

APPENDIX A

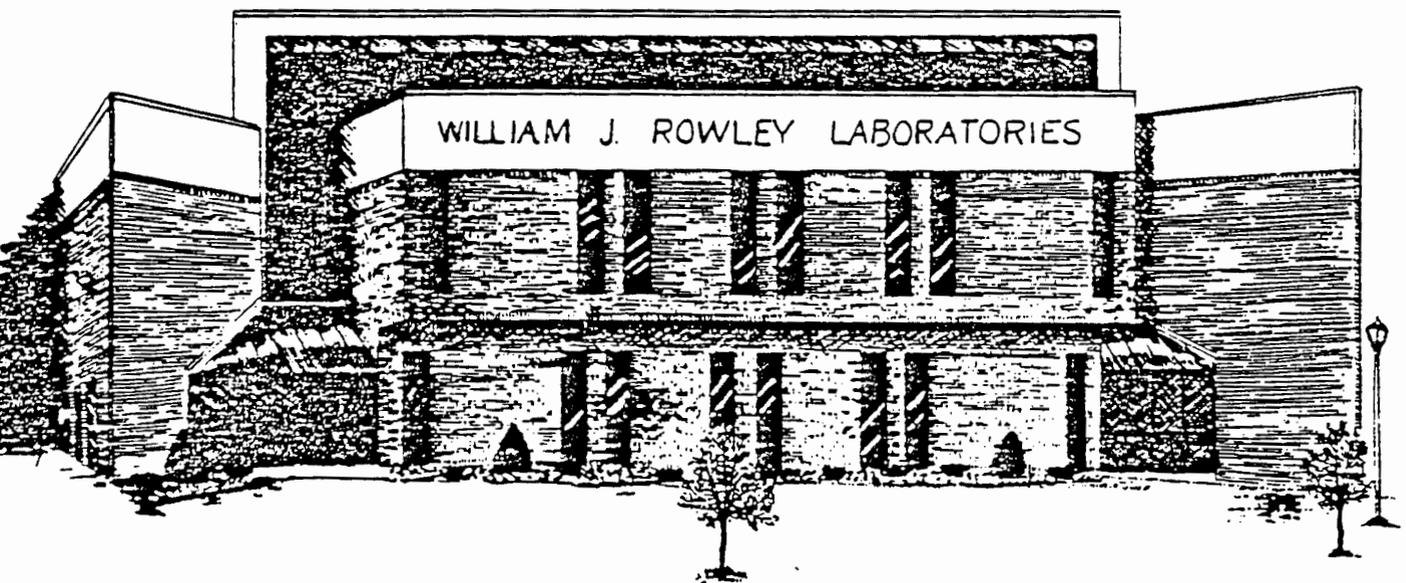
EXPOSURE AND BIOLOGICAL EFFECTS OF IN-PLACE POLLUTANTS:
SEDIMENT EXPOSURE POTENTIAL AND PARTICLE-CONTAMINANT INTERACTIONS.

ENVIRONMENTAL ENGINEERING

REPORT NO. 87-9

EXPOSURE AND BIOLOGICAL EFFECTS OF IN-PLACE
POLLUTANTS: SEDIMENT EXPOSURE POTENTIAL AND
PARTICLE-CONTAMINANT INTERACTIONS

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CLARKSON UNIVERSITY

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SECTION 1**INTRODUCTION****STATEMENT OF PROBLEM**

In spite of major efforts in the Great Lakes basin (eg. DDT and PCB bans) to reduce the impacts of toxic chemicals on human health and aquatic communities (Toxic Substances Committee 1981), surveillance and monitoring efforts continue to demonstrate the presence and impact of toxic substances in certain areas (Great Lakes WQB 1981a; Great Lakes Human Health Effects Committee 1982; Great Lakes WQB 1982; Nriagu and Simmons 1984). Problems of potential toxicity to aquatic organisms and bioaccumulation in aquatic food chains were identified for both metals and organic compounds.

In its 1985 report to the International Joint Commission, the Great Lakes Water Quality Board (1985) identified 42 areas of concern that were exhibiting significant environmental degradation and severe impairment of beneficial uses. Among these areas of concern are areas known as the Great Lakes "Upper Connecting Channels" --St. Mary's River, St. Clair River, and Detroit River. Furthermore, these three systems are among 38 of the 42 areas of concern where it is felt that in-place pollutants (ie. pollutants previously deposited in bottom sediments via external inputs followed by water column processes) are contributing to the degraded conditions.

Before agencies can establish rational control programs for toxic substances, it is necessary to identify the relative importance of in-place contamination for each of the systems of concern. Because not all systems behave identically with respect to in-place contamination, a research effort is necessary to develop a general methodology that can address questions relative to exposure and biological effects of in-place pollutants. Some integrated exposure/effects studies on in-place pollutants in the Great Lakes have already been conducted (eg. Monroe Harbor, Michigan study). However, it is probable that the connecting channels will behave differently from harbors, embayments, and estuaries relative to the resuspension and release of in-place toxic substances and subsequent biological effects. Therefore, as part of the overall Great Lakes Upper Connecting Channels Study, research on the relative significance and biological impact of in-place metals and toxic organics in the Trenton Channel of the Detroit River has been initiated.

The Trenton Channel in-place pollutants study is being conducted by the USEPA Large Lakes Research Station, located in Grosse Ile, MI, with the participation of several cooperative research institutions, including Clarkson University, Indiana

University, Manhattan College, Michigan State University, Ohio State University, Roswell Park Memorial Institute, University of California - Santa Barbara, University of Michigan, Raytheon - Grosse Ile, Michigan DNR, U.S. Fish and Wildlife Service, U.S. Army Corps of Engineers - Detroit District, and Computer Science Corporation. The overall problem being addressed by this group can best be stated in the form of a hypothesis:

Through a series of fate and transport processes, including sorption by viable and non-viable suspended solids followed by settling from the water column, toxic substances entering a water body may tend to concentrate in the bottom sediments of the system. Once bottom sediments are contaminated (termed in-place pollution), depending on their characteristics and contaminant levels, they represent a potential source of toxicity and other biological effects. These effects can manifest themselves as direct effects on benthic organisms and bottom feeders or indirectly, through resuspension of this sediment particulate matter, as acute or chronic effects on water column organisms. The spatial and temporal distribution of particulate matter caused by resuspension can be predicted from measurable hydrologic factors and sediment properties. The actual exposure level and subsequent biological uptake and toxicity during a resuspension event depend on the phase/speciation changes in the contaminant of interest that take place and how these changes affect the contaminant bioavailability. The rate at which and extent to which the phase/speciation altering interfacial processes occur are significant in predicting exposure and effects. The rate and extent of these processes can be predicted from measurable water chemistry and bottom sediment properties.

The objectives of the Clarkson research described in this interim report were developed to contribute to the testing of the above hypothesis and to the development of a methodology for evaluating the severity of above in-place pollutant scenario on a site-specific basis. The Clarkson contribution to the overall project is intended to provide the essential chemical process link between the physical investigations of sediment dynamics and the biological investigations of sediment toxicity and effects.

OBJECTIVES

The overall objective of the Trenton Channel in-place pollutant research project is to provide insight into the impact of in-place pollutants in the Upper Connecting Channels and to develop and field test an exposure/effects model for selected substances at a specific site. In order to achieve this overall objective within the framework of testing the above hypothesis, it is essential that a component of the integrated project deals

with the physico-chemical interfacial processes of in-place and resuspended sediments. Specifically, the sediment exposure potential and relevant particle-contaminant interactions are being investigated by undertaking the following specific research objectives:

1. Collect surface sediment samples from specified stations within the study area and characterize them by measurement of specific physical and chemical properties that may affect contaminant exposure/effects.
2. Perform kinetic studies of both adsorption and desorption of selected metals under controlled field and laboratory conditions. Use experimental variables for the kinetic studies that will permit an adequate process description and parameterization of the process.
3. Using the results of the above experimental work, develop a submodel for the prediction of contaminant release during sediment resuspension. This submodel would be available as an integral component of the planned overall exposure/effects model.

SCOPE OF WORK

This interim report represents the research performed during approximately the first half of this project. In an effort to accomplish the above objectives the research was planned in five phases or work plan elements:

1. physical and chemical characterization of surface sediments in the study area
2. field experiments of metals/sediment resuspension
3. laboratory experiments of metals/sediment resuspension
4. laboratory studies of metals adsorption and desorption
5. development of a kinetic model for metals aqueous/solid phase exchange during a resuspension event.

The first two element of the project have been completed and are reported in their entirety. These phases represent the more site-specific, observational aspects of the project. They were intended to give us a good characterization of the system and the extent of the problem and to aid in focusing the efforts in the last three work elements. These latter three phases of the project represent an effort to obtain a more fundamental understanding of the mechanisms responsible for the field observations.

The first work element of the project involved the collection and analysis of surface sediments at all study sampling locations for the following parameters: total and pore water metals (Cd, Co, Cr, Cu, Ni, Zn); cation exchange capacity; total organic carbon (TOC); total inorganic carbon (TIC); specific gravity; moisture content; loss-on-ignition (LOI); and

particle size distribution. The field resuspension experiments involved cooperation with the research team from the University of California - Santa Barbara in the application of a field sediment entrainment reactor to measure resuspension of sediments from intact cores along with the resultant solid and dissolved phase metals entering the overlying water during the resuspension. In all 24 field resuspension experiments were conducted during two field trips to the study area. The third phase of the project was intended to confirm the field resuspension observations under more controlled laboratory conditions under which a relatively steady-state resuspended solids concentration could be maintained for a longer period of time than in the field. A laboratory resuspension reactor was constructed for this phase; its design and some preliminary experimental results are presented in this report.

Phase four of the project involves equilibrium and kinetic batch metal sorption studies using well characterized experimental sediments from the master and control stations of the Trenton Channel study area (stations 30, 34, 53, 82, and 83). This phase is ongoing and only preliminary data are presented in this report. In addition to sediment type plans for this phase include investigation of the following experimental variables: pH, metals and solids levels, and particle shear. Some preliminary equilibrium results are presented in this report. Finally, the model is being developed in conjunction with the experimental studies. At this point we have a possible framework, which is presented in this report; however, the approach may change (probably in the direction of simplification) as more empirical results become available.

SECTION 2

CONCLUSIONS

1. The bottom sediment characterization survey, which was intended to aid in the evaluation of sediment exposure potential for the system, revealed a wide range of bottom sediment quality through the Trenton Channel study area. With respect to heavy metal contamination, some "hot spots" with especially high metals levels were observed in the vicinity of the mouth of Monguagon Creek (sites 30CR and the master station 30), in the vicinity of sites 104 and the master station 34, and at site 107. The most striking relationship among the sediment characteristics analyzed at the survey sites was the significant positive correlation between the total metal levels in the surface sediments and the organic carbon content.
2. The field resuspension shaker experiments provided some very interesting observations on sediment-water metals interactions during a resuspension event. Among them were: resuspended total metal concentrations correlated with bottom shear stress and resuspended solids; all dissolved metal levels in the overlying water during a resuspension event were inversely correlated with pH; all dissolved metal levels in the overlying water during a resuspension event tended to increase with time as long as pH was less than 7.5; and dissolved Cd, Co, Cu, and Ni decreased as the bottom shear stress increased, probably in response to higher resuspended solids.
3. Laboratory resuspension and metals partitioning experiments, although preliminary at the time of this report, have qualitatively, but not necessarily quantitatively, confirmed the field observations. In addition to water chemistry, these experiments have demonstrated the significance of sediment type (ie. properties) in governing metals adsorption and desorption. These experiments show great promise for developing an understanding of the mechanisms involved in this process, an understanding that is necessary to predict the exposure/effects profile resulting from a resuspension event.

