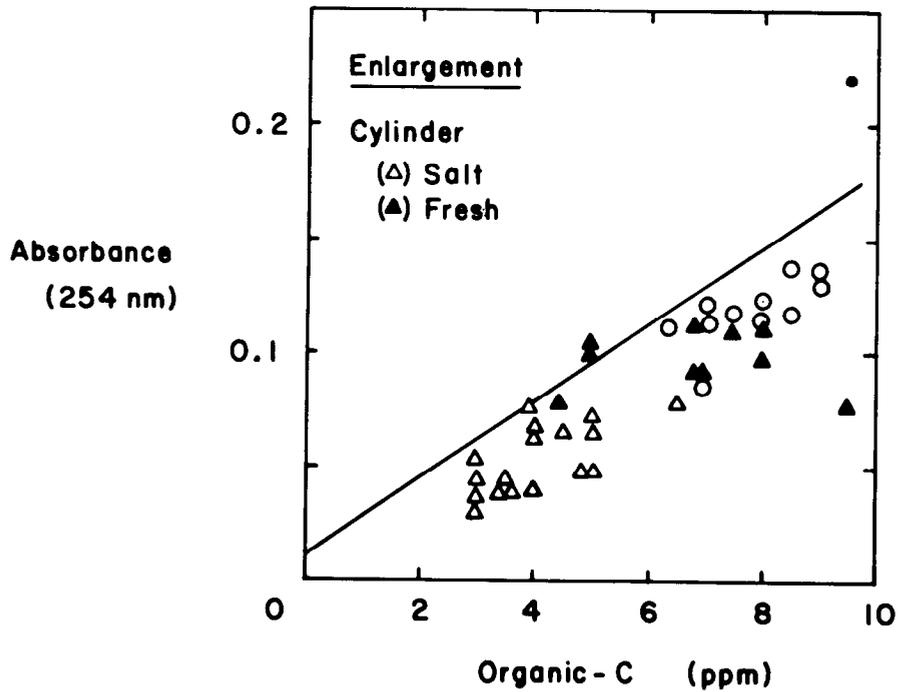
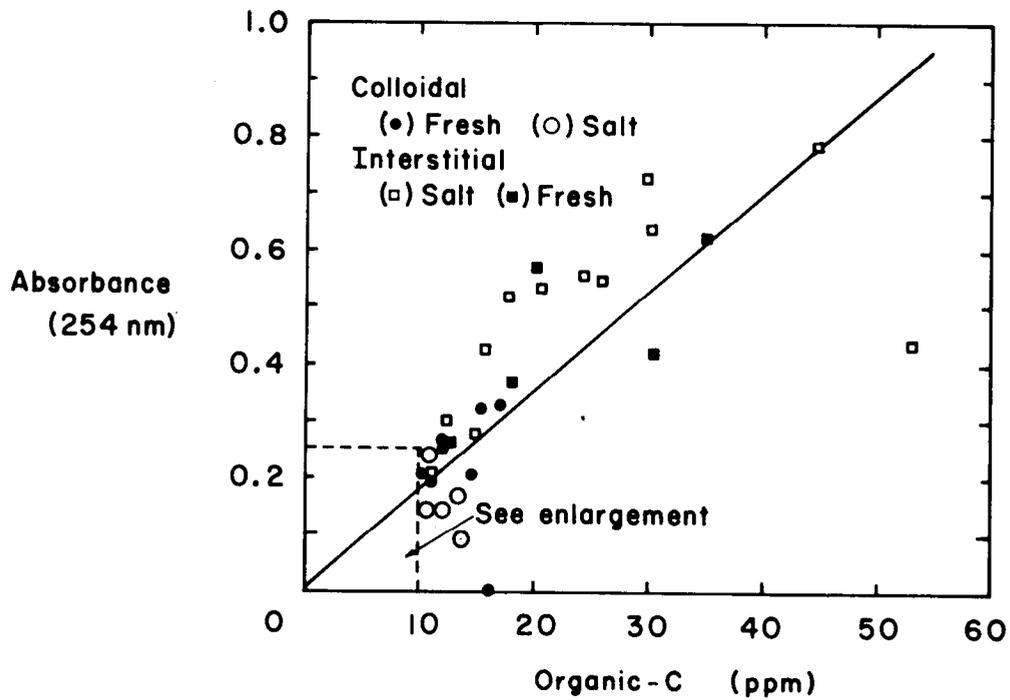


Figure 30. Absorbances at 254 nm Versus Organic-C Concentrations

ferric iron. In solutions containing large amounts of iron it might be preferable to reduce iron to the ferrous state where the subsequent correction would be much smaller. This would only be of advantage if a non-interfering reducing agent could be found. Using longer wavelengths is also a possibility, but even at 280 nm the effect of ferric iron is hardly changed from that at 254 nm.

Mattson et al. (90) have used UV for the continuous monitoring of marine surface waters and found a reasonable correlation with organic carbon. Ultraviolet measurements at fixed wavelengths are at this stage appropriate for surface waters only, as the amount of iron is usually quite low. In addition surface waters are generally homogeneous with regards to the types of organic matter they contain, at least over short distances. Thus, significant variations in the measured absorbances can generally be attributed to the changing nature and/or amounts of dissolved organic matter. Application of UV spectrophotometry to waters containing significant amounts of "interfering" substances can be quite useful, especially if applied to individual water bodies. In our own work we have attempted to show that consistencies in the UV spectra exist between samples of widely varying water quality. Application of such techniques to an individual water body, where the aqueous components are less variable, should be quite useful.

(3) Anodic Stripping Voltammetry (ASV)

(a) Cell Constant

In ASV work, a certain amount of metal ion is by necessity removed from solution during the plating step. Thus, in determining the

amount of uncomplexed or weakly complexed metal present, it is desirable to remove as little of the metal as possible so as not to greatly disturb possible equilibrium situations which may exist.

At any time the amount of metal remaining in solution, C_t , is related to the initial concentration, C_o , by (56):

$$C_t = C_o \exp(-k_c t) \quad (1)$$

where t = plating time

k_c = cell constant

Significant changes in the bulk metal ion concentration are governed by:

$$Q = nFV C_o (1 - e^{-k_c t}) \quad (2)$$

For insignificant bulk concentration changes:

$$Q = nFV k_c C_o t \quad (3)$$

where Q = the total amount of reduced species in the electrode
(coulombs)

n = the number of electrons involved in the reduction

F = Faraday constant (coulombs/equivalent)

V = the cell volume (liters)

k_c = cell constant (sec^{-1})

C_o = bulk concentration (moles/liter)

t = plating time (seconds)

Figure 31 shows a typical polarogram for a solution containing cadmium, lead, and copper. Stripping currents were linearly related to

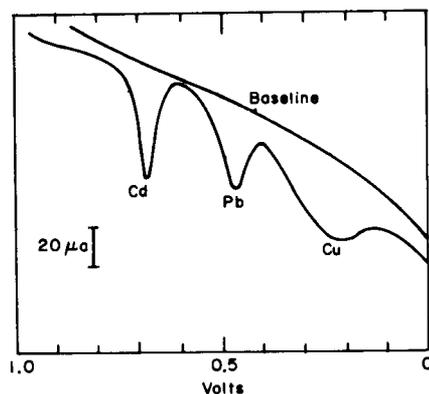


Figure 31. Typical Anodic Stripping Voltammogram of 20 ppb each Cd, Pb, Cu in Seawater. Plating Time = 1 minute (MCGE).

concentration ($R=0.999$) and were also found to be linearly related to plating times of less than ten minutes. With knowledge of the sweep rate, the area under a peak can be determined and the value of Q obtained. Substituting this value along with the other experimental parameters into Equation 3 makes possible an estimate of the cell constant, k_c . In practice most workers have used slow sweep rates to insure that the metal in the electrode is completely oxidized back into solution. In our work using very high sweep rates, it was found that only about 70% of the reduced metal is oxidized during a single sweep and Q has to be adjusted accordingly. Under the experimental conditions listed previously, values of $k_c = 10^{-3.5} \text{ sec}^{-1}$ were found indicating an approximately 4% decrease in the bulk concentration during the plating step. Increasing

the cell volume would allow the use of longer plating times with a concurrent increase in sensitivity but it was not found necessary to do so in this work. The single most important experimental variable is reproducing the MCGE so that fairly consistent cell constants are obtained. The method of standard addition has been utilized to avoid this problem but in fact the cell constants have generally been "constant" from electrode to electrode within about 10%.

(b) Results and Discussion

The effect of copper ion additions on undiluted interstitial (t=2 months) solutions is shown in Figure 32. Only the Newtown and Shooter's interstitial waters show significantly different behavior. Such behavior was also noted in the four-month Newtown and Shooter's samples with the plateau for Newtown extending out to 7 μg of added copper. Matson (56) has considered a number of cases involving labile and nonlabile complexes. As free metal ions are depleted at the electrode interface during the plating step, metal-organic complexes will tend to dissociate in order to reestablish equilibrium. If this dissociation is rapid in comparison with plating rate, then such complexes are referred to as being labile. Nonlabile complexes have, by definition, such slow dissociation rates that metals associated with these complexes are not detected (reduced) at the electrode.

The behavior of both Newtown and Shooter's can be described as follows. The initial increase in stripping current is due to the formation of labile complexes whose dissociation rates are greater than those

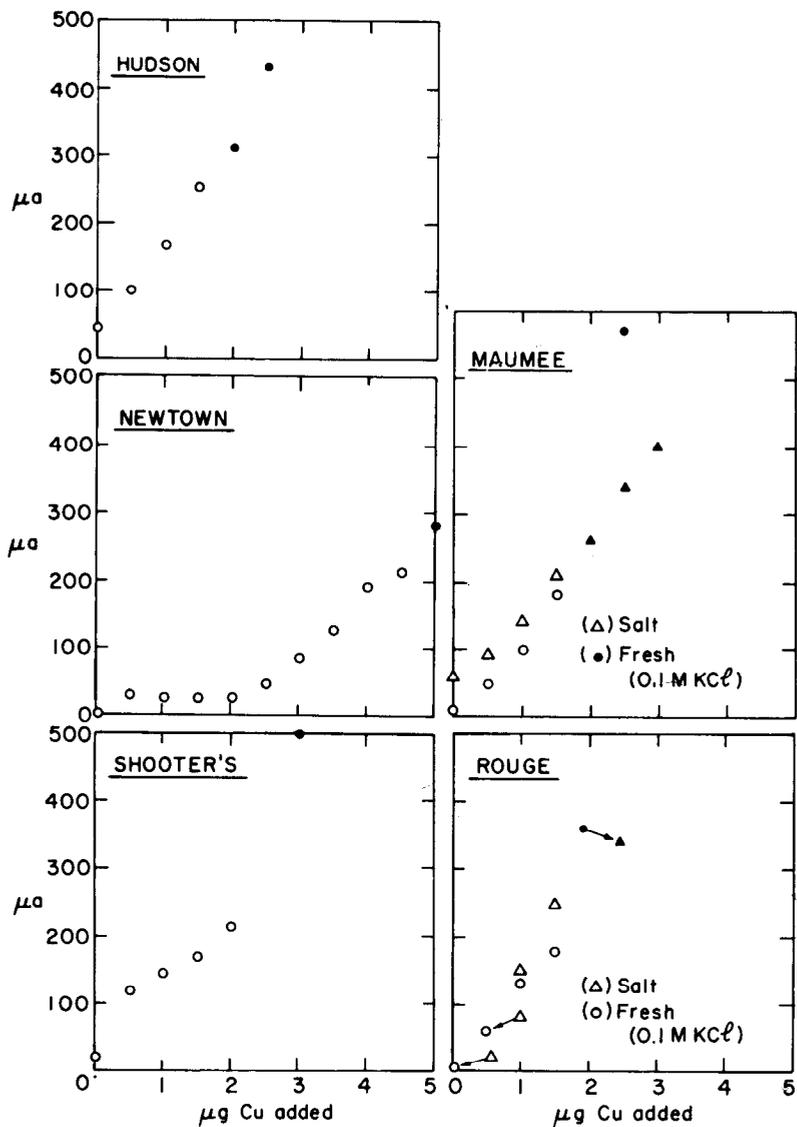


Figure 32. Titration Curves for Interstitial Waters. The closed symbols represent simultaneous addition of equal amounts of cadmium, lead and copper. Solutions were stirred for five minutes after each sample addition.

for the nonlabile complexes present. Once these labile complexes are saturated with copper, additional copper is tied up with other ligands which form nonlabile complexes, making the copper unavailable to the

electrode. Once all ligands have been saturated with copper, additional spikes of copper result in an increase in free ion in solution which is available for reduction at the electrode.

The data from the other samples investigated suggest if complexes are formed they are predominantly labile in nature. The four-month interstitial samples were not extensively investigated but there was evidence in some cases that nonlabile complexes were present where there had been none indicated in the two-month samples.

A number of samples were examined before and after hydrogen peroxide treatment to see what effect this might have on the current versus added metal ion response. In these experiments copper, lead, and cadmium were added simultaneously. For the majority of cases the same electrode was used for the unoxidized and oxidized samples so as to minimize differences which might be caused by variations from electrode to electrode. Figure 33 shows the behavior encountered.

In all these samples only two minutes of stirring takes place after the addition of the spike and before plating is initiated. The sample shown in Figure 33 is somewhat irregular in that the titration of the unoxidized sample is nonlinear ($R=0.941$ for Cu). All oxidized samples show $R > 0.99$. For the case shown in Figure 33, there are two possible explanations of why the slopes are different. If organic material is adsorbed at the electrode interface, then it can conceivably interfere with either the mass transfer and/or electron transfer process. This may result in a smaller amount of metal being reduced at the electrode in a

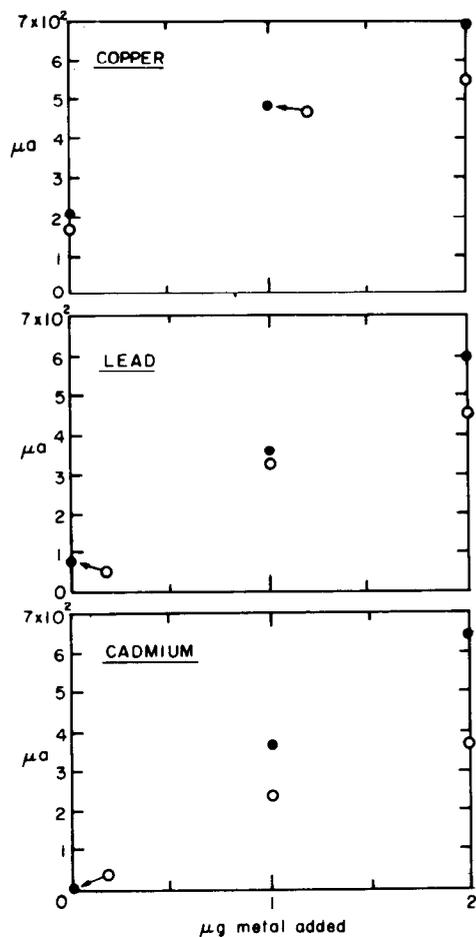


Figure 33. Effect of H₂O₂ on Titration Curves. Open Symbols Represent NO Pretreatment with H₂O₂. Metals added Simultaneously With Two Minute Stirring Period. Newtown Colloidal (t=0).

given time as compared to systems where adsorption does not occur. The results obtained on the undiluted Newtown sample (Figure 32) indicate that this is not the situation. What is indicated however is that complexation is occurring but sufficient time is not being allowed for the metal to be complexed before plating is initiated. Thus, the increased slope of the oxidized sample, indicates that the peroxide

treatment has had some effect, either by destruction of complexing ligands and/or changes in the nature of the ligands. Such changes might be chemical in nature and might affect the rates at which the ligands can complex metal ions. The data in Table 15 show the ratios of the

Table 15. Ratio of Sensitivities for Oxidized Versus Unoxidized Colloidal ($t=0$) Solutions

Sample	Cd	Pb	Cu
Hudson	1.24 \pm 0.11	1.09 \pm 0.03	0.98 \pm .06
Newtown	1.78 \pm 0.19(0.986)**	1.42 \pm 0.16(0.988)	1.30 \pm 0.39(0.941)
Shooter's	1.32 \pm 0.08	1.10 \pm 0.11	1.02 \pm 0.06
Saginaw-Salt	1.40 \pm 0.15	1.28 \pm 0.02	1.07 \pm 0.06
Fresh	2.22 \pm 0.13	1.41 \pm 0.01	---
Rouge-Salt	1.17 \pm 0.16	0.96 \pm 0.02	0.57 \pm 0.07
Fresh	1.84 \pm 0.17	1.26 \pm 0.06	1.11 \pm 0.01
Maumee-Salt	---	---	---
Fresh*	1.34 \pm 0.21(0.980)	1.39 \pm 0.13	1.50 \pm 0.19(0.983)

*Two different electrodes used.

**Correlation Coefficients of unoxidized samples. All others \geq 0.99

sensitivities (slopes of the least-square line) for the initial colloidal samples. Similar metal additions were also carried out on some interstitial solutions (Table 16). Data obtained in this manner can be explained as follows. The slope of a given titration curve is complexly related to both the rate at which metal ions become bound to ligands, their subsequent rate of dissociation during the plating step, and the rate at which free metal is reduced at the electrode. A potential reaction scheme is as follows:

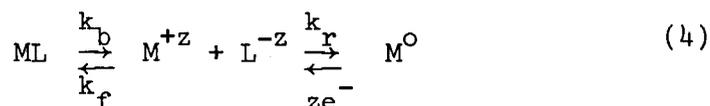


Table 16. Ratio of Sensitivities for Oxidized Versus Unoxidized Interstitial Solutions

	<u>Original</u>	<u>t = 2 months</u>	<u>t = 4 months</u>
Hudson			
Cd	1.04 \pm 0.09(0.985)**	1.09 \pm 0.10	1.79 \pm 0.05
Pb	1.07 \pm 0.02	1.06 \pm 0.10	1.37 \pm 0.04
Cu	0.95 \pm 0.02	0.95 \pm 0.12	2.23 \pm 0.05
Newtown			
Cd	1.13 \pm 0.21(0.979)	1.24 \pm 0.06*	---
Pb	1.26 \pm 0.15	0.95 \pm 0.02*	---
Cu	1.63 \pm 0.14	2.40 \pm 0.26*(0.941)	---
Shooter's			
Cd	1.05 \pm 0.01	1.16 \pm 0.23 (0.982)	---
Pb	1.07 \pm 0.16	1.08 \pm 0.08	---
Cu	1.10 \pm 0.24(0.976)	0.89 \pm 0.07	---
Saginaw-Salt			
Cd	---	1.51 \pm 0.12	---
Pb	---	1.12 \pm 0.07	---
Cu	---	0.71 \pm 0.07	---
Saginaw-Fresh			
Cd	1.35 \pm 0.2*	---	---
Pb	1.32 \pm 0.09*	---	---
Cu	1.47 \pm 0.05*	---	---
Rouge-Salt			
Cd	---	1.42 \pm 0.14	---
Pb	---	1.09 \pm 0.04	---
Cu	---	0.84 \pm 0.04	---
Rouge-Fresh			
Cd	0.83 \pm 0.09*	---	---
Pb	0.78 \pm 0.04*	---	---
Cu	0.80 \pm 0.09*	---	---
Maumee-Salt			
Cd	---	1.37 \pm 0.14	---
Pb	---	1.26 \pm 0.08	---
Cu	---	1.06 \pm 0.10	---
Maumee-Fresh			
Cd	0.84 \pm 0.21*(0.980)	---	1.67 \pm 0.12
Pb	1.18 \pm 0.11*	---	1.47 \pm 0.03
Cu	1.42 \pm 0.27*(0.965)	---	---

(Continued)

Table 16 (concluded)

	<u>Original</u>	<u>t = 2 months</u>	<u>t = 4 months</u>
Seawater			
Cd	1.11 \pm 0.05	---	---
Pb	1.03 \pm 0.03	---	---
Cu	0.86 \pm 0.09	---	---
Distilled Water			
Cd	1.08 \pm 0.06	---	---
Pb	1.10 \pm 0.02	---	---
Cu	0.95 \pm 0.02	---	---

*Two different electrodes utilized.

**Correlation Coefficients of unoxidized samples. All others \geq 0.99.

where

ML = metal-ligand complex

L^{-z} = free ligand of charge z

M^{+z} = free metal ion of charge z

M^0 = reduced metal ion in electrode

The increase in metal detected by the electrode after peroxide oxidation can be due to either, or a combination of two effects. It is assumed that the rate of reduction, k_r , is unaffected by the peroxide step. In one case, the ligand could simply have been destroyed. Alternatively, the oxidation could have chemically modified the ligand thus altering the magnitude of k_f and/or k_b . Thus, increases in the sensitivity can be due to an increase in k_b and/or a decrease in k_f . For sensitivity ratios less than one the opposite effect could have occurred. The stability constant, as defined by the ratio k_f/k_b , may be affected by peroxide oxidation, but this does not enter directly into the arguments

made above. The stability constant can remain unchanged. All that is necessary under such circumstances is that k_b change in magnitude relative to k_r .

The large increase in the ratio of sensitivities (Table 16) for Hudson interstitial solution at four months was verified by titration of the undiluted sample with copper. Sensitivities of oxidized samples generally approach those found for seawater and fresh water. The decrease in total organic carbon as a result of peroxide oxidation was variable, ranging from no decrease up to an approximately 20% decrease. The average decrease was 5% (range = 0-21). This suggests that peroxide alters the nature of the ligand material without causing significant reductions in total organic carbon.

Table 17 shows the stripping current before and after oxidation of the samples. Negative values reflect the fact that the unoxidized samples are often higher in free metal ion. This suggests that the complexing ability has been increased by peroxide oxidation or that the blank levels obscure many of the low levels encountered. Lead blanks are quite high, apparently due to the leaching of lead from container walls during the oxidation procedure. This precluded accurate determination of low lead levels. Large increases in specific metals with time as determined by ASV are in agreement with atomic absorption data.

Several inferences can be drawn from the data. Sizable amounts of the various metals appear in various samples and oxidation with peroxide increases the amount detected in a number of cases. Ligands of an

Table 17. Stripping Current Before and After Peroxide Treatment (μa) μa in Unoxidized, μa in Oxidized (ppb in oxidized**)

	<u>Interstitial</u>		<u>Colloidal</u>	
	<u>Orig.</u>	<u>t = 2</u>	<u>t = 4</u>	<u>t = 0</u>
Hudson				
Cd	0,0	5,6(7)	5,4(4)	0,0
Pb	3,*	8,*	48,21(38)	23,13(19)
Cu	9,5(27)	4,6(11)	284,235(207)	12,21(27)
Newtown				
Cd	*,*	2,18(7)	*,*	9,6(5)
Pb	*,*	10,102(80)	6,*	88,70(75)
Cu	*,*	*,18(5)	*,*	148,223(243)
Shooter's				
Cd	3,5(4)	1,2(2)	*,*	3,0
Pb	*,*	*,*	*,*	22,7(1)
Cu	*,*	*,3(6)	*,*	12,27(35)
Saginaw-Salt				
Cd	--	3,*	25,26(26)	3,*
Pb	--	2,*	*,*	8,*
Cu	--	*,1(3)	*,*	10,10(8)
Saginaw-Fresh				
Cd	*,5(10)	--	25,53(45)	2,7(14)
Pb	*,*	--	270,542(641)	9,11(83)
Cu	*,*	--	542,865(1090)	*,0
Rouge-Salt				
Cd	--	*,*	7,8(4)	*,*
Pb	--	2,1(13)	*,*	22,2(21)
Cu	--	*,*	*,*	0,6(18)
Rouge-Fresh				
Cd	0,5(14)	1,5(6)	5,2(4)	2,11(21)
Pb	3,*	0,*	140,222(390)	49,83(211)
Cu	*,0	*,*	224,470(2350)	*,15(55)
Maumee-Salt				
Cd	--	0,3(2)	5,2(1)	--
Pb	--	6,*	*,*	--
Cu	--	*,30(57)	*,*	--
Maumee-Fresh				
Cd	0,3(8)	1,2(3)	7,8(10)	2,*
Pb	*,*	*,*	8,*	11,*
Cu	*,*	*,*	28,53(112)	*,3(10)

*Blank exceeds sample.