SECTION 3

RECOMMENDATIONS

At this point in our studies we have identified two general areas of research that must be pursued further in order to understand the problem of biotic exposure assessment from sediment-bound contaminants. They are briefly described below:

1. A knowledge of the fluxes of contaminants from sediments is absolutely necessary in any mass balance study of contaminants in aquatic systems, since it is potentially a major exposure route. In order to determine the spatial and temporal exposure of water column biota to an in-place contaminant, there are several physical and chemical processes that must be understood at a mechanistic level. Otherwise, generalization from site-specific observations will not be possible. These processes include: the resuspension and subsequent deposition of the particulate matter; the particle-particle interactions of resuspended sediments (i.e. aggregation-disaggregation); and the interfacial processes which determine the phase/speciation of a contaminant either in-place or in-suspension. Furthermore, there are several potentially significant interactions between these physical and chemical processes. For example, it is well known that chemical properties, such as pH and ionic content, can affect particle aggregation. We must strive to understand the kinetics of these processes on the basis of fundamental, measureable properties of a sediment-water system, because the characteristic times of these processes are on the same order as the time scale of resuspension events. This understanding can then lead to the development of combined physico-chemical mathematical model of sediment transport and contaminant transport/transformation during a resuspension event. Essential components of this model would be (a) the settling velocity distributions; (b) the rates of aggregation and disaggregation; (c) the rates of resuspension and deposition and the associated particle size distributions; and (d) the rates and extent of sorption/desorption reactions in the resuspension medium.
2. The second research area is one that must be better understood for the refinement of toxics food chain models. The problem is one of predicting the spatial and temporal distribution of contaminants between the two main fractions of suspended particulates in most aquatic systems: biotic and abiotic. The abiotic particulate matter is primarily allochthonous in origin, low in organic carbon and has a relatively high density, while the biotic solids are primarily autochthonous primary producers, contain significantly higher organic carbon and have a much lower density. Experimental studies at

Clarkson have demonstrated that the extent of partitioning of hydrophobic organic compounds to particulate matter depends a great deal on the type of solid sorbent in the system (DePinto, et al., 1986; McCann, 1986). These studies showed that the primary characteristic of the solid type in governing partitioning was the organic content of the solid. For example, hexachlorobenzene exhibited partition coefficients about an order of magnitude higher in suspensions of Cyclotella (~35% carbon) than in suspensions of river bottom sediments (1-5% carbon). Furthermore, in bioavailability experiments algae maintained in contact with sediment-bound hexachlorobiphenyl demonstrated a significant uptake from the sediment phase. This exchange of material, which has major implications relative to toxic organic chemicals transport, bioaccumulation, and toxicity is attributed to the preferential sorption of nonpolar organics to higher organic carbon particulate matter. In addition to differences in partitioning, the two solid types also have very different vertical transport characteristics because of, among other things, their density differences (Bonner, 1983); these differences will, of course, impact the accuracy of contaminant mass balance calculations. Therefore, more studies are needed in the following areas: the kinetics of contaminant uptake and release from particulate matter as a function of the solid phase properties, the rate and extent to which sediment-bound contaminants become bioavailable to various trophic levels, and the field measurement of the distribution of a contaminant between biotic and abiotic particulate matter for purpose of model calibration and field testing.

SECTION 4

METHODS

SEDIMENT SAMPLE AND EXPERIMENT LOCATIONS

A general description of the Trenton Channel study area is not presented in this report as it would be redundant to the overall project description. This section does indicate the location of all sediment sampling sites for the Clarkson contribution to the overall project, including stations for the sediment characterization survey as well as for the field and laboratory experimental aspects of the Clarkson study.

The stations included in the Trenton Channel study are shown in Figure 1. The indicated station numbers are consistent with those used by the other project participants. As indicated in the scope of work our study was divided into four study elements: sediment characterization, field resuspension experiments, laboratory resuspension experiments, and laboratory metal adsorption/desorption experiments. The bottom sediment stations used in these study elements are listed in Table 1.

EXPERIMENTAL APPROACH

Sediment Characterization

Sample Collection and Storage--

Clarkson personnel, in conjunction with the Environmental Protection Agency's Large Lake Research Station (LLRS) at Grosse Ile, Michigan collected sediment and sediment pore water samples for physical and chemical characterization during the week of May 12 -16, 1986. Samples of sediments and pore water were collected from 26 stations in the study area. Replicate (to check for variability) and large volume samples were also taken at the master and reference stations.

A stainless steel ponar dredge was used for sampling sediments. Ponar grabs attempted at stations 49A, 54A, 52A, and 38 were unsuccessful in obtaining sediment material. All sediment samples were homogenized in a large pan and a representative sample taken for analyses. The sediment samples were stored in new acid washed 125 ml Nalgene Polymethylpentene wide mouth jars. The interstitial water samples were collected using a Nalgene vacuum filtering apparatus and 0.45 um cellulose acetate membrane filters. Interstitial water samples were stored in acid washed 30 ml Nalgene Polyethylene bottles. All water samples were immediately preserved by the addition of one to two drops of Baker Instra-analyzed nitric acid to a pH <2. Attempts were made to filter the sediment immediately after sampling but this proved to be too difficult on the small boat used to collect the samples. It was decided that filtering would be done as soon as possible aboard the large EPA research vessel present during

SEDIMENT SAMPLING SITES: PHYSICO-CHEMICAL CHARACTERIZATION

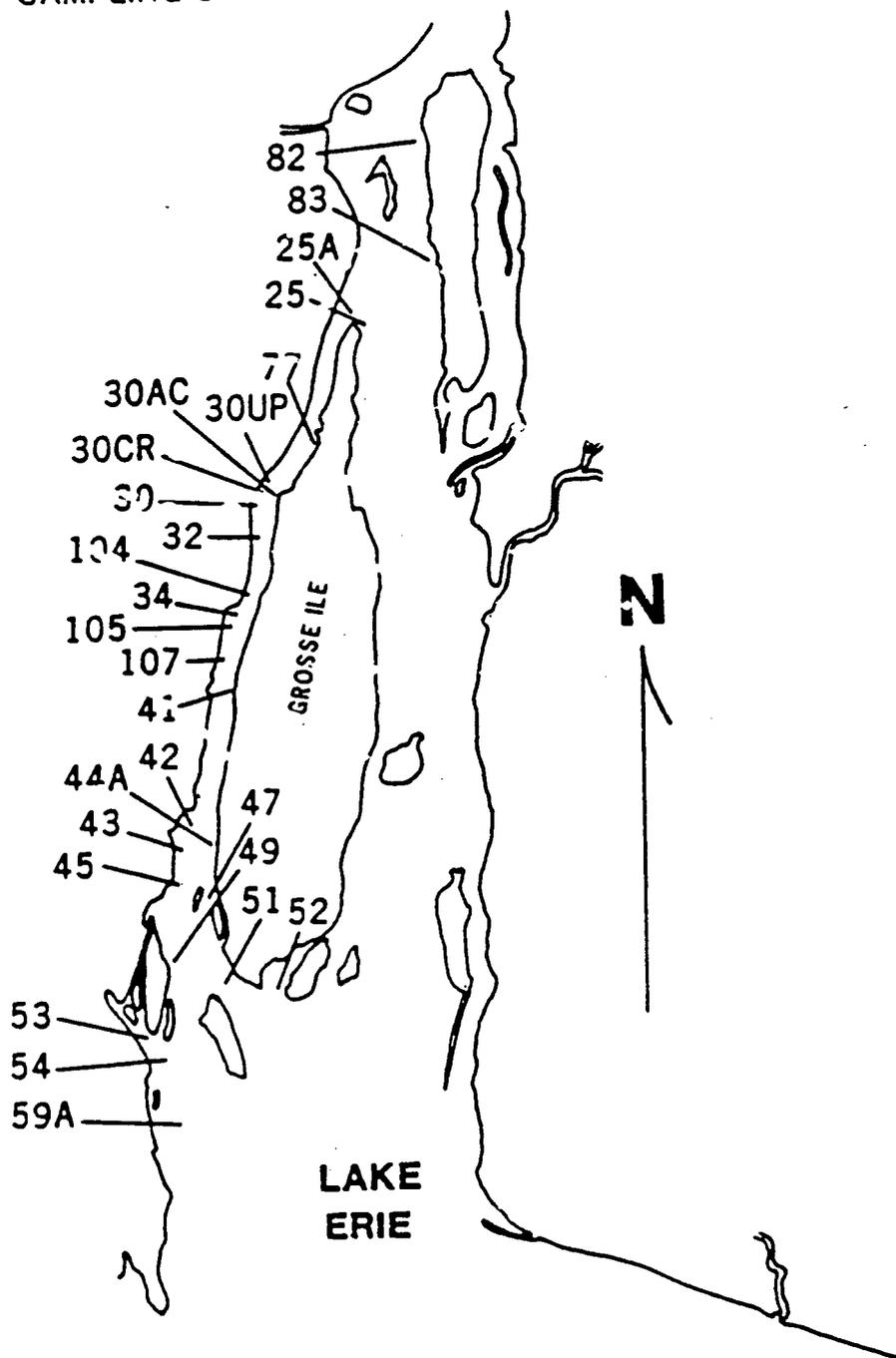


Figure 1. Map of Trenton Channel study showing location of sediment sampling stations

Table 1. Listing of Detroit River (Trenton Channel) Sampling Stations (North to South) and Purposes of Sample Collection.

Station	Study Element			
	Sediment Characterization	Field Resuspension Experiments	Lab Resuspension Experiments	Lab Partitioning Experiments
82 (control)	*	*	*	*
83 (control)	*	*	*	*
25A	*			
25	*			
77	*			
30 WP	*			
30 AC	*			
30 CR	*			
30 (master)	*	*	*	*
32	*			
104	*			
34 (master)	*	*	*	*
105	*			
107	*			
41	*			
42	*			
44A	*			
43	*			
45	*			
47	*			
49	*			
51	*			
52	*			
53 (master)	*	*	*	*
54	*			
59A	*			

sampling or at the LLRS laboratory. All samples collected were to be stored and transported in a cooler with ice to maintain a temperature close to 4° C.

Upon receiving the sediment samples at the Clarkson laboratory they were homogenized by shaking and stirring with a teflon stir rod, (which was cleaned and rinsed between mixing of samples). A portion of the sample, approximately 30 ml, was transferred to an acid washed polyethylene bottle for immediate determination of sediment moisture content, loss on ignition, and particle size distribution. The remainder of the sediment was placed in an enclosed hood to air dry. After air drying the sediments were pulverized with a mortar and pestal. The air dried sediment was used to determine specific gravity, total organic carbon, total inorganic carbon, total heavy metals, and cation exchange capacity.

Physical Characterization--

Sediment physical characteristics that were determined included sediment moisture content, loss on ignition (LOI), specific gravity and particle size distribution (PSD). A description of the methods and procedures used for each of the analysis is included in the general analytical methods section.

Chemical Characterization--

Sediment chemical characteristics included in the survey were total organic carbon (TOC), total inorganic carbon (TIC), total and interstitial sediment heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn), and cation exchange capacity (CEC). A description of the methods and procedures used for each of the analysis is included in the general analytical methods section.

Field Sediment/Metals Resuspension Experiments

Introduction--

Field sediment/metals resuspension experiments were performed in conjunction with the University of California - Santa Barbara and LLRS. There were two field trip dates for this purpose, May 12-16, 1986 and September 2-5, 1986. The experiments were carried out on the EPA Bluewater research vessel using a portable entrainment reactor designed and constructed by personnel from UCSB. The experiments were performed using sediment from the project master stations, 53, 30, 34 and the reference station, 83.

Reactor Design--

The portable entrainment reactor constructed by UCSB consists of a cylindrical plastic chamber, inside of which a horizontal grid plate oscillates vertically (Figure 2). The cylinder is 27.9 cm high and has an outside diameter of 12.7 cm and an inside diameter of 11.7 cm. A sampling port is located at 12.7 cm from the bottom. The oscillating grid plate is made of

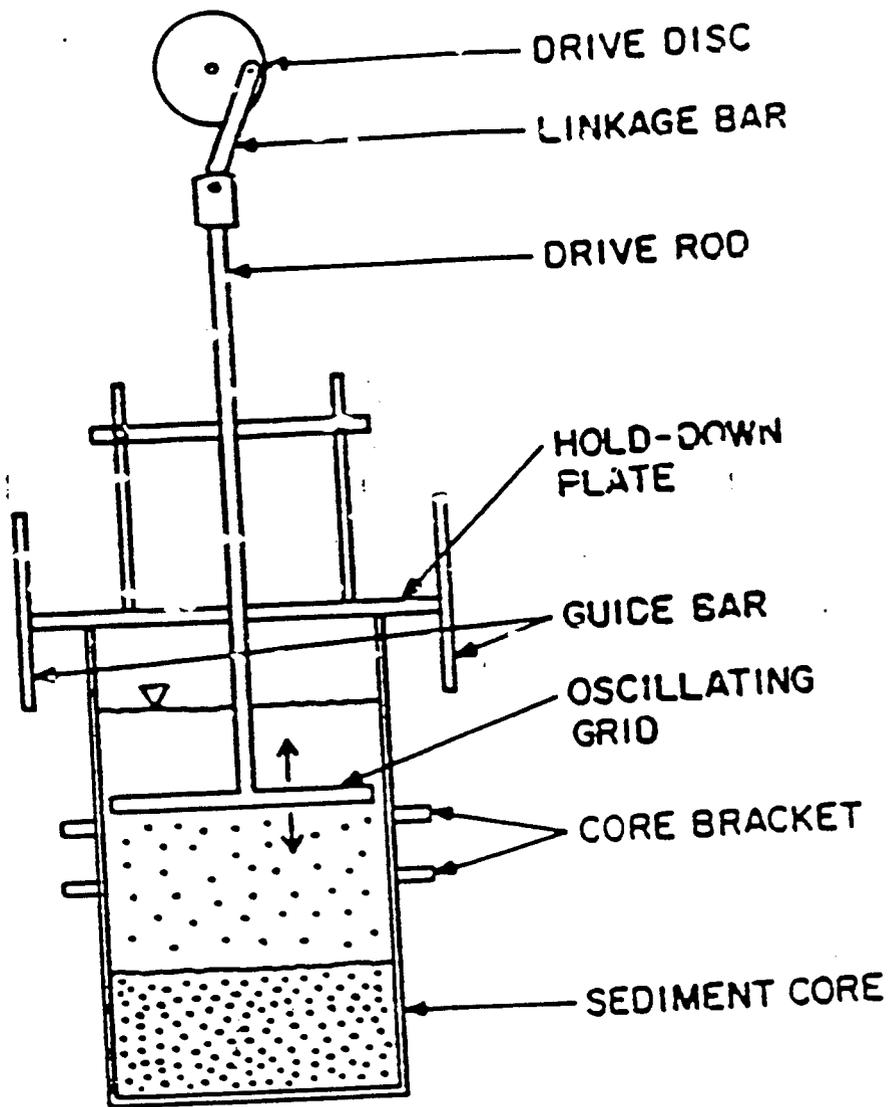


Figure 2. Schematic of field shaker resuspension apparatus

an 11 cm diameter plexiglass plate 0.6 cm thick. The grid has 1.2 cm diameter holes drilled 1.5 cm from center to center. The grid is oscillated by a 1/8 horsepower motor controlled by a solid state rheostat. The grid's vertical displacement when oscillating is 2.54 cm. The cylindrical core is held in place during a run by a scissors jack and a hold down plate. More detail of the reactor design can be found in Lick (1985).