**Corrected for sample volume.

unspecified nature can be altered by peroxide while leaving the total organic carbon present relatively unaffected. The resistance of the organic material to complete oxidation (i.e. conversion to CO_2) suggests that the bulk material is relatively stable; an EDTA solution (460 ppm as organic-C) was reduced to 320 ppm organic-C by identical treatment. Similarly, a 1300-ppm organic-C solution of a polymeric dextran ($\text{MW}=2 \times 10^6$) was reduced by 100 ppm organic-C when the quantity of peroxide was doubled to account for the larger initial concentration. Since the actual samples rarely exceeded 15 ppm organic-C, the quantity of peroxide should not be a limiting factor. Finally, the complexing ability of a solution is not related to total organic carbon but perhaps may be related to components of the organic carbon present. Whether the complexing capacity of the solutions is due to truly soluble organic ligands or colloidal material, both organic and inorganic, could not be determined.

(4) Organic Fractionation

The technique by which the various chemical fractions were isolated is shown in Figure 7. Briefly, the chloroform-extractible neutral fraction would be expected to contain nonpolar compounds such as aromatic and aliphatic hydrocarbons, chlorinated hydrocarbons, and possibly esters. The chloroform-extracted acid fraction should contain both strong and weak acids such as carboxylic acids and phenols. The other three fractions are classical operational definitions. Because of the origin of the interstitial waters, it is to be expected that these so-called humic fractions will contain some nonhumic materials. The

amounts of each fraction found in the interstitial waters is shown in Table 18¹. The recovery of organic carbon is generally unsatisfactory. The largest single loss might be expected to occur in the initial ammonium sulfate-acetone extraction. Although this procedure completely removed colored material from the aqueous phase, it is still possible that some organic material remained. Because the aqueous phase is saturated with acetone, it proved impossible to confirm this. Volatile materials may have been lost during subsequent vacuum drying steps. Qualitative analysis of vapors above the Newtown and Shooter's sediments by gas chromatography-mass spectrometry showed significant amounts of volatile, petroleum derived hydrocarbons, including oxygen containing species.

Table 18. Distribution of Organic Carbon in Original Interstitial Waters

	Organic Carbon (mg/l)*					
	Hudson	Newtown	Shooter's	Saginaw	Rouge	Maumee
Chloroform-extractible Neutrals	1.0	0.9	1.3	0.6	0	0.4
Chloroform-extractible Acids	0.8	1.9	1.6	1.3	2.8	0.8
Humic Acid	2.7	1.0	1.8	1.1	1.0	0.8
Hymatomelanic Acid	1.4	0.8	2.7	0.6	0.3	0.5
Fulvic Acid	7.1	---	3.9	---	---	---
Total Organic Carbon Found	13.0	---	11.3	---	---	---
Total Original Organic Carbon	55	33	47	37	198	33

*Calculated assuming organic matter contains 50% carbon

¹A laboratory accident resulted in the total loss of four fulvic acid fractions.

Infrared spectra of the various chemical fractions are shown in Figure 34. Several absorption bands are common to most of the spectra and for simplicity the more frequently encountered ones are shown below. Interpretation is based upon Stevenson and Butler (104).

<u>cm⁻¹</u>	<u>Interpretation</u>
3300	H-bonded OH
2900	Aliphatic C-H
1720	C=O stretch of -COOH and ketonic C=O
1610	Aromatic C=C and H-bonded C=O
1500	Aromatic C=C
1460	C-H deformation of CH ₂ or CH ₃ groups
1390	O-H deformation, CH ₃ bend, or C-O stretch
1250	C-O stretch and OH deformation of COOH

(a) Hymatomelanic Acids (KBr Pellet)

All samples are similar in their absorptions at approximately 3300, 1720, and 1610 cm⁻¹. Aliphatic C-H (2900 cm⁻¹) either is minor or obscured in the Hudson and Shooter's samples. Medium to strong bands at 1400 cm⁻¹ are found for all samples except Newtown. The small band at 2340 cm⁻¹ is spurious.

(b) Chloroform-Extractable Acid Fraction (Chloroform Smear)

The water peak in the 3000-3500 cm⁻¹ is greatly reduced and the remaining absorption is perhaps due to trace amounts of tightly bound water involved in hydrogen bonding or hydrogen bonding involving the solid itself. The spectra are almost identical and show essentially C-H and C=O functionality.