Sediment is located at the bottom of the reactor with water overlying it. The grid oscillates in the water creating turbulence which resuspends the sediment. The amount of sediment resuspended is dependent on the applied shear stress which is related to the frequency of the grid oscillation (Tsai and Lick, 1985). A calibrated laboratory flume (Fukuda and Lick, 1980) was used to determine the equivalent shear stresses produced by the oscillating grid. The calibration is based on the idea that, given the same environmental conditions, the entrainment reactor and the laboratory flume will maintain equivalent amounts of resuspended sediment for a given shear stress (Tsai and Lick, 1985).

Experimental approach--

Sediment cores, two to four from each station, were taken from the river bed using the cylinder core of the entrainment reactor and a fitted base and cap. The cores were collected in a fashion that produced the least possible disturbance to the sediment and overlying water. The intact cores, collected in this manner, were then brought aboard the research vessel and placed in the entrainment reactor apparatus.

The parameters of interest during an experimental run were the frequency of oscillation; time of sampling; suspended solids; pH; and total and dissolved resuspended as well as total and interstitial bottom sediment heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn). Two grid frequencies of oscillation were used, 0.08 sec/stroke and 0.14 sec/stroke. Samples of the overlying water were taken from the reactor over time from a sampling port located 12.7 cm from the bottom of the reactor. After sampling, an equivalent volume of river water was added to the reactor to maintain a constant water column depth. At each sampling time a volume of approximately 50 ml of overlying water was drawn off the reactor and split into two aliquots. One portion was used to determine pH, suspended solids and total heavy metals. The pH was measured immediately upon sampling using a Fisher Accumet Mini pH meter (Model 640 with a glass combination electrode). The other portion was filtered immediately through an acid rinsed 0.45 μ m cellulose membrane filter for analysis of dissolved metals. A sample of the sediment layer at the bottom of the reactor was taken after an experimental run was completed for analyses of total sediment metals and interstitial metals. This sediment sample was homogenized, and an aliquot was filtered immediately for analysis of interstitial metals. After measurement of the pH and filtering was completed all the aqueous samples were acidified to a pH <2 with Baker Instra-analyzed

nitric acid. All samples were stored in a cooler with ice to maintain a temperature of approximately 4° C. Analyses of the suspended solids, total heavy metals, dissolved heavy metals, interstitial heavy metals and sediment heavy metals were performed upon return to Clarkson University. The methods used are included in the general analytical methods section.

Laboratory Sediment/Metals Resuspension Experiments

Introduction--

In order to illustrate the mechanisms operating in the field resuspension experiments under more controlled conditions and to obtain data for parameterizing a model of metal adsorption/desorption kinetics during sediment resuspension, we decided to supplement the field experiments with similar laboratory experiments. The laboratory sediment/metals resuspension experiments have several potential advantages over the field studies. First, the lab experiments can be conducted over a longer period of time, permitting observation of potential long-term metals uptake or release. Second, the lab experiments can be more carefully controlled, particularly in terms of water chemistry and are more easily replicated. This gives the potential of a more deterministic analysis of the results. In any event we strived to run the laboratory experiments under conditions as close as possible to those existing during the field shaker experiments, i.e. shear stress, sediment type, depth of overlying water, and with overlying water with similar water chemistry as in the Detroit River. Presented below is a description of the apparatus and experimental design for this ongoing phase of the study.

Reactor Design--

To determine physical and chemical reactions and interactions during resuspension of sediments in the laboratory, a sediment entrainment reactor was constructed. The reactor is designed after a laboratory annular flume as described by Fukuda and Lick (1980), but approximately 1/5 the size. A schematic of the reactor is presented in Figure 3.

The reactor consists of two plexiglass cylinders, a 15.24 cm (6 in.) O.D. cylinder placed inside a 29.21 cm (11.5 in.) I.D. cylinder. The reactor channel is 6.98 cm (2.75 in.) wide and 14.6 cm (5.75 in.) in diameter, (measured from the center of the reactor to the outside edge of the channel). A plexiglass ring approximately the same width as the channel is supported by several rods connected to a drive shaft in such a manner that it rotates on the water surface. The ring is supported so that its depth in the reactor can be varied. A Tekmar 1/8 hp, variable speed motor with digital readout is used to drive the ring. Sampling ports are located at 6, 9, and 11.5 cm from the bottom of the reactor. The cut off tip of a 5 ml wide bore glass pipet is secured in the sampling port located 9 cm from the bottom of the reactor. This port can be used for sampling of the overlying water. The end of the pipet tip is located at approximately one-half the channel width, allowing a representative sample of

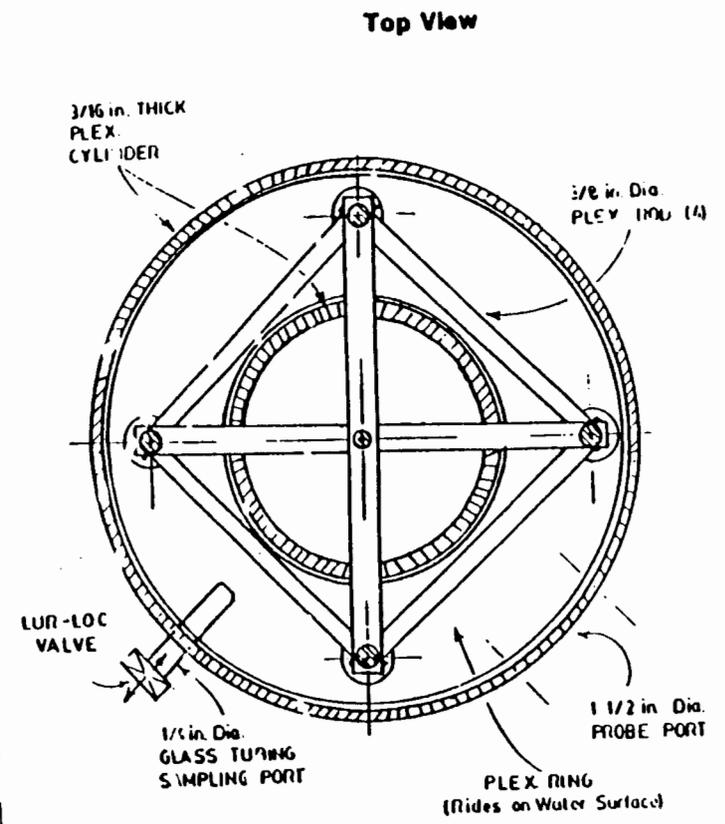
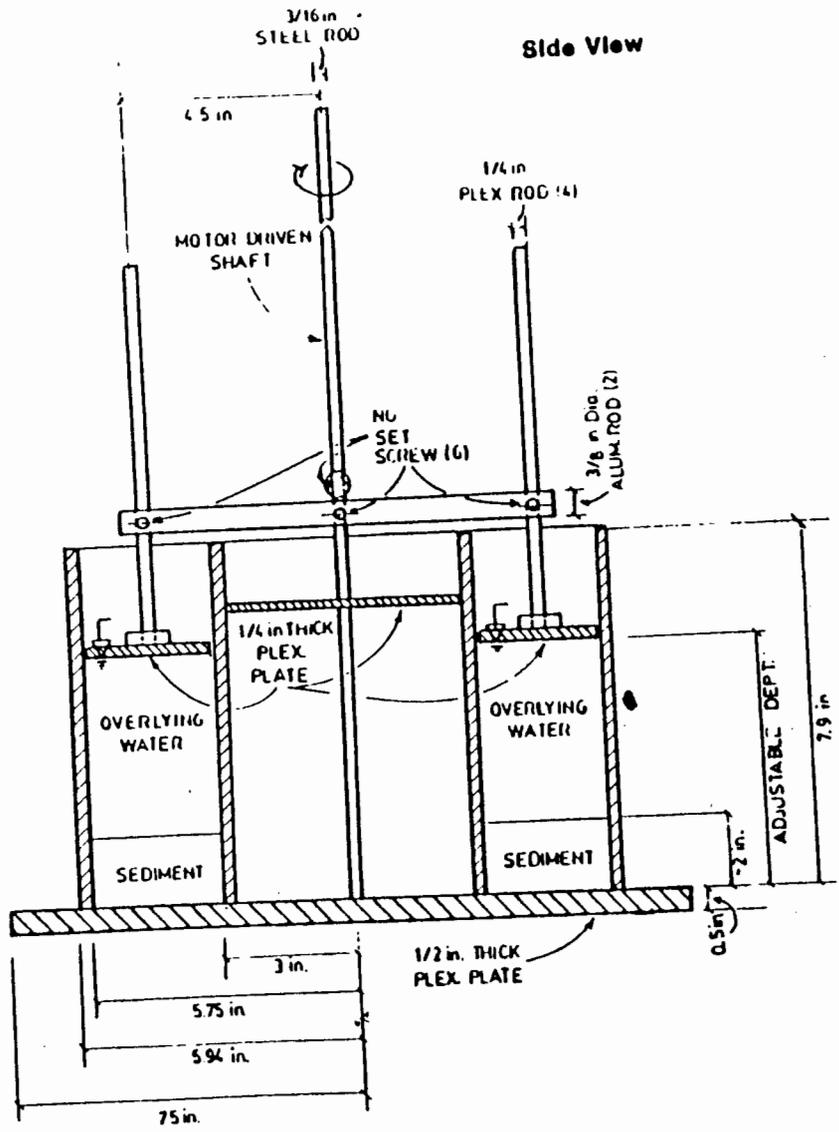


Figure 3. Schematic of laboratory resuspension reactor

the average overlying water in the reactor channel to be taken for analysis. A 1.5 inch diameter port is located at 13 cm from the bottom of the reactor, 90° upstream from the sampling ports. This port can be used for placement of a velocity meter or a pH probe. The pH electrode or velocity meter is held in place by a rubber stopper through which a hole has been bored. Finally, an automatic refill apparatus is used to maintain a constant depth of the overlying water.

Sediment is placed in the bottom of the reactor and then filled with the overlying water to a predetermined depth. By applying a rotational force to the ring, shear stress will be transmitted through the overlying water to the sediment bed causing resuspension of the sediment. The subsequent bottom shear will be calculated from the azimuthal velocity or by correlation of the amount of resuspended solids with that found in the UCSB calibrated annular flume.

Experimental Design--

The resuspension of bottom sediments and the subsequent metal-sediment interactions that can take place are dependent on several parameters. Those that appear to be most significant include shear stress; physical and chemical characteristics of bottom sediments, sediment compaction; and overlying water chemistry, including total metal content pH and ionic strength. The laboratory resuspension reactor is currently being operated in a manner that permits the investigation of these parameters in a systematic way. Consequently, the experimental variables for these experiments are the rotational velocity of the ring and the subsequent bottom shear stress, pH, metals content of the system, and the sediment type. During any given experiment the overlying water in the reactor is monitored for suspended solids, total and dissolved metals (Cd, Cr, Pb), and pH as a function of time. A sample of the bottom sediment in the reactor is collected prior to each experiment and analyzed for moisture content, total and pore water metals. Some preliminary experiments have been conducted, but not yet evaluated, with this reactor; the results of these experiments are presented in the next section.

Metals Adsorption/Desorption Experiments

Introduction--

The kinetics and equilibrium tendencies of metals-Trenton Channel sediment interactions are being studied independent of the physical aspects of bottom sediment entrainment and deposition. In this phase of the experimentation we are using batch systems with very carefully controlled chemical conditions. We are also using carefully prepared experimental sediment samples from each of the master and reference stations in the study; in this way we can be sure to have reproducible sediment characteristics among experiments performed using sediments from a given station. Presented below is a description of the methods used for the experiments conducted to date in this phase of the study. As with the laboratory resuspension

experiments this phase of the study is still in its early stages. To date two types of experiments have been conducted in this phase of the study: classical metal adsorption isotherms and pH stat experiments aimed at observing the tendencies of metal-sediment interactions as a function of pH (in essence this second approach is a good method for producing a pH adsorption edge).

Experimental Sediment Preparation--

A lyophilization procedure was used to prepare experimental sediments that could be stored for relatively long time periods without experiencing significant changes in their characteristics. The procedure is as follows. The contents of 2 L bottles of wet sediment samples from stations 30, 34, 53, 82, and 83 were individually added to a 4 liter pail and homogenized by stirring for 20 minutes with a plastic trowel. The samples were then lyophilized in the following manner. Samples were added in small increments to a 600, 900, or 1200 ml Labconco lyophilization flask and the flask was rotated as it was submerged in a liquid nitrogen bath to freeze the samples onto the walls of the flask. This procedure increases the speed of the lyophilization process and prevents flask breakage due to expansion. The samples were lyophilized for 48 to 72 hours. The lyophilized sediments were removed from the flasks with a Teflon coated bar and ground with a mortar and pestle. The samples were next added to 1 liter wide-mouth polyethylene screw top bottles and stored in a constant temperature room at 4° C.

Adsorption Isotherm Experiment--

Adsorption isotherms were conducted by preparing an experimental sediment suspension containing 1.0 ± 0.05 g/L of sediment, 0.1 N NaNO_3 as an ionic strength adjuster, and 0.01 M BES (N,N-bis(2-hydroxyethyl) -2-aminoethanesulfonic acid) ($(\text{HOCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{SO}_3\text{H}$) ($\text{pK}_a = 7.15$ at 20° C) as a pH buffer. Forty ml aliquots of this suspension were dispensed into 50 ml centrifuge tubes and spiked in triplicate with various levels of individual metals (Ni, Cd, and Pb to date). After adjustment to a pH of 7.2, the tubes were agitated for 24 hours. At this time the final pH was measured and the total and "dissolved" (obtained by centrifugation) metal concentrations were determined.

pH Stat Experiments--

The procedure for conducting the pH stat experiments involved maintaining a 200 ml volume of a 1 g/L sediment suspension at different pH levels with microcomputer-controlled microliter additions of HNO_3 or NaOH and sampling the suspension for total and "dissolved" metal concentrations (Cd and Pb) after the equilibration period at each pH. In the initial experiments no metal spikes were made to the suspension; only the behavior of the "native" metals on the experimental sediments was being observed as the system was equilibrated at several pH values from 8.6 down to 5. These experiments are an attempt to confirm the pH-related behavior of the metals noted in the field shaker

experiments (see Section 5).

ANALYTICAL METHODS

Sample Handling Procedures

All sample containers, glassware, apparatus and all materials used to store or transfer samples or reagents used for the analysis of trace metals were prepared in the following manner: washed with soap and hot water, rinsed with tap water three to five times, soaked in 30% v/v nitric acid for a minimum of 30 minutes, rinsed three to five times with deionized/distilled water, then inverted and allowed to drip dry. All acid washed apparatus was stored inverted either in closed cabinets or in sealed plastic containers. When a container was used for storage of samples or reagents the container was rinsed with a portion of the sample or reagent prior to filling.

Filters that were used in the collection of samples for trace metals analyses were prepared in the following manner: placed on the filter apparatus and with vacuum applied, rinsed with distilled water, rinsed with 10% v/v nitric acid and then rinsed with copious amounts of distilled water. The waste was then discarded and the receiving vessel was then rinsed with distilled water.

Deionized/distilled water was used for all dilutions and preparation of all samples and reagents. Aqueous samples that were to be analyzed for trace metals were acidified to a pH < 2 by the addition of ~ 0.2% v/v of concentrated Baker Instra-analyzed nitric acid. All samples collected were stored in a dark constant temperature room at 4° C to minimize evaporation, chemical reactions and biological activity.

Sediment Moisture Content

A representative sample of sediment was placed in a tared crucible and weighed. The sample was dried at 103° C to a constant weight, approximately three hours. The sample is then placed in a dessicator, cooled and weighed again. The sediment moisture content is determined by the following formula:

$$\frac{\text{weight of wet sediment (g)} - \text{weight of dry sediment (g)}}{\text{weight of wet sediment (g)}} \times 100$$

Loss on Ignition (LOI)

The residue from the sediment moisture content procedure is ignited to a constant weight in a muffle furnace at 550° C, approximately one hour. The sample is cooled, placed in a dessicator and then weighed again. The loss on ignition is

determined by the following formula:

$$\frac{\text{weight of wet residue(g)} - \text{weight of ignited residue(g)}}{\text{weight of wet residue(g)}} \times 100$$

Specific Gravity

The specific gravity of the sediment samples was determined by pycnometric methods. A 50 ml pycnometer bottle was filled with degased distilled water and weighed (designated as W_{wb}). A vacuum was applied to the pycnometer bottle to degas the distilled water. The bottle and distilled water were maintained at room temperature throughout the analysis to insure that thermal expansion did not affect the determination. After weighing the bottle filled with water, a portion of the water was poured off to compensate for the volume of soil added. A sediment sample dried at 103°C and weighed (designated as W_s) was then added to the pycnometer bottle. When necessary the cohesive sediment samples were dispersed prior to oven drying by mixing with water into a thin batter. A vacuum was then applied to the pycnometer bottle to remove any dissolved or trapped air bubbles. Degased distilled water was added to top off the pycnometer bottle to the correct volume. The weight of the sample, water and bottle was then determined (designated as W_{wbs}). The specific gravity is determined by the following equation (assuming that the specific gravity of water at room temperature is equal to unity):

$$\frac{W_s}{W_{wb} + W_s - W_{wbs}}$$

Particle Size Distribution (PSD)

Particle size distribution was determined by wet sieving with a vacuum applied. Each sediment sample was prepared in two ways; with and without the addition of a dispersing agent. Approximately 5 to 10 grams of sediment sample was used for each portion. A solution of sodium hexametaphosphate, (40 g/L) was used as the dispersent. The dispersed sediment sample was placed in a beaker then covered with the dispersing agent and allowed to soak for at least 12 hours. This slurry was then further dispersed by placing in a blender and mixing for one minute.

A micro-sieve set with eight interchangeable brass mesh screens was used for the wet sieving. The brass mesh screens had sieve openings of 710, 500, 355, 250, 180, 125, 90, 63. Additional nylon mesh screens with sieve openings of 20, 10, 5, and 1 micron were used. The wet sieving procedure outlined by Black (1965) was followed.

Suspended Solids

Suspended solids were determined by vacuum filtration of a known volume of sample. The volume was chosen to produce at least 2.5 mg but less than 250 mg of retained solids. A 0.45 um cellulose acetate membrane filter dried at 103° C, dessicated and preweighed was used. After filtering, the filter and retained solids were dried to a constant weight at 103° C, then dessicated and weighed. The suspended solids were determined by dividing the weight of the retained solids by the aliquot volume.

Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC)

Both total organic carbon and total inorganic carbon were determined by wet combustion and gravimetric methods. The apparatus and procedure were taken from Black (1965).

Total Sediment Metals

Sediments were digested by the nitric acid digestion procedure outlined in EPA Method 3050 (see Appendix E). A 1 g air-dried and pulverized sediment sample was used. Nitric acid was used for the final reflux. The final digested sample was filtered to remove solids to minimize clogging of the nebulizer.

Total sediment heavy metals were analyzed using a Perkin-Elmer Zeeman/5000 Atomic Absorption Spectrophotometer by flame atomic absorption. The instrument was set up using the recommended conditions as outlined in Perkin-Elmer's manual of flame atomic absorption recommended conditions. At the beginning of each analytical run, the burner head settings were optimized while aspirating a copper standard solution. The Zeeman/5000 was then set up for the particular metal to be analyzed and a standard calibration control was performed using five fresh standards in the expected concentration range. Blanks and standards were prepared with the same matrix and additions of reagents, on a molar or v/v basis, as the samples analyzed. The average of two to three replicate readings was used as the metal concentration of the sediment. The National Bureau of Standards river sediment #1645 was carried through the same process as the samples and used as a quality control check sample. Quality control as outlined at the end of Method 3050 was followed to further insure accurate results.

Dissolved Metals

Total dissolved metals in filtered water column or pore water samples were determined by digesting a 10 ml sample according to EPA Method 3020 nitric acid digestion (outlined in Appendix E).

Furnace atomic absorption was used to analyze the dissolved metal concentrations. The Zeeman/5000 mentioned above is equipped with a Perkin-Elmer AS-40 Auto-Sampler and a HGA-400

Graphite Furnace for use in the furnace mode. Pyrolytically coated graphite tubes with platforms were used in the furnace. The spectrophotometer was set up using the recommended conditions as outlined in the Perkin-Elmer manuals. Optimization of furnace settings was carried out for all the metals prior to analysis.

At the beginning of each day the furnace was cleaned and calibrated and the auto-sampler aligned. Prior to each run a standard calibration control was performed using at least five standards made up fresh that day. Blanks and standards were prepared with the same matrix and additions of reagents, on a molar or v/v basis, as the samples analyzed. During each run recalibration was performed at least every ten samples. A known standard was analyzed during the run to insure calibration control. The graphite tube was replaced as needed, indicated by decreasing absorbance for a known standard.

pH

An Orion Research Digital Ionalyzer, Model 501 and a Sargent Welch ground junction glass combination electrode were used for all pH determinations. The electrode was soaked in 1M KCl solution when not in use. Calibration of the meter and electrode was performed prior to and after pH determinations using certified pH buffer solutions.

Cation Exchange Capacity (CEC)

Sediment cation exchange capacity was determined using the procedure outlined by Polemio and Rhoades (1977). The method is a two step procedure whereby the cation exchange sites are saturated with Na by equilibrating the soil with an ethanol solution of 0.4N NaOAc - 0.1N NaCl titrated to a pH of 8.2, followed by extraction with 0.5N MgNO₃. The total Na and Cl in the extracted solution were determined by flame atomic absorption.

SECTION 5

RESULTS AND INTERPRETATION

BOTTOM SEDIMENT CHARACTERIZATION

The bottom sediment characterization results, tabulated as raw data in Appendix A and summarized in Table 2, are discussed in the following section. The focus of the discussion is identification of patterns of variability, both among sampling sites and among the various quantities measured. This has been done by describing the sediment data from several perspectives: (1) analysis of data variability among sampling sites: ranges, numerical and spacial distributions of sediment quantities, and cluster analysis; and, (2) analysis of data variability among sediment characteristics: bivariate correlation and multivariate factor and cluster analyses. SAS (Version 5, SAS Institute, Inc. Cary, N.C.), implemented on an IBM 4341, was used for the statistical workup of the data.

Comparisons Among Sites

A summary of the sediment characterization results is presented in Table 2. Though not indicated by the results in Table 2, univariate tests indicated the data among sampling sites for most of the sediment variables were log-normality distributed. Exceptions to the log-normal trend were noted for: (1) particle size distribution, as most samples had large weight percents of very small particles; (2) most porewater metals, due to multimodality; (3) total carbon and organic carbon, for which the distributions of log-transformed data tended to be uniform; and (4) a few sediment-porewater partition coefficients (Co, Ni). The results given in Table 2 are not log-transformed data.

To provide one view of differences among sample sites, sediment data are presented in Figures 4-8 for particle size distribution, specific gravity, total organic carbon, and cation exchange capacity. For certain of the sample sites (eg. Site 30), multiple entries have been plotted on some graphs. The multiple entries represent replicate collections from the site and differences between replicates indicate the magnitude of intrasite (plus analytical) variability. This, in turn, may be used as a rough yardstick for judging the significance of differences among sites.

Differences in levels of heavy metals among the study sites may be viewed longitudinally through the study region in Figures 9-12. It should be noted that logarithmic scales have been used for the metal concentration axes on these figures. Some "hot spots" of especially high metal contamination were observed: (1) the vicinity of site 30CR (mouth of Monguagon Creek), including the master site, site 30; the vicinity of site 104 and site 34, the latter also being a master site; and site 107. As shown in Figure 7, sediments from

Table 2.
Summary of Characterization Results.