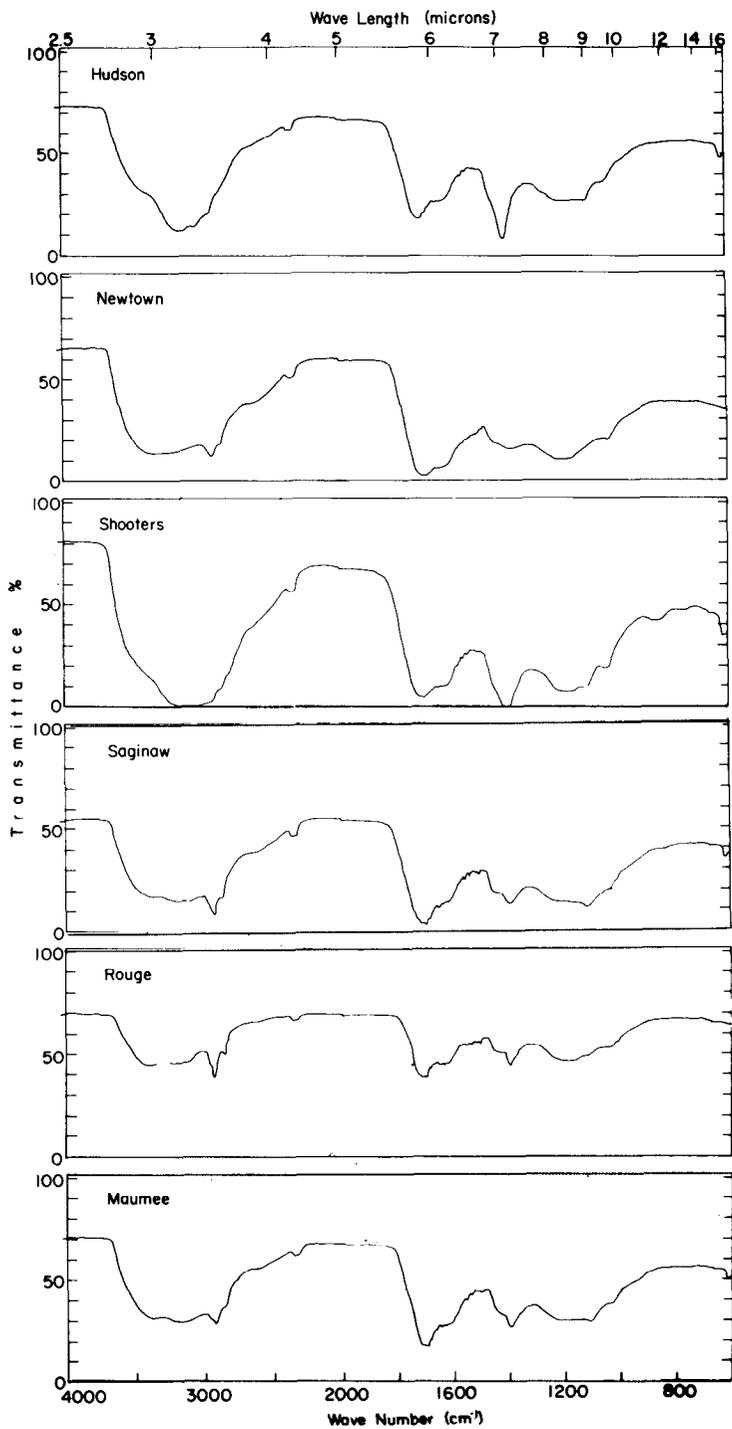


Figure 34a. Infrared Spectra of Organic Fractions. Hymatomelanic Acid Fractions

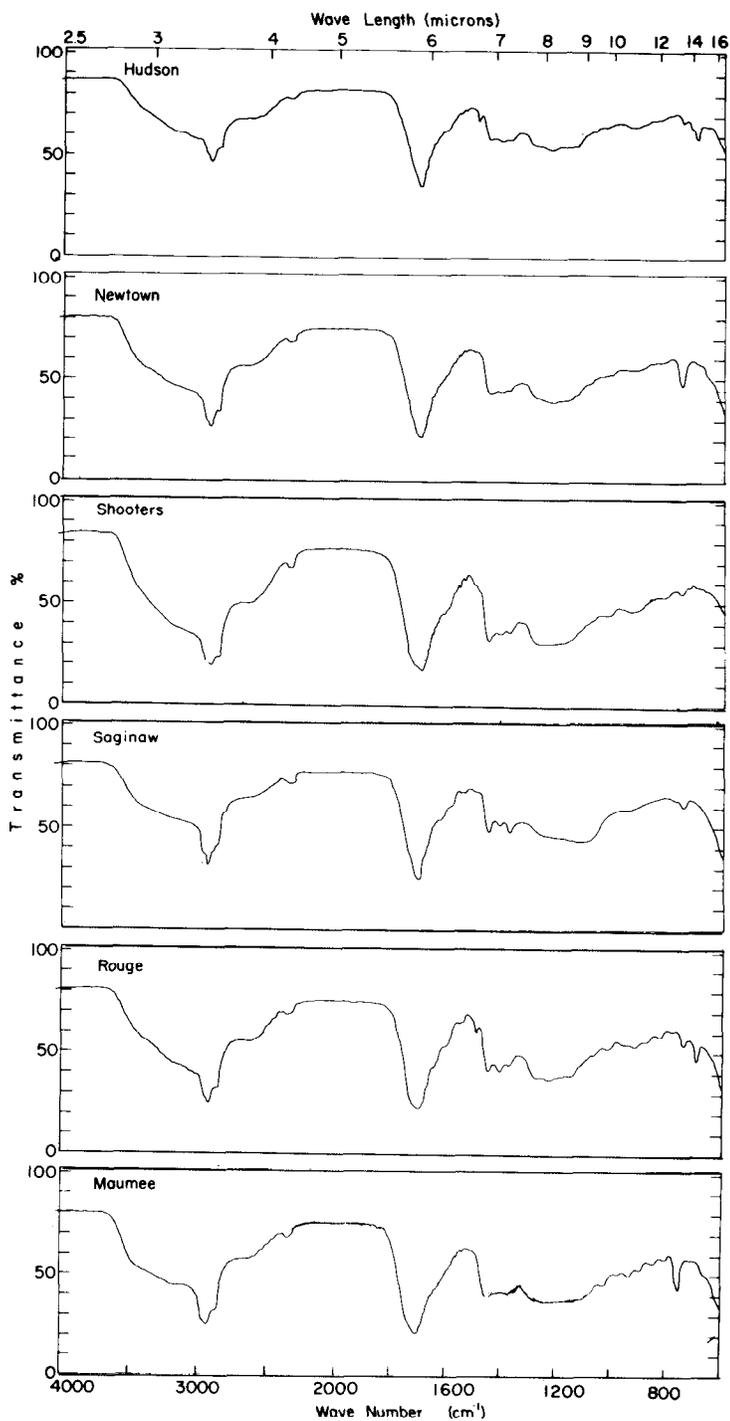


Figure 34b. Chloroform-Extractable Acid Fraction

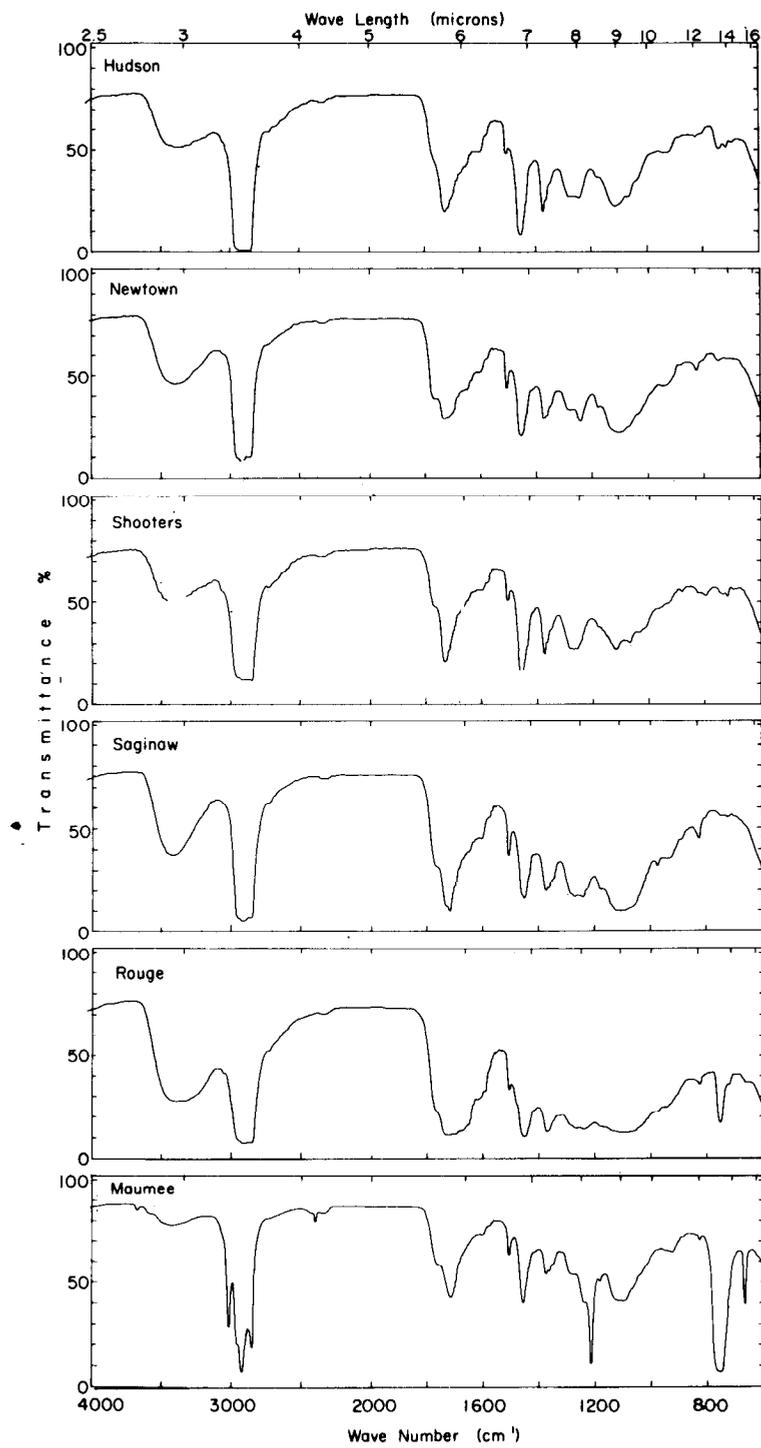


Figure 34c. Chloroform-Extractable Neutral Fraction

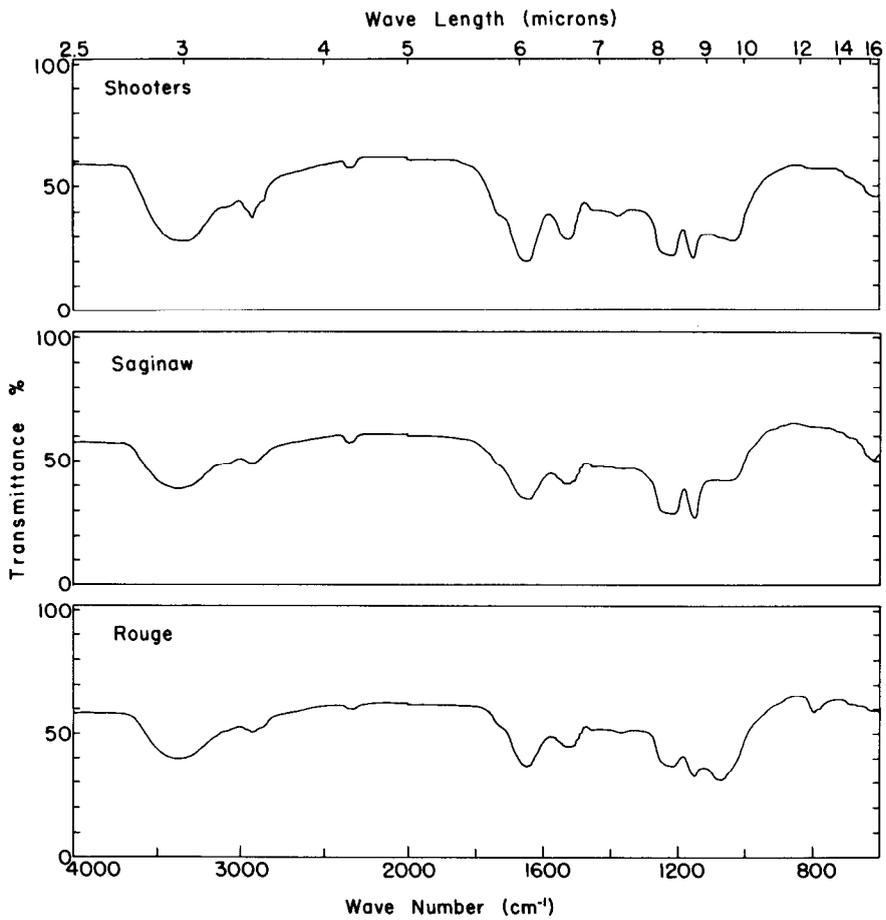


Figure 34d. Representative Humic Acid Fractions

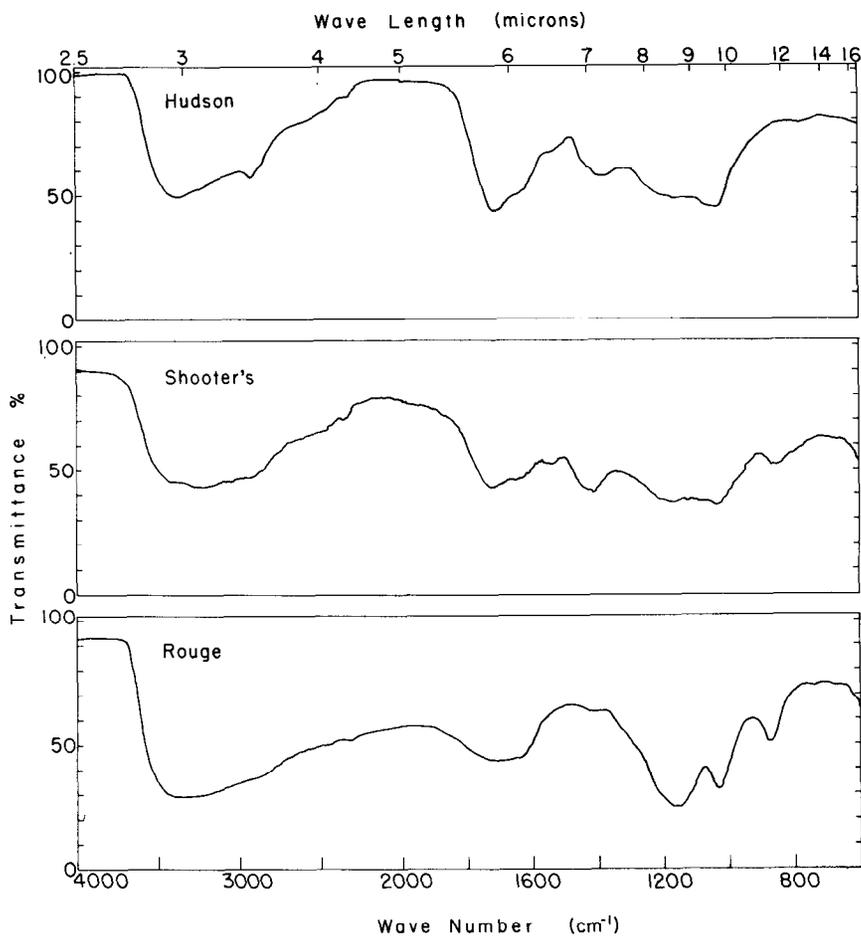


Figure 34e. Fulvic Acid Fractions

(c) Chloroform-Extractable Neutral Fraction (Chloroform Smear)

Numerous well-defined peaks are evident. This fraction is a minor component of the total organic carbon present and the bands at 1760, 1720, 1290, 1240, 1215, and 1100 cm^{-1} indicate a highly oxygenated system containing carbonyl, alcoholic, and possibly ester and epoxide linkages. Little evidence is found for carboxylic acid groups. The large peak at 750 cm^{-1} is undoubtedly due to substituted benzene groups. Maumee represents an interesting case in that the spectrum shows numerous well-defined bands. This may be due to the presence of a relatively large amount of chemically similar components.

(d) Humic Acids (KBr Pellet)

Only three of the humics are shown. The other three were similar but less well defined. Several new peaks are evident. The 1720 cm^{-1} peak has become a shoulder on the 1650 cm^{-1} peak. The peaks at 1650 cm^{-1} and 1530 cm^{-1} are attributed to peptides and proteins (amide linkages) and were also found in a lake humic acid by Goh and Stevenson (105). The peaks at 1150 cm^{-1} and 1230 cm^{-1} are probably due to C-O stretch, possibly phenolic in nature.

(e) Fulvic Acids (KBr Pellet)

Of the three fulvic acid spectra shown, only Hudson has an apparently significant absorption at 2920 cm^{-1} . Generally, the humic acids have greater absorption at this wavelength as they are less oxygenated than the fulvic acids. The increased absorption at 1720 cm^{-1} compared to 1650 cm^{-1} for the Hudson and Shooter's is indicative of the increased

predominance of carbonyl groups and is the reverse of the situation encountered with the humic acids. Weak absorptions at 1540 cm^{-1} and 1650 cm^{-1} may be indicative of amide groups.

The carboxylate anion absorbs at 1400 cm^{-1} and 1550 cm^{-1} and may also be contributing to the spectra.

The Rouge sample is quite different from other two samples. Only two broad absorption bands are encountered above 1600 cm^{-1} . The other three bands probably reflect some phenolic and/or carbohydrate oxygen or compounds peculiar to this specific location.

The Rouge sample was unlike the other fulvics, having the appearance of an oil. Water could not be removed at 30° and the sample had to be dried over phosphorus pentoxide (the other two fulvic samples were also dried over P_2O_5). The broadness of the absorption band at 3000 cm^{-1} may reflect a highly oxygenated mixture of compounds capable of sorbing large amounts of water.