VARIABLE	N	MEAN	STD DEV	MEDIAN	MINIMUM	MAXIMUM
TCD	34	10.93235	9.47736	8.20000	1.000000	41.0000
TCO	34	15.40882	6.29051	14.35000	4.500000	30.2000
TCR	34	96.35294	74.44538	87.50000	23.000000	389.0000
TCU	34	55.24118	41.71448	40.00000	11.400000	186.1000
TNI	34	56.09412	34.50667	45.60000	19.600000	175.0000
TPB	34	104.88235	102.62930	75.50000	10.000000	448.0000
T?N	34	621.11765	899.50447	372.00000	71.000000	4080.0000
PCD	45	6.79778	6.61975	4.10000	0.800000	27.2000
PCO	45	1.89111	3.39738	0.90000	0.000000	14.2000
PCR	45	1.20889	0.57557	1.10000	0.300000	2.5000
PCU	45	10.22667	12.82892	4.50000	0.700000	58.7000
PNI	45	13.31556	11.99591	8.40000	2.100000	48.1000
PPB	45	5.05333	5.86672	4.80000	1.000000	27.5000
PZN	45	16.09333	8.43778	13.60000	2.600000	42.3000
CEC	29	0.86069	0.39229	0.81500	0.330000	2.0500
TC	34	5.28529	2.95688	4.50000	1.700000	10.7000
TC	34	1.02353	0.51819	0.90000	0.200000	2.5000
SG	29	2.46793	0.15999	2.43000	2.210000	2.7900
I2O	29	38.92690	14.29041	34.86000	10.700000	76.0100
LOI	29	5.94828	3.60730	4.40000	1.300000	13.1000
D/10	28	98.96750	2.38958	99.89500	90.270000	99.9900
D63	28	70.46571	26.09737	78.55500	11.070000	97.4200
D1	28	58.41357	24.49280	66.56500	7.150000	89.3000

Range of Particle Size Distributions

Trenton Channel Sediment Samples

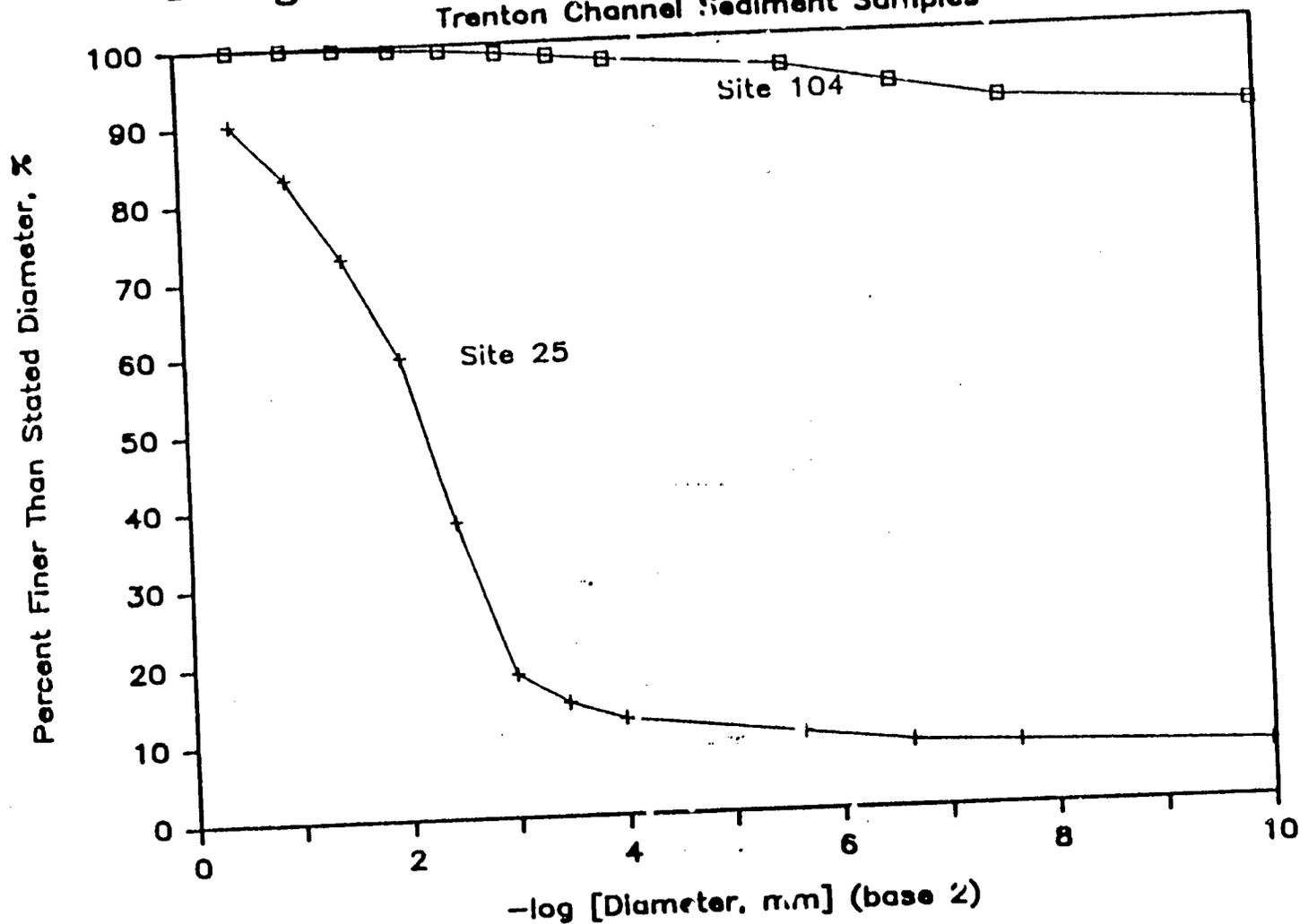


Figure 4. Particle size distribution curves for surface sediments from stations 25 and 104

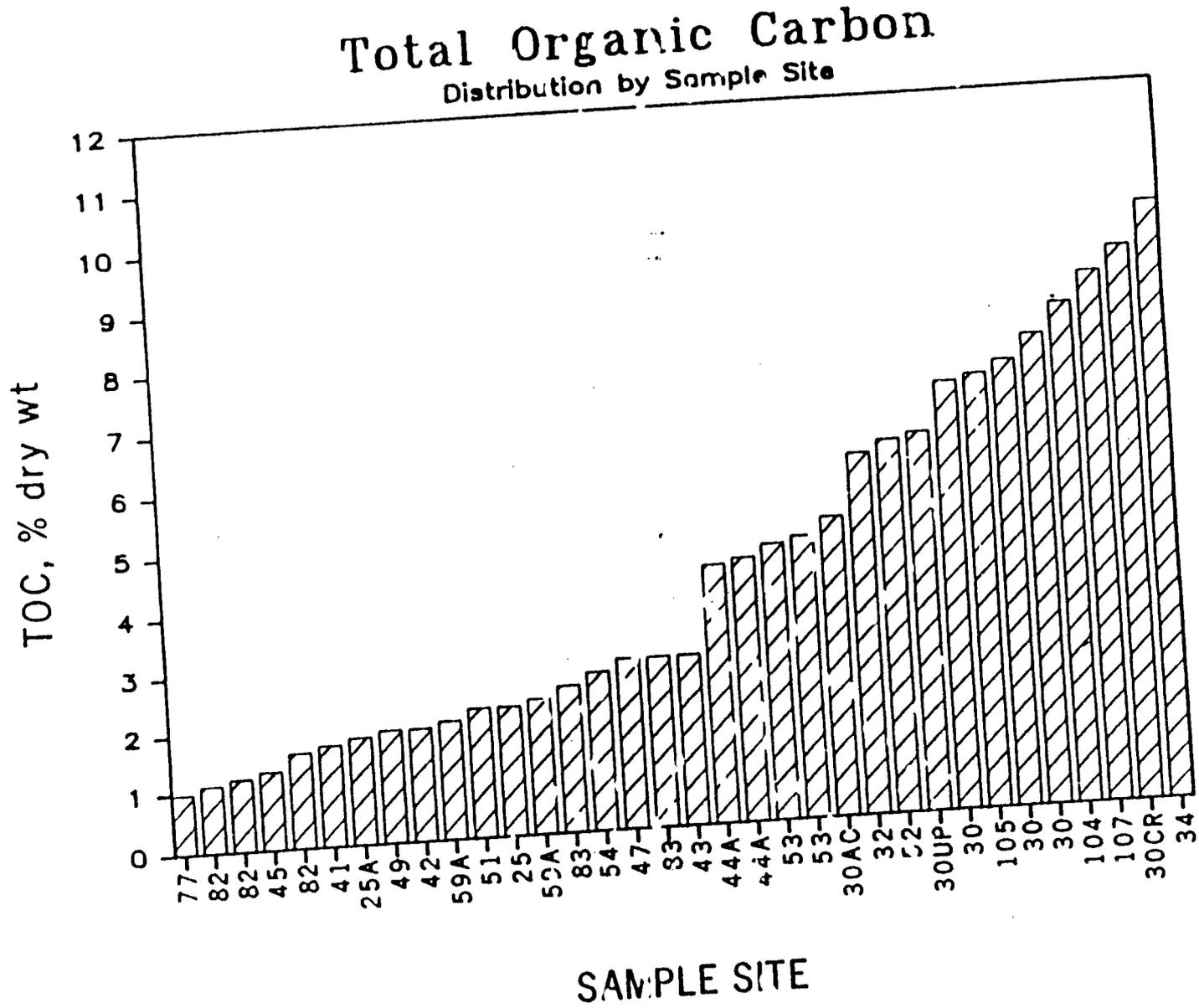


Figure 7. Distribution of sediment total organic carbon by site

Cation Exchange Capacity

Distribution by Sample Site

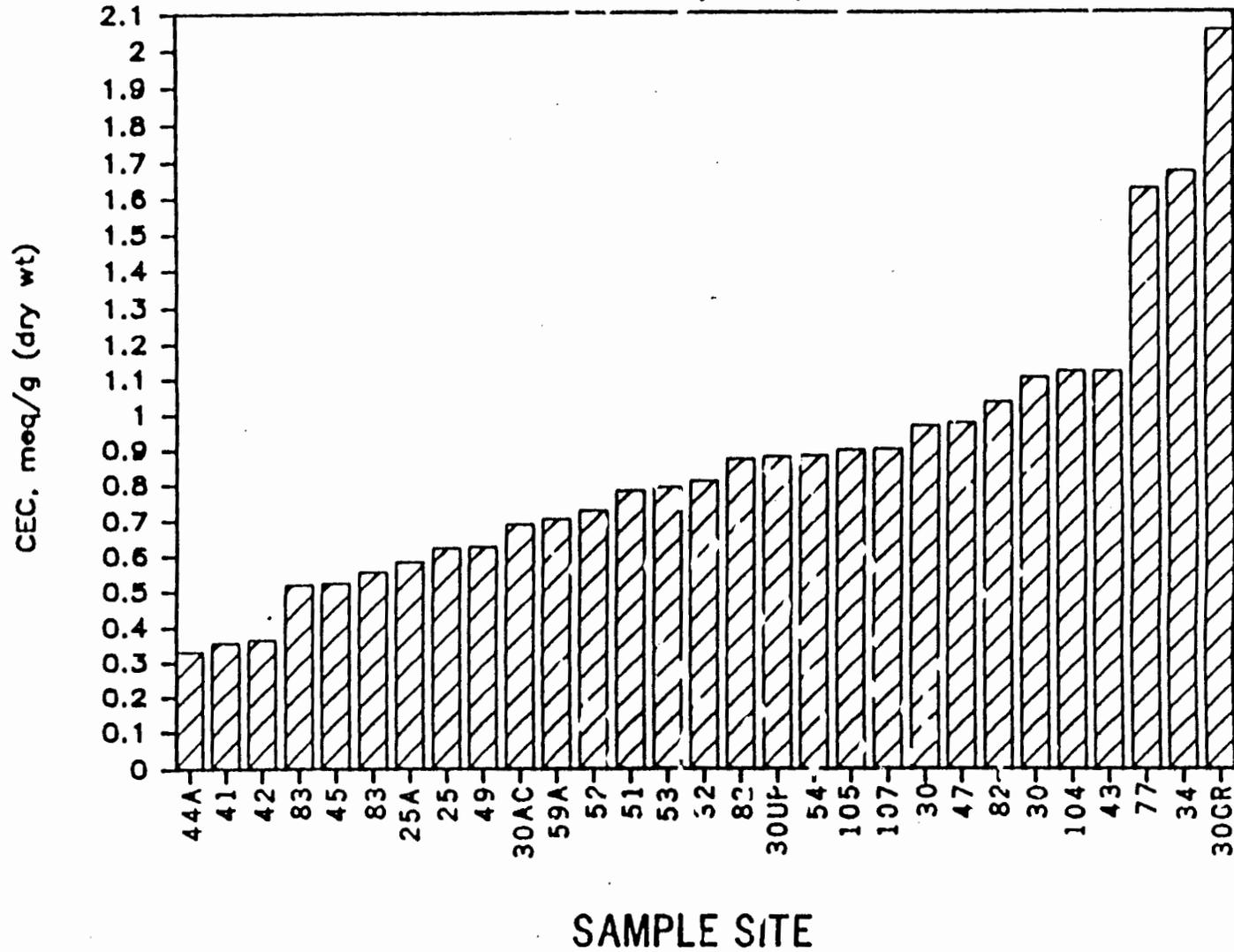


Figure 8. Distribution of cation exchange capacity in survey sediments by site

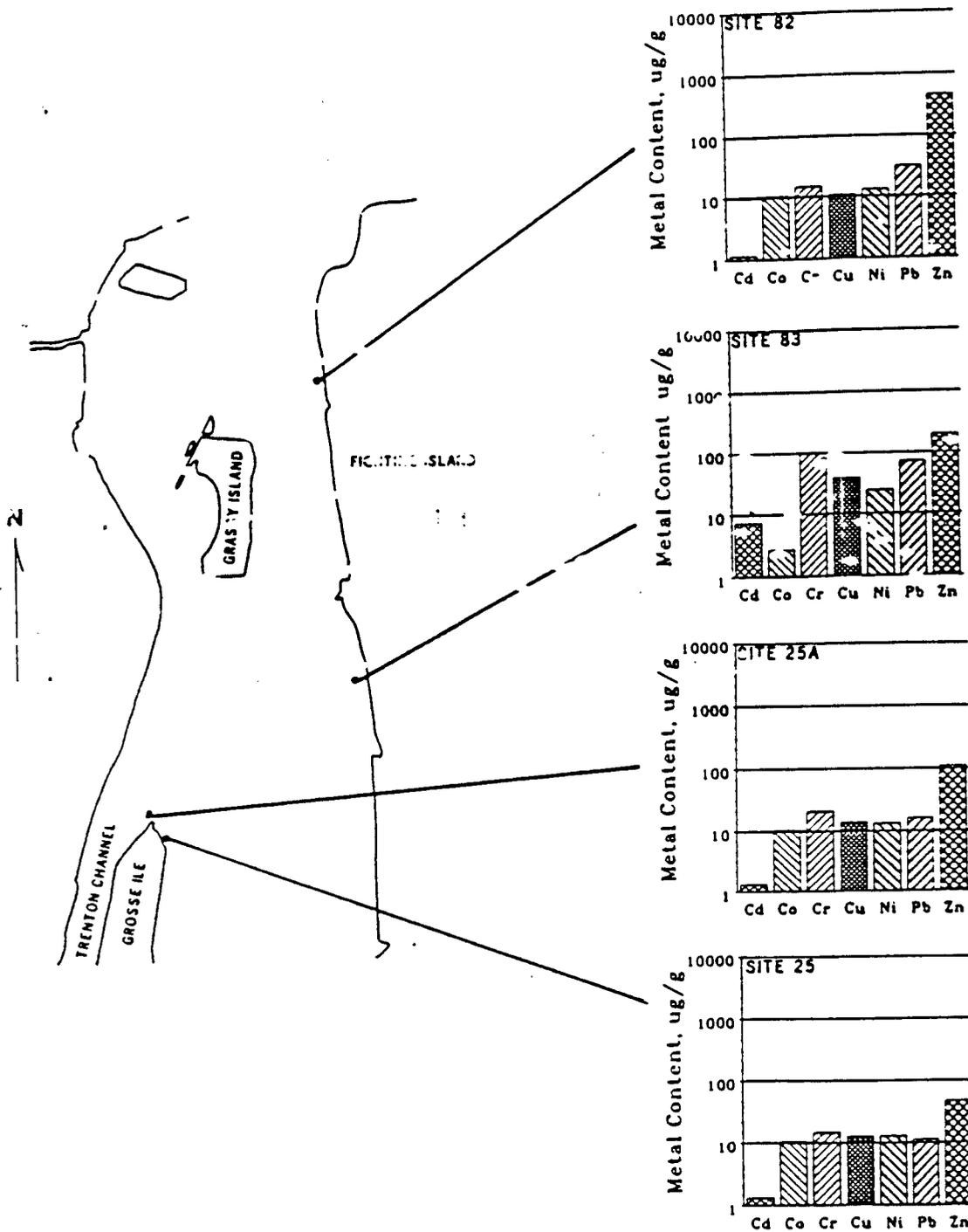


Figure 9. Heavy metal concentrations in surface sediments of selected Trenton Channel stations

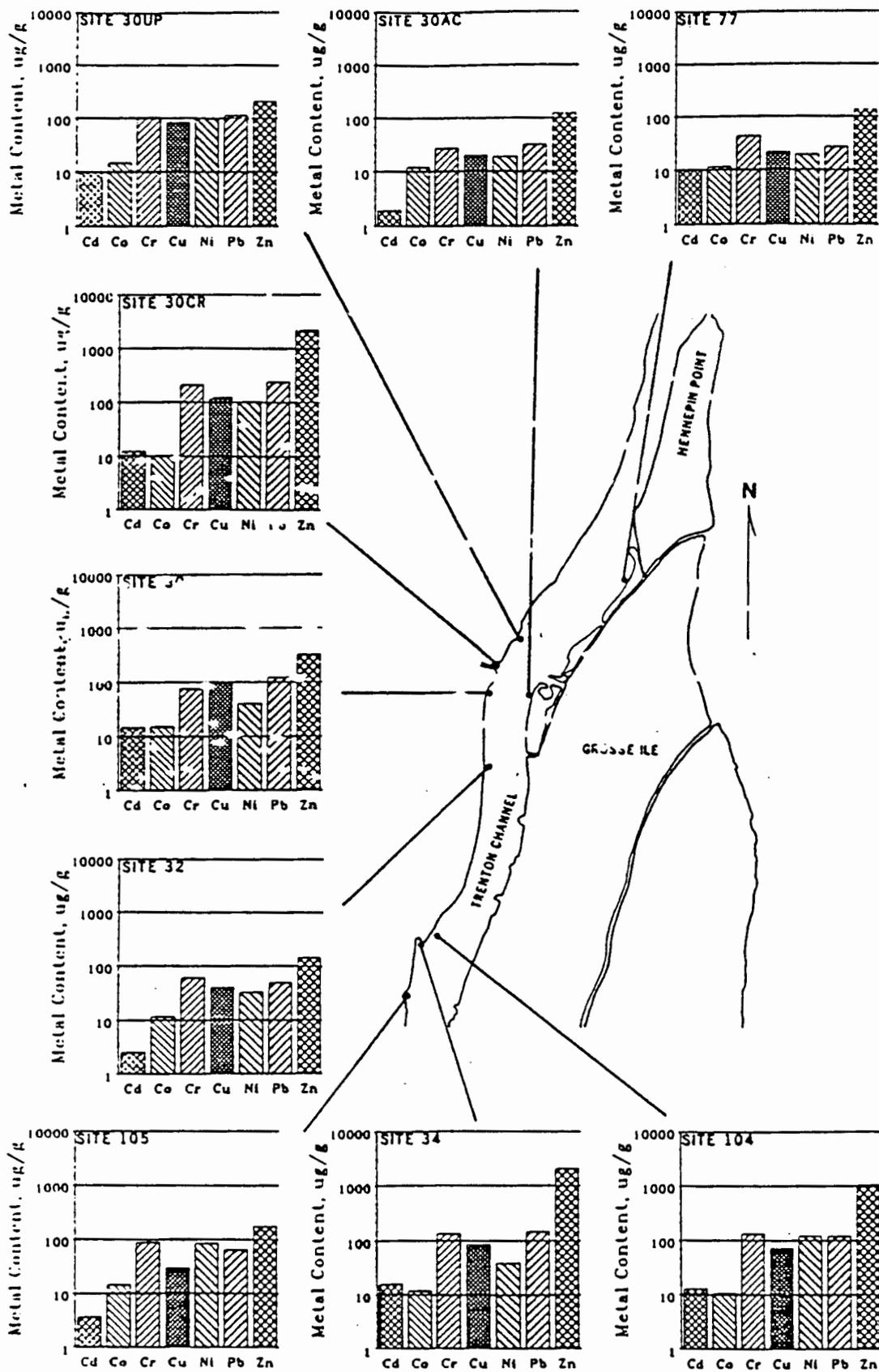


Figure 10. Heavy metal concentrations in surface sediments of selected Trenton Channel stations

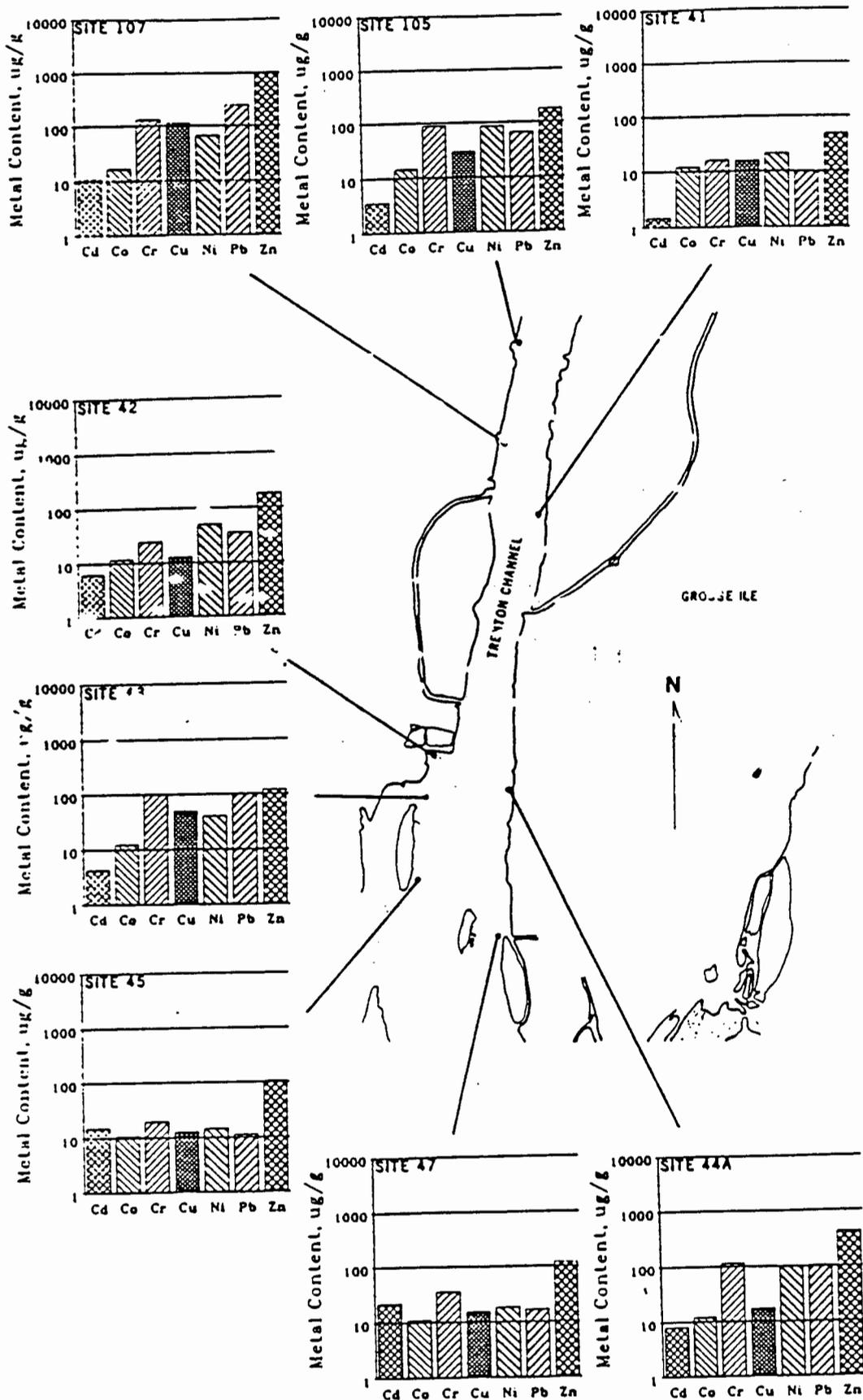


Figure 11. Heavy metal concentrations in surface sediments of selected Trenton Channel stations

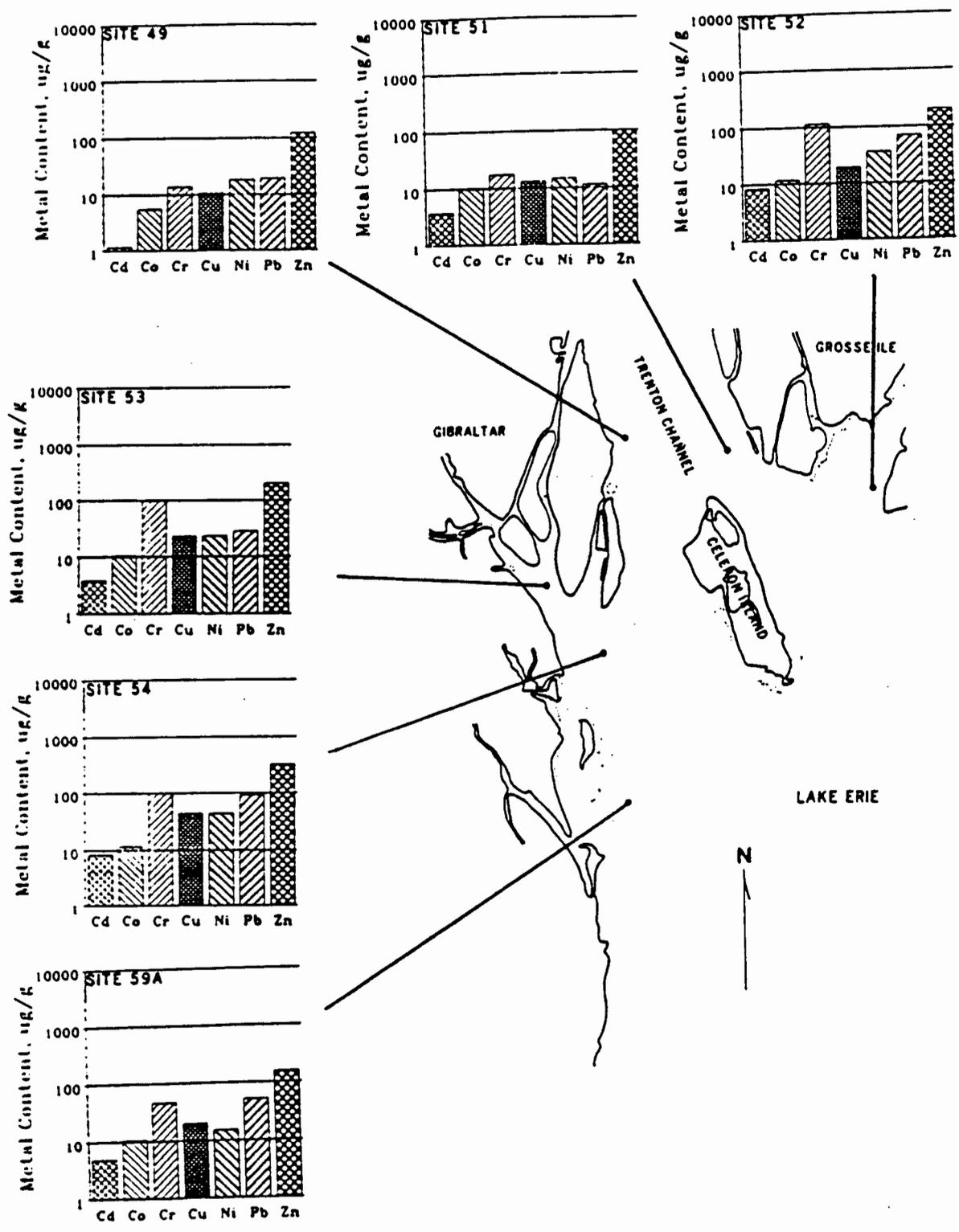


Figure 12. Heavy metal concentrations in surface sediments of selected Trenton Channel stations

these sites also contained the highest levels of total organic carbon.