Results of ultrafiltration experiments on the humic and fulvic fractions are shown in Figures 35 and 36. The data are in general agreement with the findings of other workers with respect to the fact that fulvic acids are generally of lower molecular weight than humic acids. The dextran standard T-10 (molecular weight 10,000) is shown only to demonstrate membrane performance. As was discussed in the introduction, determination of molecular weights of humic materials by gel permeation is difficult, one of the reasons being the lack of suitable standards. Since ultrafiltration (and gel permeation) fractionate

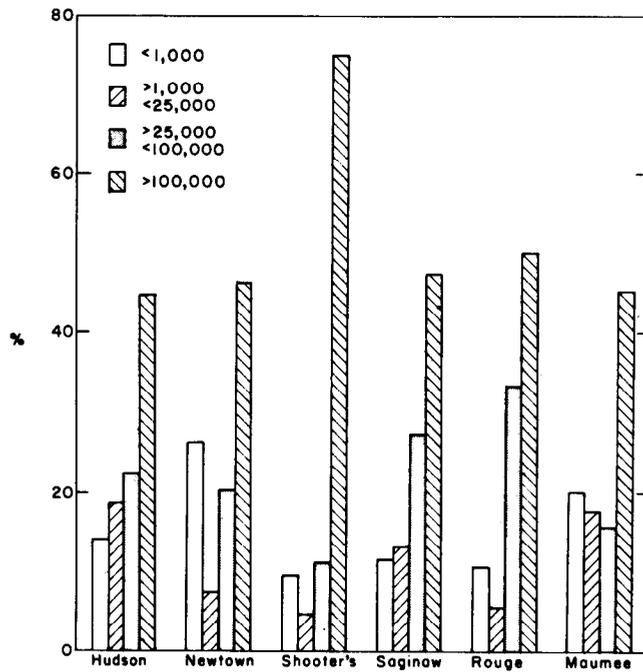


Figure 35. Molecular Weight Distribution of Humic Acids by Ultrafiltration

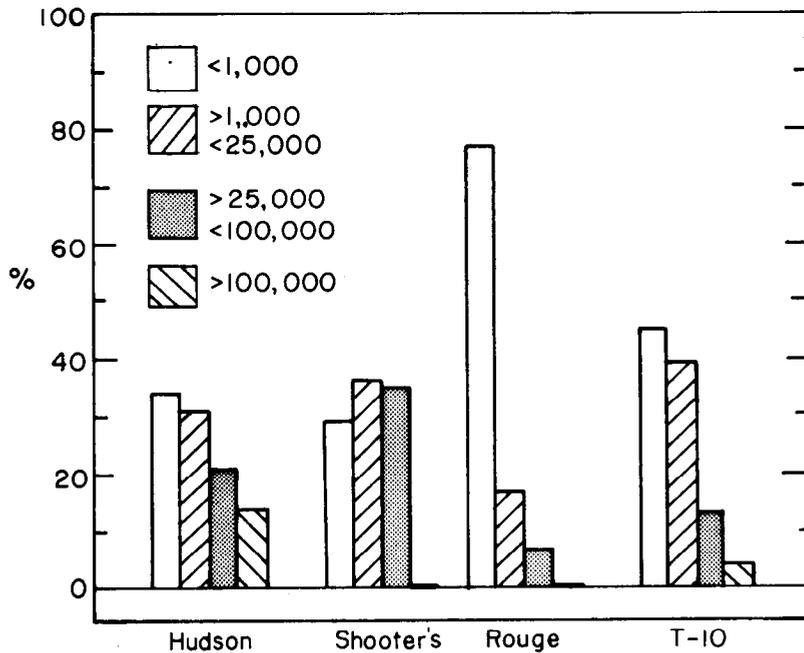


Figure 36. Molecular Weight Distribution of Fluvic Acids by Ultrafiltration (T-10 is a Dextran Standard, MW = 1×10^4)

materials based on molecular size, conversion of such data to molecular weight requires standards of known molecular weight. Molecular shapes in solution must be comparable to the unknown material to allow accurate calibration. Although ultrafiltration cannot produce a continuous fractionation pattern such as found in gel permeation, the relatively low surface area of a membrane compared to a gel column helps to minimize adsorption effects.

Fulvic acid is generally considered to have an average molecular weight of approximately 700 (21). The Hudson and Shooter's fulvic samples show a lower percentage of material being retained by the 1000 nominal molecular weight membrane than the Rouge fulvic. This is in part due to some minor losses encountered when these samples (Hudson and Shooter's) were initially purified with the PSAL membrane (500 nominal molecular weight). It was the results obtained with the Rouge fulvic and the PSAL membrane that necessitated the abandonment of this procedure. However, the overall distribution of material in Hudson and Shooter's suggests that these fractions are somewhat different than the Rouge fulvic (as was also found in the infrared spectra) and implies quite different sources for the "fulvic" fraction.

In gel permeation, the distribution coefficient, k_D , is defined as:

$$k_D = \frac{V_e - V_o}{V_t - V_o}$$

where

V_e = peak elution volume

V_t = total volume of gel column

V_o = column dead volume (as measured with a totally excluded solute)

Values of the distribution coefficient range from $k_D=0$ for complete exclusion of a solute to $k_D=1$ for complete inclusion of a solute. Values of $k_D>1$ are possible for solutes which are adsorbed on the gel column. For the purpose of discussion, we shall define an additional parameter, α , as the peak width at half height measured in milliliters. Table 19 summarizes the results of the gel permeation work. Peak heights, h , are shown only to give an approximate idea of the relative contribution of various peaks within a sample. They are not strictly comparable from one sample to another due to differences in initial concentrations.

The gel permeation results for the fulvic samples show reasonable agreement with the ultrafiltration results. The data in Table 19 show that the Hudson and Shooter's fulvic acids have relatively broad distributions (αJh), while the Rouge fulvic shows a major peak ($h>J_a$) of low molecular weight. This is in agreement with the ultrafiltration data and for Rouge suggests a quite different source for the organic matter as compared to Hudson and Shooter's.

The humic acid chromatograms were often more complex than the fulvic chromatograms. Multiple peaks were observed and, due to the limited amount of humic acids available, low concentrations might have prevented all peaks from being detected. All samples show that some material is excluded by the gel ($k_d \approx 0$) as would be expected from the ultrafiltration data. The presence of multiple peaks is in agreement with what is often found by other workers using similar procedures. The ultrafiltration data did not clearly predict that multiple peaks would be

Table 19. Gel Chromatographic Data for Organic Fractions
 ($V_o = 90$ ml, $V_t = 276$ ml)

<u>Sample</u>	<u>k_D</u>	<u>h (arbitrary units)</u>	<u>α (ml)</u>
FULVIC ACIDS			
Hudson	0.41	25	44
Shooter's	0.41	25	54
Rouge	1.0	115	15
HUMIC ACIDS			
Hudson	0.04	14	29
	0.28	5	70
	0.72	96	14
	0.82	17	17
Newtown	0	6	10
	0.68	14	12
Shooter's	0.01	7	14
	0.80	8	14
Saginaw	0.02	20	13
	0.35	13	72
	0.79	15	22
Rouge	0.01	7	21
	0.77	11	17
Maumee	0	11	77

observed. This may be due to the inherent limitations of ultrafiltration (i.e. lack of sufficiently narrow fractionation ranges) or possible disruption of humic colloidal properties similar to those discussed in Section C(2). The Hudson sample is unusual in that a large narrow peak ($h > \alpha$) is observed at a position indicative of low molecular weight. Such a peak was not observed in ultrafiltration data and may therefore indicate a gel-solute interaction.

(5) Elutriate Test

The elutriate test (72), as previously indicated, is a method for assessing the potential effects disposing of dredged material may have on water quality at a disposal site. Briefly, fixed ratios of sediment and disposal site water are shaken together for one-half hour, filtered, and parameters of interest determined in the water (referred to as the standard elutriate). These same parameters are measured on filtered disposal site water. If the concentration of a component in the standard elutriate exceeds 1.5 times the value found for the disposal site water above, then the sediment is considered potentially polluting with regards to this component. The modifications to the standard elutriate test utilized in this study have been discussed elsewhere and values referred to as initial colloidal or colloidal ($t=0$) are in fact the modified standard elutriate. Table 20 summarizes the findings for a number of components.

The changes in these parameters with time have already been discussed. It is obvious that at the actual time of disposal the various components will exceed the critical 1.5 value if the disposal site water is oxygen deficient. The addition of anoxic sediments to water often results in the depletion of dispersal site dissolved oxygen so that the trends observed here may reflect the situation at an actual disposal area. With time, levels of most components will drop significantly even in the absence of an expanding mixing zone. Attempts to relate concentrations found in the standard elutriate with corresponding sediment parameters were unsuccessful.

Table 20. Modified Elutriate Test Ratios, All Sediments

Sample	NH ₄ -N	Ortho-P	Organic-C	Fe	Mn	Pb	Cu	Ni	Cd	Cr	Zn	COD
Hudson	36*	3	2.6	126	72	5.8	6.6	1	1.4	4	3.6	---
Newtown	68	17	3.4	35	9.5	1	55	12.6	1.1	7.1	14.8	---
Shooter's	70	19	2.8	33	11.5	1	6.6	2.9	1.1	1	2.3	---
Saginaw-Salt	130	2	4.8	219	112	4.2	3.5	1.6	1	2.5	2.3	---
Fresh	80**	2**	3.1	1413	182	13.8	5.2	11.7	-	174	115	8
Rouge-Salt	88	3	4	251	52	3.0	6.6	4.9	1	1	3.9	---
Fresh	80**	0.5**	2.9	676	1	1	18.2	13.8	3.2	126	132	5
Maumee-Salt	48	<0.1	3.3	380	81	6.9	43	22	1	1	7.2	---
Fresh	40**	1**	2.7	550	55	2.5	7.2	11.7	2.8	36	10.7	7

*>1.5 denotes potentially polluting

**Concentration in lake disposal site water below detection. Number shown is relative to concentration found in marine disposal water.

NOTE: The data for Mn, Pb, Cu, Ni, Cd, Cr, and Zn in the Detroit-Fresh samples were determined using diluted samples and subsequently corrected.

Other methods have also been devised, based upon sediment organic carbon and nitrogen, with the aim of identifying potentially troublesome sediments. Figure 37 shows two such schemes (101). Disregarding the Detroit-Salt cases, it can be seen from the data in Table 7 that Newton,

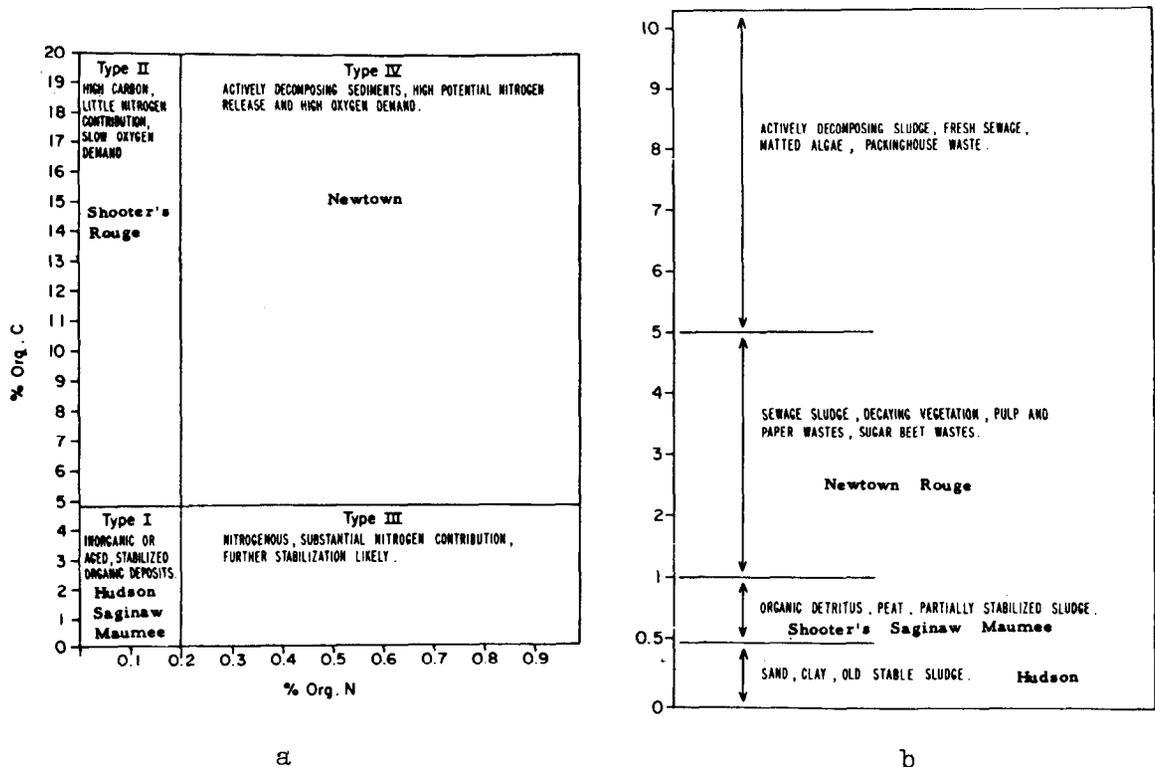


Figure 37. Two Arbitrary Sediment Classification Schemes. In 'b' the Vertical Axis is Organic Sediment Index (OSI). After Ballinger and McKee (101), reprinted with permission from Journal Water Pollution Control Federation, Vol. 43, 1971, pp 216-227.