A hierarchical cluster analysis was performed to summarize similarities and differences among sampling sites and, in effect, sort the sites by "relatedness" with respect to the measured characteristics. To eliminate redundancy, composite sediment variables such as partition coefficients, which combined total and porewater metal concentrations, and total organic carbon, which combined total and inorganic carbon, were dropped from the data set prior to clustering. The results of the cluster analysis is shown as a dendrogram in Figure 13. The distribution of sites represents a multivariate ranking that corresponds, approximately, to the degree of sediment contamination by heavy metals and correlated quantities, such as organic matter, moisture, and others as described in the next section. It may be observed that the master sites (sites 30, 34, and 53) and reference sites (sites 82 and 83) were among the more contaminated of the sampled sites.

Relationships Among Sediment Characteristics

An all-pairwise analysis of rank correlation (Kendall's tau-b) among the measured and derived sediment variables is tabulated in Appendix B. Presented in Figures 14-20 are illustrations of the relationships between several of the sediment variables in the characterization data set.

Generally, cation exchange capacity did not correlate well with total sediment metal content. For example, the computed correlation between Total Zn and cation exchange capacity was significant from a statistical viewpoint ($p < 0.05$) but the correlation was largely spurious as may be seen from the data in Figure 14.

The distribution of sediment metals between porewater and sediment solids did not yield a consistent relationship among samples from the different sampling sites. An example of the observations on sediment-water partitioning is shown in Figures 15 and 16; the correlation between porewater and total metal levels was virtually nonexistent. While care in sampling was exercised to avoid dilution of porewater with river water, some dilution may have occurred to obscure existing relationships. Nonetheless, it should be pointed out that analysis of resuspension and other processes involving solid-solution partitioning of metals and sediments should be predicated on knowledge of the sediment character in the immediate vicinity of interest.

Sediment metal levels generally correlated well among all metals (Figure 17); however, total sediment levels of Co and Zn provided a notable exception to this rule (Figure 18). All metals correlated significantly and positively with total organic carbon (Figure 19), a condition that may account for the high

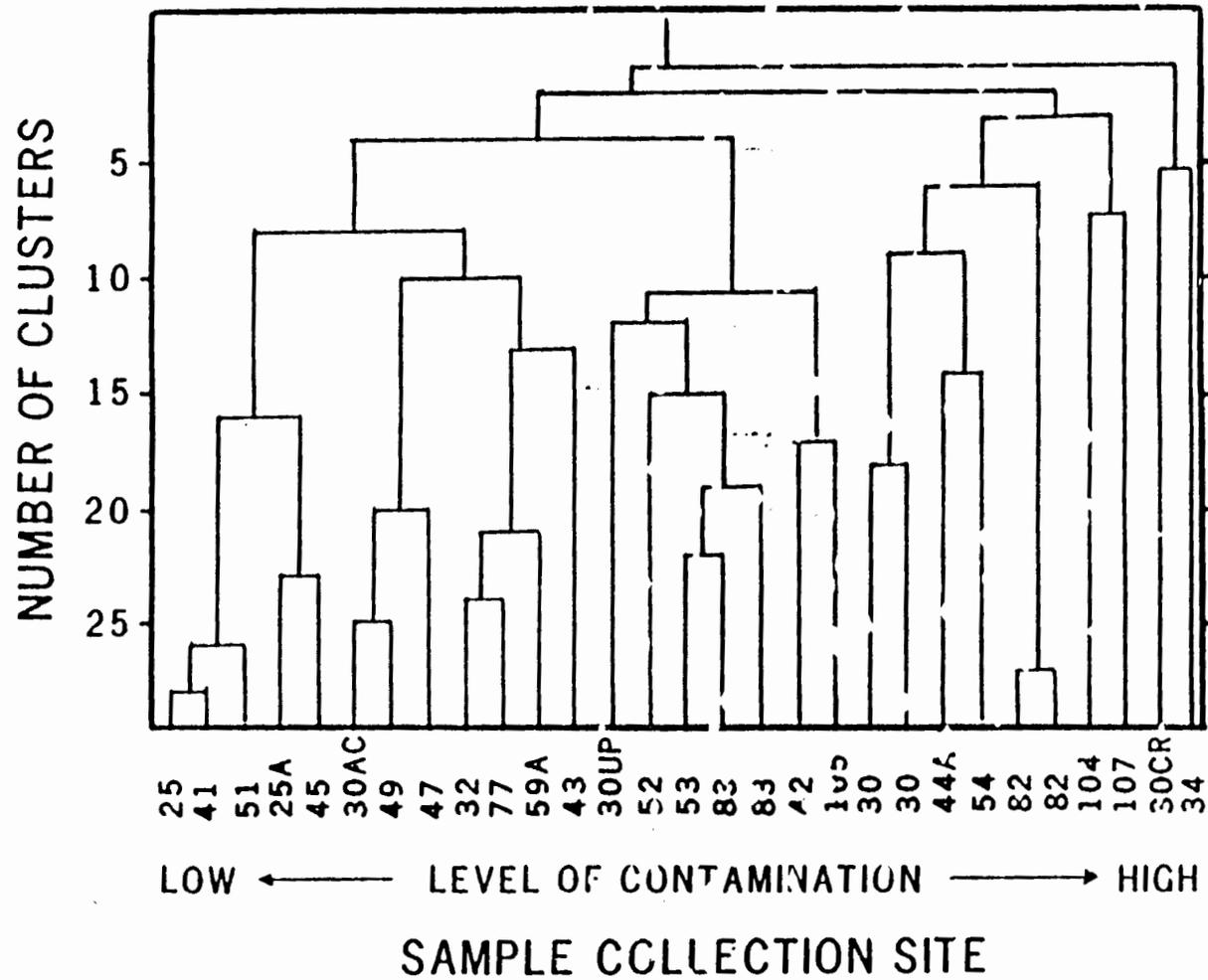


Figure 13. Dendrogram of similarities among sediment samples from Trenton Channel, as determined by Ward's minimum variance cluster analysis