Rouge, and Saginaw release N into the water column while the Hudson, Shooter's, and Maumee sediments release only small amounts. It can be seen that under the experimental conditions utilized neither the elutriate test or the other two schemes is entirely satisfactory. The Organic

Sediment Index (Figure 37b) might be useful, however, as a technique for crudely classifying the long term effect of sediments.

With regards to predicting the results of the modified elutriate test, the Organic Sediment Index may be useful (Figure 38). Only the

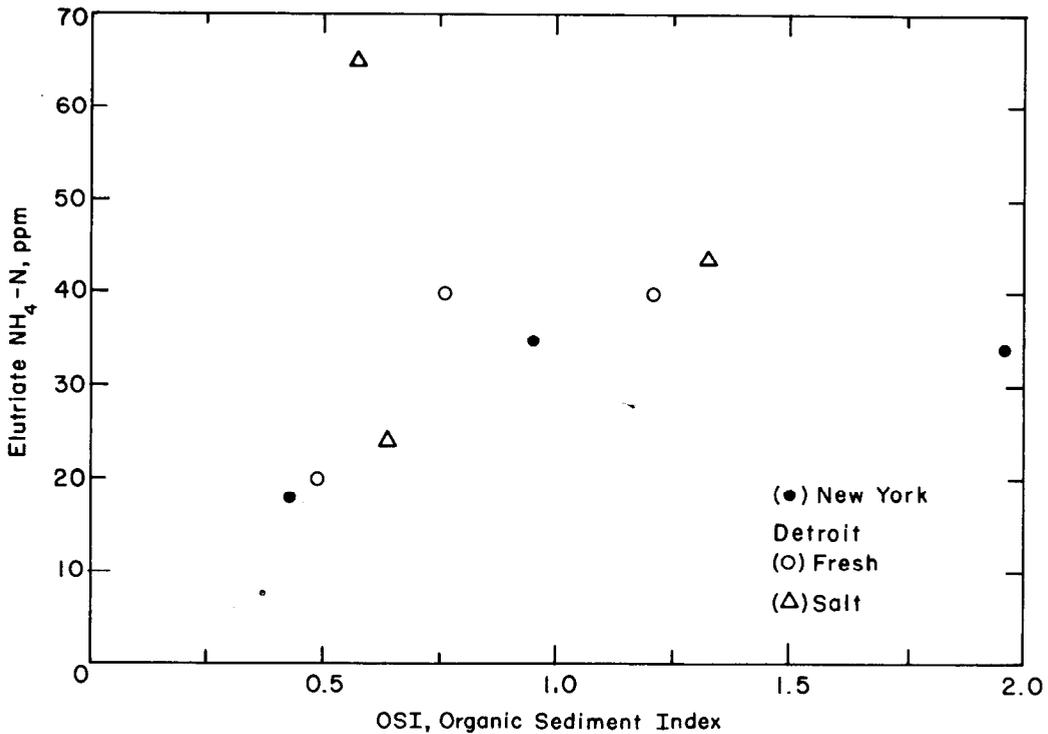


Figure 38. Comparison of Elutriate Test $\text{NH}_4\text{-N}$ with Organic Sediment Index

behavior of Newtown and Saginaw-Salt are significantly different while the result for Saginaw-Fresh is only slightly greater than anticipated. OSI values were calculated from average organic-C and organic-N values. The correlation is somewhat surprising. If $\text{NH}_4\text{-N}$ concentration in the

interstitial water reasonably reflects the concentration of $\text{NH}_4\text{-N}$ in the residual water associated with the sediment (30-40% by weight) after dewatering and prior to mixing with disposal site water, then this residual water $\text{NH}_4\text{-N}$ cannot account for the concentration of $\text{NH}_4\text{-N}$ in the standard elutriate. The Organic-C/Organic-N ratio may be used in place of the OSI but the correlation is not as good. Agreement between the $\text{NH}_4\text{-N}$ levels and sediment total nitrogen or sediment organic nitrogen is poor.

Examination of elutriate test data for organic-C, ortho-P, and metals with corresponding sediment parameters showed no correlation. In addition, no clear evidence for the existence of correlations between sediment and/or elutriate test data with interstitial water or overlying water concentrations was found.

Organic Sediment Index has no firm theoretical basis. Ballinger and McKee (101) reasoned that sediments can behave differently although having similar organic C/N ratios. Thus, it seemed preferable to utilize some parameter which reflected the magnitude of each quantity. Hence, the use of the product sediment organic-C and sediment organic-N as opposed to the ratio. Even some sediment total metals show some correlation with either OSI or C/N, or both (Table 21).

Table 21. Correlation Coefficients of Total Sediment Metals with OSI and C/N*

	<u>Zn</u>	<u>Cd</u>	<u>Pb</u>	<u>Cu</u>	<u>Ni</u>	<u>Cr</u>
OSI	0.928	0.903	0.741	0.457	0.803	0.524
C/N	0.977	0.80	0.922	0.492	0.951	0.614

*Based upon data for five of the original sediments. The sixth, Newtown, contained such large amounts of metals that it obscured any potential correlation.

V. SUMMARY AND CONCLUSIONS

A. Summary of Long-Term Experimental Results

To assist the reader, the results of the long-term experiments are summarized below.

Brackish Riverine Sediments (New York) in Seawater

(1) Colloidal Phase - Cu, Fe, Zn, Pb, Cr, and Ni decrease with time.

More Zn and Ni remain in solution with the Newtown sediment as does Cu for both Newtown and Shooter's. These two samples released only small amounts of iron to the aqueous phase. Both of these sediments contained significant amounts of hydrocarbons. Cd increases slightly with time and Mn remains high and relatively unchanged with time. $\text{NH}_4\text{-N}$ levels decrease although slowly with Newtown and Shooter's and $\text{NO}_3\text{-N}$ levels increase for all three sediments. Particulate-N is a source of soluble-N in Newtown. Only Newtown and Shooter's contained significant quantities of ortho-P and this decreased slightly with time as a result of precipitation by the small amount of iron present. Organic-C levels decreased to a constant level above baseline concentrations although Newtown at first decreased then increased. Inorganic-C (UV) increased in all samples with time.

(2) Interstitial Water - All metal concentrations increase with time although the increases are smaller or more variable for Cu, Fe, Zn, Pb, and Cd in Newtown and Shooter's. Chromium fluctuates in Hudson. $\text{NH}_4\text{-N}$ first rises then falls in Shooter's and with

Newtown and Hudson initially rises and levels off. $\text{NO}_3\text{-N}$ levels are low in Newtown and Shooter's and show little change. Hudson, $\text{NO}_3\text{-N}$ levels increase with time. Ortho-P increases in Newtown and Shooter's. Organic-C increases initially and then remains constant.

- (3) Water Overlying Sediment - Initially anoxic conditions followed by maintenance of an oxic state result in all metal concentrations decreasing with time except for cadmium and manganese, which tend to increase. $\text{NH}_4\text{-N}$ in Newtown initially increases and then remains constant. $\text{NH}_4\text{-N}$ in Hudson and Shooter's remains constant for a time and subsequently decreases. Newtown $\text{NO}_3\text{-N}$ increases slightly with time while in Hudson and Shooter's a similar increase is followed by a decrease. Ortho-P increases slightly and then remains constant except for Newtown where the P level continues to increase. Organic-C concentrations remain unchanged and at uncontaminated seawater levels. Inorganic-C (UV) increases slightly.

Riverine Sediments (Detroit) in Fresh Water

- (1) Colloidal Phase - All metal concentrations decrease with time except for Rouge Zn where a significant amount remains in solution. Also, Saginaw Cd increases and Maumee Cr at first decreases and then increases. $\text{NH}_4\text{-N}$ levels decrease and $\text{NO}_3\text{-N}$ levels increase in all samples. Ortho-P decreases. Organic-C decreases to a constant level in Saginaw and Maumee but fluctuates,

decreasing then increasing, in Rouge. Inorganic-C (UV) increases in all samples.

- (2) Interstitial Water - All metal levels increase with time except for Maumee Cd and Ni where the initial increase is followed by an apparent decrease. $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ increase in all three samples. Ortho-P increases in Saginaw and remains below detection limits in Maumee and Rouge. Organic-C rises then decreases in Maumee while in Rouge no decrease occurs.
- (3) Water Overlying Sediment - Initially anoxic conditions followed by maintenance of an oxic state did not result in predictable metal behavior. Concentrations decreased in all cases except for: Rouge, where Zn, Cr, and Ni fluctuated, Cu decreased but not to baseline levels and Pb and Cd decreased; Maumee, where Pb and Cd fluctuated and Cu and Cr decreased but did not return to baseline levels; and Saginaw, where Cd fluctuated. $\text{NH}_4\text{-N}$ levels remained at zero for Maumee, increased then decreased for Rouge, and increased and remained constant for Saginaw. $\text{NO}_3\text{-N}$ levels increased for Rouge and decreased slightly for the others. Ortho-P increased slightly in Saginaw but not in Maumee and Rouge. Organic-C concentrations for all samples showed small fluctuations around the uncontaminated freshwater level. Inorganic-C (UV) increased for Rouge and only slightly increased for Maumee and Saginaw.

Riverine Sediments (Detroit) in Seawater

- (1) Colloidal Phase - Generally all metal concentrations decreased except for: Saginaw Zn which did not decrease significantly, Cr and Pb which fluctuated, Ni and Mn which remained constant, and cadmium which increased; Maumee Pb which fluctuated, Cr, Cd, and Mn which remained constant and nickel which decreased; and Rouge Pb which fluctuated, Cr and Mn which remained unchanged, and Ni which decreased slightly. $\text{NH}_4\text{-N}$ remained high and constant and $\text{NO}_3\text{-N}$ low and constant. Ortho-P decreased, Organic-C decreased and remained constant. Inorganic-C (UV) increased slightly.
- (2) Interstitial Water - Fe, Cd, Cr and Mn increased; Cu and Pb remained unchanged; and Zn and Ni were variable. $\text{NH}_4\text{-N}$ increased in Rouge and, after an initial increase, Maumee and Saginaw decreased. $\text{NO}_3\text{-N}$ levels were erratic. Ortho-P increased in Rouge and showed little or no increase in Saginaw and Maumee. Organic-C initially increased in all samples, leveled off in Rouge, and decreased in Saginaw and Maumee.
- (3) Water Overlying Sediment - Initially anoxic conditions followed by maintenance of an oxic state resulted in a decrease in most metal concentrations. Exceptions are: Saginaw Zn which remained constant, Pb which fluctuated, and Mn and Cd which increased; Maumee Cd and Cr which fluctuated and Mn which increased; and Rouge Cd and Mn which increased. $\text{NH}_4\text{-N}$ increased in Rouge and, following an initial increase, decreased

in Saginaw and Maumee. $\text{NO}_3\text{-N}$ levels remained low in Rouge and increased slightly in Saginaw and Maumee. Ortho-P increased in Rouge but not in the other samples. Both organic-C and inorganic-C showed slight increases with time.

B. Summary of Characterization Experiments

- (1) Ultraviolet absorbance measurements at 254 nm showed a positive correlation with soluble organic-C.
- (2) Chemical oxygen demand data showed a positive correlation with soluble organic-C. Data were in reasonable agreement with the theoretical chemical oxygen demand of fulvic acid. Rouge River interstitial water showed a significantly larger chemical oxygen demand than predicted.
- (3) Anodic stripping data indicated the presence of non-labile ligands in interstitial waters of the Newtown and Shooter's sediments. This was not observed for the other samples. Labile ligands are indicated for all samples. The chemical nature of these ligands could not be determined.
- (4) Soluble organic carbon from the original interstitial waters was fractionated into five chemical classes based on solubility.
- (5) Infrared spectra of all fractions were obtained. Comparable fractions from different locations had, for the most part, similar spectra. Fulvic acid spectra differed substantially from published spectra. The Rouge sample was most notable in this respect.

(6) Ultrafiltration and gel permeation data were comparable for the fulvic acid samples. Rouge fulvic acid consisted primarily of low molecular weight species. Comparison of the two methods with the humic acid fractions was not as consistent.

C. Conclusions

Based upon the results obtained in this study, it is concluded that there is no evidence to suggest that total sediment organic carbon directly controls the release of either metals or nutrients during sediment disposal operations. No positive correlation was found between soluble organic carbon and levels of either metals or nutrients released during dispersal operations. A positive correlation appears to exist between soluble organic carbon and the chromium and lead concentrations in freshwater disposal site interstitial solutions.

The indirect effects of sediment organic carbon are more difficult to quantitate. Two sediments (Newtown and Shooter's) which were observed to contain significant amounts of petroleum hydrocarbons exhibited atypical behavior with regards complexing capacity and iron and ortho-P concentrations in dispersal and interstitial waters. Field investigations utilizing similar types of sediments should address this possible relationship in more detail. The product of sediment organic carbon and sediment organic nitrogen was found to be useful in predicting the release of ammonium-nitrogen during the dispersal operation.

The disposal of freshwater sediments in fresh water may lead to high concentrations of heavy metals for short periods of time. Disposal

of the same sediments in saline waters may temporarily disrupt the nitrification process in the dispersal water.

In general low levels of cadmium were transported out of the sediment into the overlying water column. For seawater media, manganese may be transported into the water column. Additionally, low levels of ortho-phosphate and, in some cases, ammonium nitrogen, were transported into the water column.

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APPENDIX A: ADDITIONAL ANALYTICAL DATA

Analytical data collected on the sediments at t=0 months and not reported elsewhere are shown in Tables A-1 through A-3. Data on the original interstitial water are contained in Tables A-4 and A-5. Data which were presented graphically are tabulated in Table A-6.

Table A-1: Total Metals, Sediment (mg/kg dry weight)

	<u>Zn</u>	<u>Cu</u>	<u>Cr</u>	<u>Ni</u>	<u>Pb</u>	<u>Cd</u>
Hudson	238	157	155	47	171	4
Newtown	4289	4684	616	767	481	53
Shooter's	416	431	342	68	177	11
Saginaw-Salt	234	73	71	46	79	6
Fresh	233	70	58	44	69	9
Rouge-Salt	530	180	178	99	388	14
Fresh	539	181	198	98	391	14
Maumee-Salt	174	61	73	59	85	9
Fresh	171	55	64	61	81	9

Table A-2. Extractable Metals (HCl), % of Total; 0, 2, 4 months

	Cu			Zn			Cr			Ni			Pb			Cd		
	0	2	4	0	2	4	0	2	4	0	2	4	0	2	4	0	2	4
Hudson	0.10	0.99	0.40	0.05	2.0	0.01	7.0	16.1	2.4	<0.01	0.66	0.05	1.4	11.9	1.9			
Newtown	<0.01	0.02	1.02	0.01	0.02	0.28	0.29	2.6	1.1	<0.01	0.03	0.04	0.13	0.40	0.09			
Shooter's	0.05	0.19	0.37	0.02	0.91	1.5	6.8	12.4	10.7	<0.01	0.02	0.06	0.69	0.23	0.50			
Segitow-Salt	0.16	0.08	0.32	0.06	0.52	0.02	4.0	2.2	2.7	<0.01	0.04	0.13	2.0	2.2	0.82			
Fresh	0.15	0.13	0.73	0.06	0.08	0.04	5.2	4.5	2.5	<0.01	0.12	0.09	1.0	1.6	0.62			
Reuge-Salt	0.08	0.10	0.31	0.02	0.02	0.02	3.7	7.4	3.2	<0.01	0.01	<0.01	0.74	0.93	0.29			
Fresh	0.06	0.08	0.92	0.02	0.01	0.01	4.0	6.6	3.1	<0.01	>0.01	0.04	0.68	1.2	0.35			
Maumee-Salt	0.27	0.13	0.32	0.05	0.02	3.1	4.0	2.1	1.3	<0.01	0.02	0.04	1.3	1.2	0.54			
Fresh	0.28	0.20	0.53	0.05	0.09	0.03	2.5	5.0	1.9	<0.01	0.04	0.30	0.99	3.3	0.67			

Table A-3. Additional Sediment Analytical Data

Sample	CEC*	Iron Oxides(%)**	Exchangeable Cations (mg/kg dry weight)						pH	TVS(%)***
			Ca	Mg	K	Na	Fe	Mn		
Hudson	28.0	1.61	2,703	3921	472	6201	854	30	7.0	6.4
Newtown	29.8	0.78	2,050	2668	664	7249	1825	186	7.1	15.1
Shooter's	30.2	0.91	4,209	3260	573	6222	1208	62	6.9	7.2
Saginaw-Salt	22.8	0.51	8,509	2171	343	4577	827	98	---	---
--Fresh	18.3	0.64	8,270	627	64	74	469	116	6.8	5.7
Rouge-Salt	16.2	1.27	9,289	1672	294	3468	1067	79	---	---
Fresh	19.2	1.49	9,924	768	96	69	269	81	7.0	9.3
Maumee-Salt	32.3	1.05	11,489	2501	527	4545	877	125	---	---
Fresh	26.7	1.10	15,594	1592	203	109	1004	187	7.0	6.1

* Cation Exchange Capacity meq/100g dry weight

** as Fe₂O₃

*** Total Volatile Solids

Table A-4. Total Heavy Metals in Original Interstitial Water

<u>Sample</u>	<u>Zn(ppm)</u>	<u>Mn(ppm)</u>	<u>Cu(ppm)</u>	<u>Cr(ppb)</u>	<u>Cd(ppb)</u>	<u>Ni(ppb)</u>	<u>Pb(ppb)</u>	<u>Hg(ppb)</u>
Hudson	0.262	7.91	0.062	20.8	2.5	12.3	7.5	1.34
Newtown	0.051	0.40	0.051	6.2	2.2	40.2	8.0	1.75
Shooter's	0.119	1.04	0.060	9.5	9.2	21.4	4.6	1.30
Seginaw	0.171	2.56	0.019	4.4	5.8	21.7	6.2	2.71
Rouge	0.210	2.86	0.022	1.7	3.9	11.1	9.1	2.09
Maumee	0.228	4.14	0.046	1.5	4.2	11.8	3.7	3.66

Table A-5. Additional Data, Original Interstitial Water (mg/l)

<u>Sample</u>	<u>Alkalinity (as CaCO₃)</u>	<u>Ortho-P</u>	<u>Organic-C</u>	<u>NH₄-N</u>	<u>Kjeldahl-N</u>	<u>NO₃-N</u>	<u>Fe(Total)</u>	<u>Fe⁺²</u>	<u>COD</u>
Hudson	77	0.3	55	56	53	<2	---	---	270
Newtown	76	26	33	98	99	<2	0.2	<0.1	295
Shooter's	61	58	47	95	95	<2	0.2	<0.1	295
Saginaw	56	1.8	37	92	88	<2	21	6	105
Rouge	69	0.3	198	92	91	<2	103	70	650
Maumee	47	0.2	33	46	35	<2	40	26	71

Table A-6. Solution Analytical Data, Long Term Experiments
(Interstitial Values (t=0) are Uncontaminated Waters)

		Ortho-P (mg/l)								
Sample	t =	Colloidal			Overlying Water			Interstitial Water		
		0	2	4	0	2	4	0	2	4
Hudson		0.6	0	0.1	0	0.2	0.2	0.2	0	0.1
Newtown		3.3	1.3	1.8	0	0.3	0.7	0.2	4.3	6.7
Shooter's		3.8	2.6	2.7	0.1	0.4	0.4	0.2	16.2	15.8
Saginaw-Salt		0.4	0.1	0.1	0	0.1	0.1	0.2	0	2.5
	Fresh	0.4	0.1	0.1	0.2	0.3	0.4	0	-	2.0
Rouge-Salt		0.7	0	0.1	0	0.2	0.5	0.2	3.4	6.8
	Fresh	0.1	0	0.1	0	0	0.1	0	0	0.1
Maumee-Salt		0	0	0.1	0	0	0.1	0.2	0.6	0.7
	Fresh	0.2	0	0.1	0	0.1	0.1	0	0.9	0.2

$\text{NH}_4\text{-N}$ (mg/l)

		$\text{NH}_4\text{-N}$ (mg/l)								
Sample	t =	Colloidal			Overlying Water			Interstitial Water		
		0	2	4	0	2	4	0	2	4
Hudson		18	0.3	0	1	1	0.5	0.5	16.5	16.6
Newtown		34	18	0	0	4	3.6	0.5	15.3	6.3
Shooter's		35	21	0	0	0.5	0	0.5	30.5	14.6
Saginaw-Salt		65	63	62	0	6	2	0.5	21	10.1
	Fresh	40	1	0	0	3	3.6	0	--	8.8
Rouge-Salt		44	37	40	1	5	6.4	0.5	13	16
	Fresh	40	0.4	0	0	4	0	0	30	21.2
Maumee-Salt		24	26	22	0	5	1	0.5	16.2	3.4
	Fresh	20	1	0	0	0	0	0	12.5	4.5

Table A-6. (Cont.)

$\text{NO}_3\text{-N}$ (mg/l)

Sample	t =	Colloidal			Overlying Water			Interstitial Water		
		0	2	4	0	2	4	0	2	4
Hudson		0.3	13.5	11.8	0.2	2.2	0.9	0.2	0.9	3.4
Newtown		0.1	19.4	51	0.2	0.2	0.8	0.2	0.8	0.4
Shooter's		1.1	9.0	25.6	0.2	2.6	0.4	0.2	0.5	0.5
Saginaw-Salt		0.2	0.8	0	0.2	0.2	4.7	0.2	0.9	0.3
Fresh		0	25.5	34.5	34.3	1.2	1.0	1.2	-	14.2
Rouge-Salt		0.1	0.5	0	0.2	0.1	0.7	0.2	1.4	2.4
Fresh		0	23.2	30.8	1.2	0.9	4.2	1.2	0.7	3.4
Maumee-Salt		-	0.7	0	0.2	0.2	5.3	0.2	86	0.8
Fresh		0.5	11.3	1.2	1.2	2.0	1.5	1.2	1.6	4.4

Organic-C (mg/l)

Sample	t =	Colloidal			Overlying Water			Interstitial Water		
		0	2	4	0	2	4	0	2	4
Hudson		10.5	7	6.5	3.5	3.5	3	4	18	23.5
Newtown		13.5	9	14	5	5	4	4	12	15.5
Shooter's		11	7.5	7	4	3	3	4	12.5	14
Saginaw-Salt		19	12	8.5	3	4	5	4	24.5	22
Fresh		17	12	12	7	5	8	5.5	-	27
Rouge-Salt		16	8	8.5	3.5	5	6.5	4	26	30.5
Fresh		16	11	14.5	9.5	4.5	8	5.5	12	18
Maumee-Salt		13	8	9	4	4.5	4	4	20.5	14
Fresh		15	10.5	9.5	7	5	7.5	5.5	20	14

Table A-6. (Cont.)

Manganese (mg/l)

<u>Sample</u>	<u>t =</u>	<u>Colloidal</u>			<u>Overlying Water</u>			<u>Interstitial Water</u>		
		<u>0</u>	<u>2</u>	<u>4</u>	<u>0</u>	<u>2</u>	<u>4</u>	<u>0</u>	<u>2</u>	<u>4</u>
Hudson		2.8	2.9	2.2	0.11	0.77	1.05	0.05	4.1	5.9
Newtown		0.37	0.42	0.48	0.16	0.16	0.14	0.05	0.45	0.29
Shooter's		0.45	0.65	0.69	0.02	0.30	0.43	0.05	0.79	1.2
Saginaw-Salt		4.5	4.2	4.1	0.66	0.62	0.91	0.05	3.7	3.9
Fresh		3.6	0.02	0.01	0.24	0.01	0.01	0.01	-	0.32
Rouge-Salt		2.1	1.8	1.6	0.36	0.65	0.72	0.05	1.6	1.4
Fresh		0.01	0.01	0.01	0.06	0.09	0.10	0.01	0.41	0.97
Maumee-Salt		3.3	3.5	3.4	0.31	0.44	0.68	0.05	5.7	6.9
Fresh		1.1	0.02	0.01	0.03	0.01	0.01	0.01	0.21	0.25
Control-Salt		0.04			0.05			0.05		
Fresh		0.02			0.01			0.01		

Copper (µg/l)

<u>Sample</u>	<u>t =</u>	<u>Colloidal</u>			<u>Overlying Water</u>			<u>Interstitial Water</u>		
		<u>0</u>	<u>2</u>	<u>4</u>	<u>0</u>	<u>2</u>	<u>4</u>	<u>0</u>	<u>2</u>	<u>4</u>
Hudson		13	8	4	12	7	10	5	3	217
Newtown		110	45	26	100	9	7	5	2	8
Shooter's		13	10	7	26	10	6	5	8	1
Saginaw-Salt		7	2	2	5	5	3	5	3	2
Fresh		57	21	14	5	5	5	3	-	1040
Rouge-Salt		13	6	4	71	3	12	5	3	3
Fresh		200	26	18	11	4	12	3	3	1000
Maumee-Salt		85	2	2	15	4	4	5	32	4
Fresh		79	12	7	45	5	5	3	9	205
Control-Salt		2			5			5		
Fresh		11			3			3		

Table A-6. (Cont.)

Zinc (µg/l)

<u>Sample</u>	<u>t =</u>	<u>Colloidal</u>			<u>Overlying Water</u>			<u>Interstitial Water</u>		
		<u>0</u>	<u>2</u>	<u>4</u>	<u>0</u>	<u>2</u>	<u>4</u>	<u>0</u>	<u>2</u>	<u>4</u>
Hudson	68	46	50	83	74	30	30	86	380	
Newtown	443	265	140	101	69	40	30	66	30	
Shooter's	69	44	30	93	71	30	30	141	40	
Saginaw-Salt	69	83	50	65	104	90	30	208	40	
Fresh	1131	34	10	17	14	10	10	-	660	
Rouge-Salt	117	52	10	123	64	30	30	81	50	
Fresh	1329	161	40	37	11	20	10	31	1090	
Maumee-Salt	216	43	20	59	63	30	30	195	80	
Fresh	108	7	10	24	15	10	10	35	80	
Control-Salt	30			30			30			
Fresh	10			10			10			

Iron (mg/l)

<u>Sample</u>	<u>t =</u>	<u>Colloidal</u>			<u>Overlying Water</u>			<u>Interstitial Water</u>		
		<u>0</u>	<u>2</u>	<u>4</u>	<u>0</u>	<u>2</u>	<u>4</u>	<u>0</u>	<u>2</u>	<u>4</u>
Hudson	12.6	0.32	0.15	0.47	0.26	0.14	0.10	8.0	17.1	
Newtown	3.5	0.36	0.18	0.38	0.32	0.11	0.10	0.52	0.33	
Shooter's	3.2	0.31	0.14	0.39	0.34	0.10	0.10	0.32	0.59	
Saginaw-Salt	21.9	0.29	0.09	0.48	0.33	0.10	0.10	10.4	13.2	
Fresh	42.0	0.07	0.01	0.44	0.01	0.01	0.03	-	2.2	
Rouge-Salt	25.3	0.34	0.12	0.43	0.33	0.14	0.10	0.39	1.3	
Fresh	20.5	0.04	0.01	0.70	0.01	0.01	0.03	0.24	6.4	
Maumee-Salt	38.2	0.30	0.12	0.46	0.32	0.13	0.10	23.0	21.8	
Fresh	16.0	0.07	0.02	0.37	0.04	0.01	0.03	0.15	0.11	
Control-Salt	0.10			0.10			0.10			
Fresh	0.03			0.03			0.03			

Table A-6. (Cont.)

		Chromium ($\mu\text{g}/\ell$)								
		<u>Colloidal</u>			<u>Overlying Water</u>			<u>Interstitial Water</u>		
<u>Sample</u>	<u>t =</u>	<u>0</u>	<u>2</u>	<u>4</u>	<u>0</u>	<u>2</u>	<u>4</u>	<u>0</u>	<u>2</u>	<u>4</u>
Hudson		28	3	4	8	3	4	5	9	5
Newtown		49	7	5	6	8	5	5	6	9
Shooter's		3	3	5	5	3	3	5	5	6
Saginaw-Salt		17	3	13	10	4	3	5	4	6
Fresh		168	2	1	7	1	1	1	-	6
Rouge-Salt		11	3	10	16	4	5	5	8	11
Fresh		124	6	2	3	1	2	1	2	4
Maumee-Salt		2	2	2	10	3	19	5	6	12
Fresh		36	1	2	4	3	2	1	4	2
Control-Salt		7			5			5		
Fresh		1			1			1		

		Cadmium ($\mu\text{g}/\ell$)								
		<u>Colloidal</u>			<u>Overlying Water</u>			<u>Interstitial Water</u>		
<u>Sample</u>	<u>t =</u>	<u>0</u>	<u>2</u>	<u>4</u>	<u>0</u>	<u>2</u>	<u>4</u>	<u>0</u>	<u>2</u>	<u>4</u>
Hudson		3.8	3.8	3.9	2.1	4.6	3.9	2.9	3.6	6.3
Newtown		3.1	6.3	4.2	2.6	3.5	2.7	2.9	4.2	2.7
Shooter's		3.1	3.5	3.2	2.5	4.2	7.1	2.9	4.2	7.3
Saginaw-Salt		1.4	3.7	7.5	1.9	3.9	6.6	2.9	5.5	6.5
Fresh		-	4.6	4.6	0.8	3.1	1.9	2.2	-	8.1
Rouge-Salt		1.6	10.0	2.5	2.5	3.7	6.9	2.9	5.5	5.0
Fresh		8.3	2.3	3.2	1.0	3.5	11.4	2.2	4.0	4.4
Maumee-Salt		1.0	3.3	2.4	2.4	5.9	3.4	2.9	2.7	3.3
Fresh		7.2	1.5	1.7	1.1	3.0	2.3	2.2	4.5	2.7
Control-Salt		2.8			2.9			2.9		
Fresh		2.6			2.2			2.2		

Table A-6. (Concluded)

		Nickel ($\mu\text{g}/\ell$)								
Sample	t =	Colloidal			Overlying Water			Interstitial Water		
		0	2	4	0	2	4	0	2	4
Hudson		6	7	8	9	10	7	10	12	30
Newtown		89	110	117	17	32	8	10	45	30
Shooter's		20	9	7	17	9	8	10	50	39
Saginaw-Salt		11	14	10	10	7	10	10	29	11
Fresh		71	11	10	19	6	7	6	--	10
Rouge-Salt		34	21	14	17	9	10	10	42	16
Fresh		82	21	8	14	6	10	6	6	54
Maumee-Salt		153	10	7	14	13	7	10	122	13
Fresh		71	11	6	15	6	5	6	42	14
Control-Salt		7			10			10		
Fresh		6			6			6		

		Lead ($\mu\text{g}/\ell$)								
Sample	t =	Colloidal			Overlying Water			Interstitial Water		
		0	2	4	0	2	4	0	2	4
Hudson		17	2	6	28	4	6	5	21	21
Newtown		57	13	7	5	5	13	5	2	9
Shooter's		43	2	8	3	2	3	5	4	4
Saginaw-Salt		6	10	5	21	2	12	5	3	3
Fresh		290	2	2	28	2	2	2	-	170
Rouge-Salt		20	5	6	15	44	6	5	3	10
Fresh		48	5	12	2	2	3	2	4	53
Maumee-Salt		3	2	8	34	2	7	5	4	8
Fresh		290	2	10	5	2	9	2	2	35
Control-Salt		3			5			5		
Fresh		12			2			2		

APPENDIX B: PARTICLE-SIZE ANALYSIS AND MINERAL IDENTIFICATION

(1) Particle Size Analysis

The original dewatered sediment was thoroughly mixed and 500 grams allowed to air dry. After drying the material was broken up and passed through a #10 sieve (2mm). Approximate amounts of >2 mm material are shown in Table B-1. All subsequent calculations are based on the material which passed through the sieve.

Table B-1. Approximate Amounts of Sediment Retained by #10 Sieve

Hudson	0%
Newtown	15%
Shooter's	2%
Saginaw	3%
Rouge	6%
Maumee	2%

After the determination of the specific gravity, sediments were washed through a #200 sieve to determine the percent sand and the material passing through the sieve was taken for use in hydrometer grain-size analysis. Gradation curves for the less than #200 material are shown in Figure B-1.

(2) X-ray Analysis

At the end of the 24-hour settling period used in the hydrometer analyses the aqueous phase was siphoned off (to 1-1/2" above the water-sediment interface) and oven dried for use in X-ray analysis. Powder

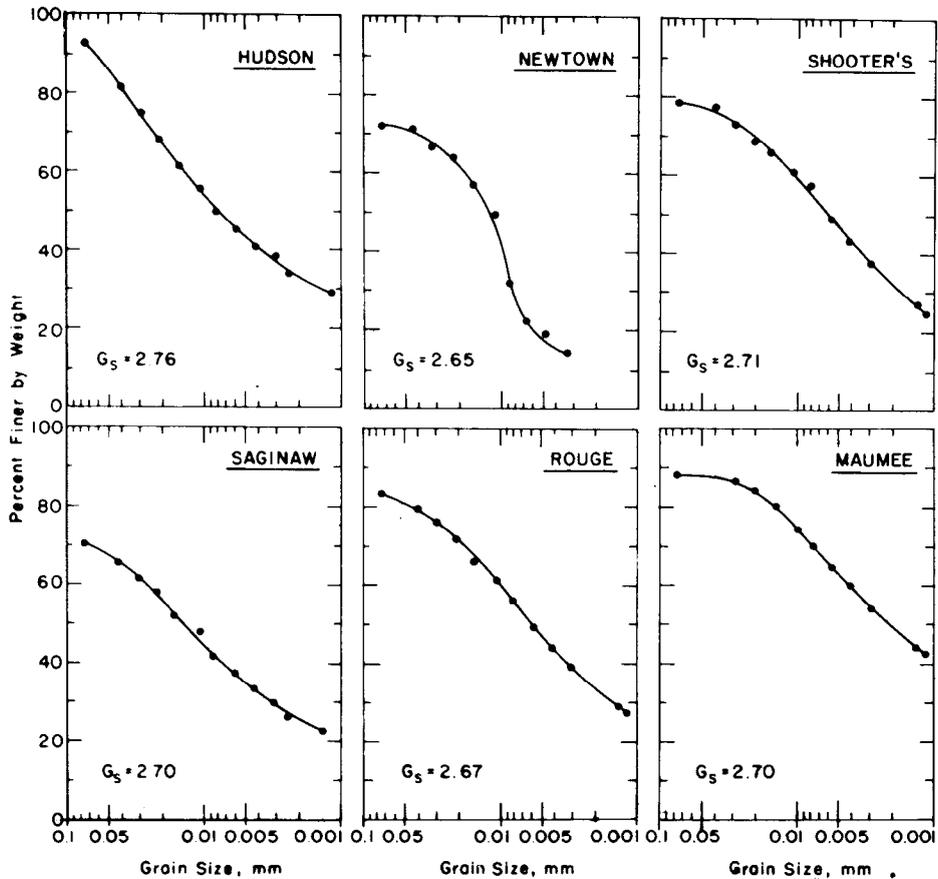


Figure B-1. Gradation curves for original sediments (G_s is the specific gravity of the sediment)

diffraction data were obtained on both normal and glycolated samples using a Norelco x-ray diffractometer. Major and minor components identified are shown in Table B-2.

Table B-2. Clay-Size Minerals Identified in Sediments

<u>Sample</u>	<u>Major Components</u>	<u>Minor Components</u>
Hudson	Quartz, Olivine, Illite	Chlorite, Feldspar
Newtown	Chlorite, Illite, Feldspar	Quartz, (Tremolite)?
Shooter's	Olivine, Quartz	Montmorillonite, Illite
Saginaw	Quartz	Chlorite, Illite, Pyroxene
Rouge	Quartz, Illite	Chlorite, (Talc)?
Maumee	Quartz	Feldspar (Andulucite, Chlorite, Muscovite)?

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