Dependence of Sediment Metal Content On Cation Exchange Capacity

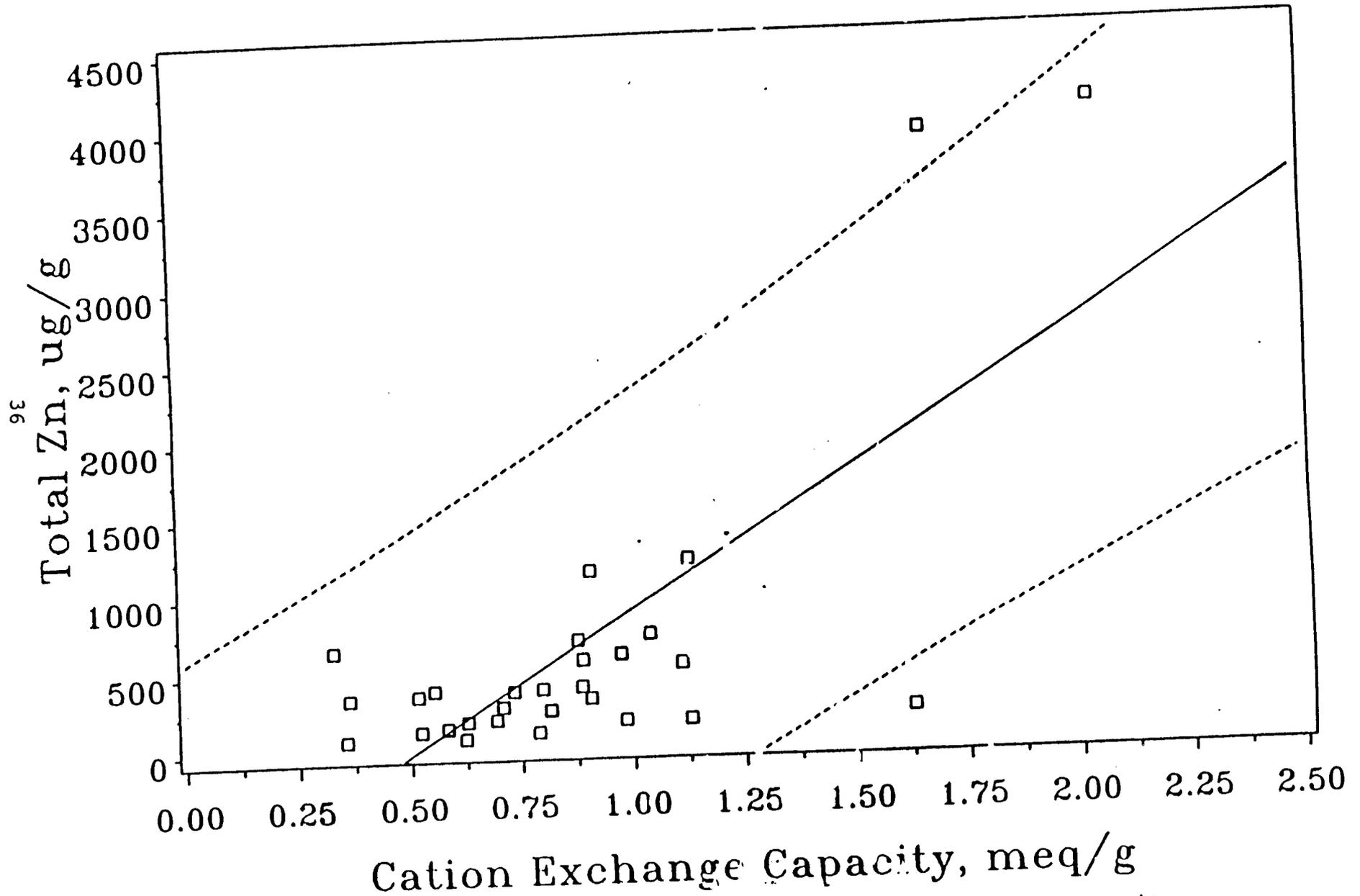


Figure 14. Dependence of total sediment Zn on cation exchange capacity

Porewater Metal Dependence On Total Metal Level in Sediment: Co

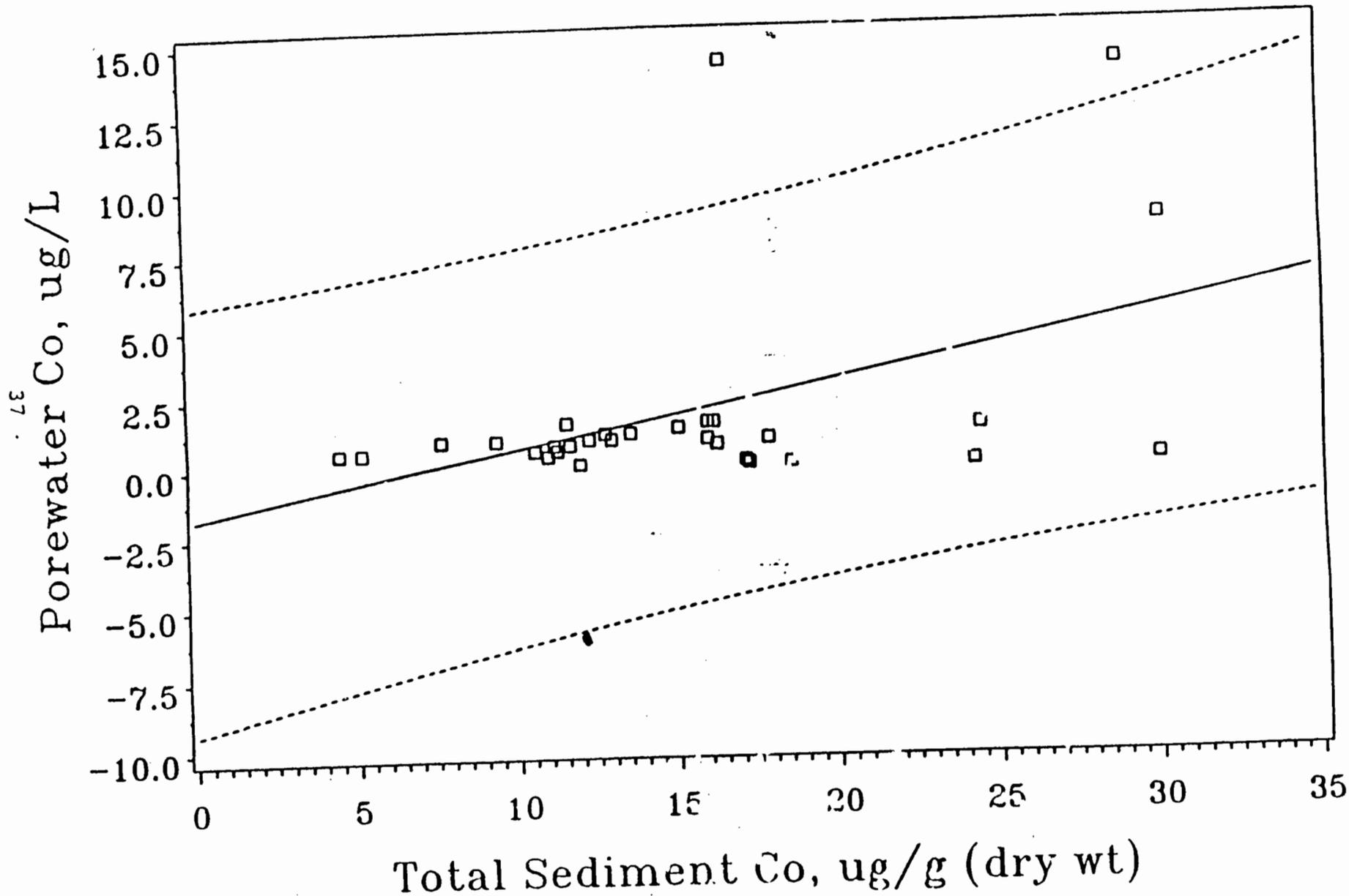


Figure 15. Dependence of porewater Co on total sediment Co

Porewater Metal Dependence On Total Metal Level in Sediment: Pb

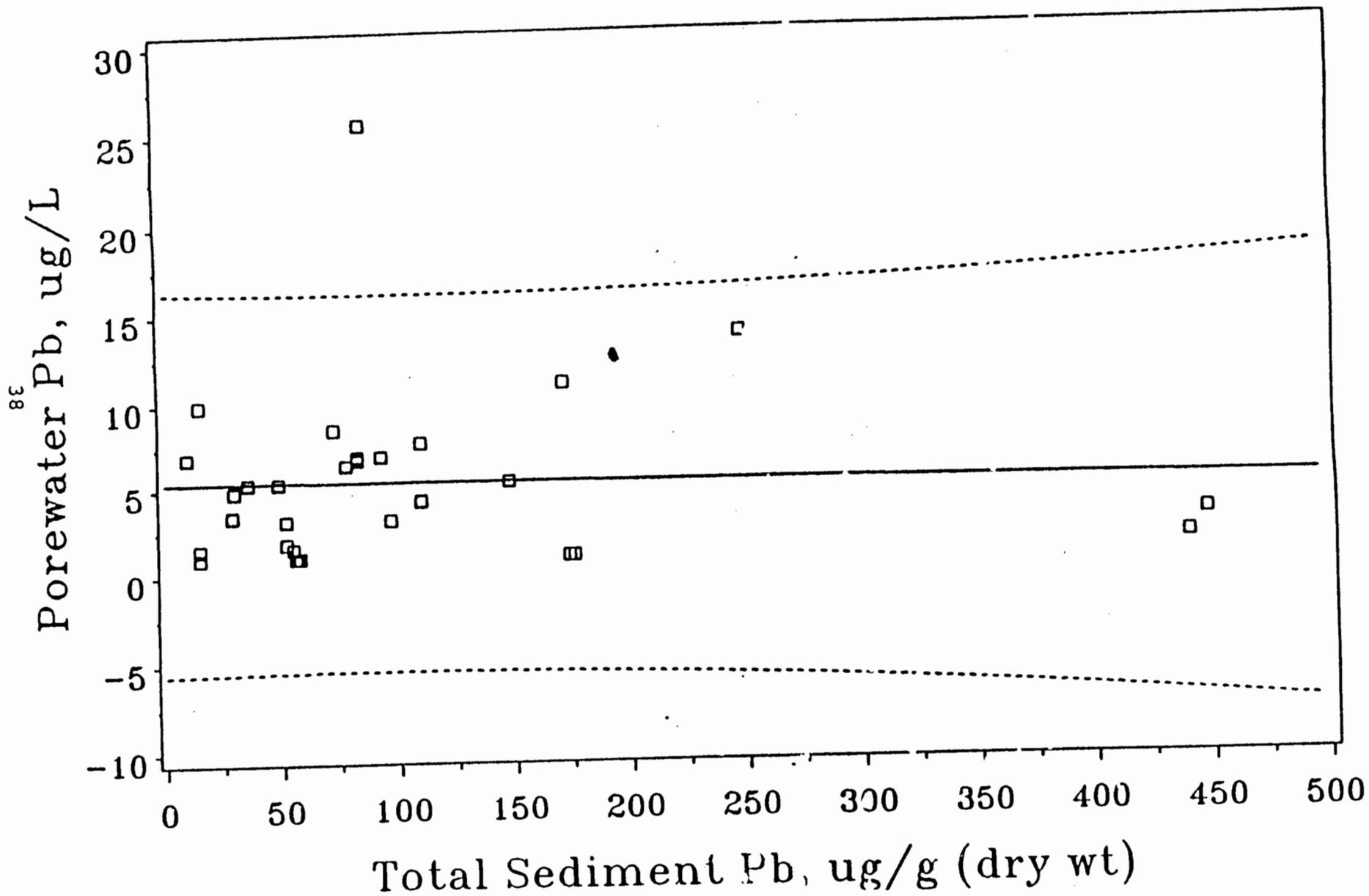


Figure 16. Dependence of porewater Pb on total sediment Pb

Interdependence of Sediment Metal Content Total Cu and Total Pb

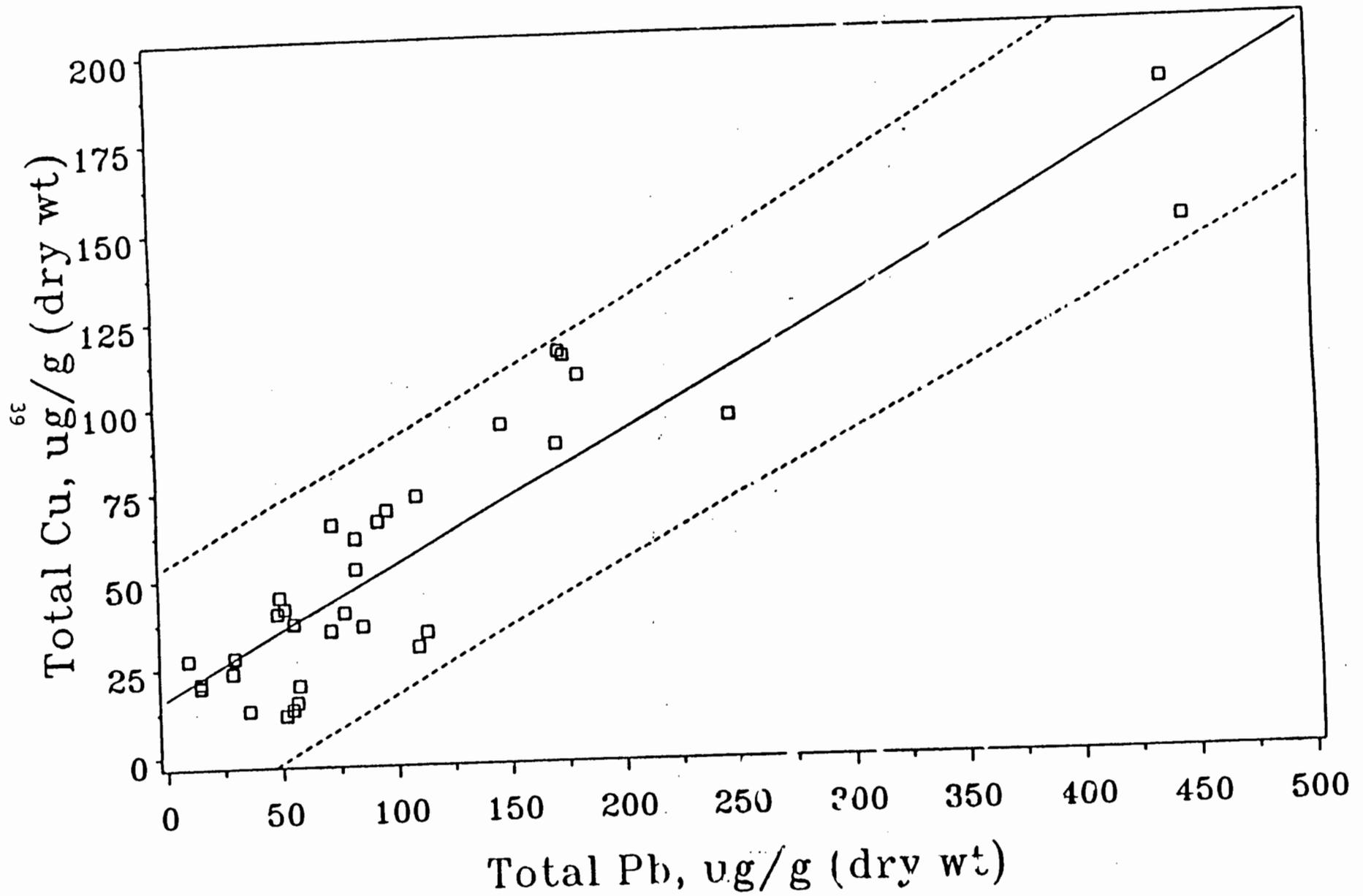


Figure 17. Interdependence of total sediment Cu and Pb

Interdependence of Sediment Metal Content Total Co and Total Zn

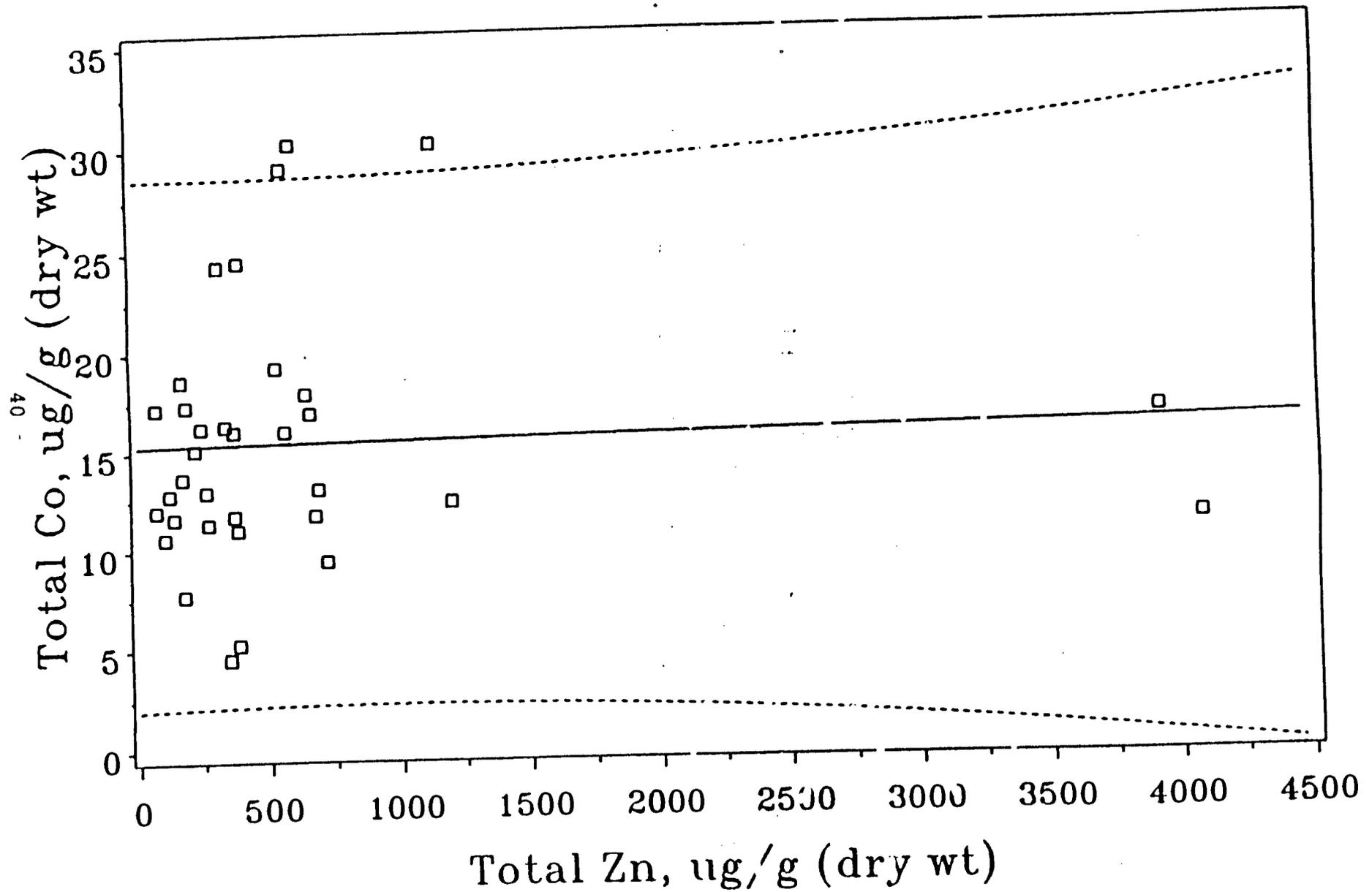


Figure 18. Interdependence of total sediment Co and Zn

Dependence of Sediment Metal Content On Total Organic Carbon Content

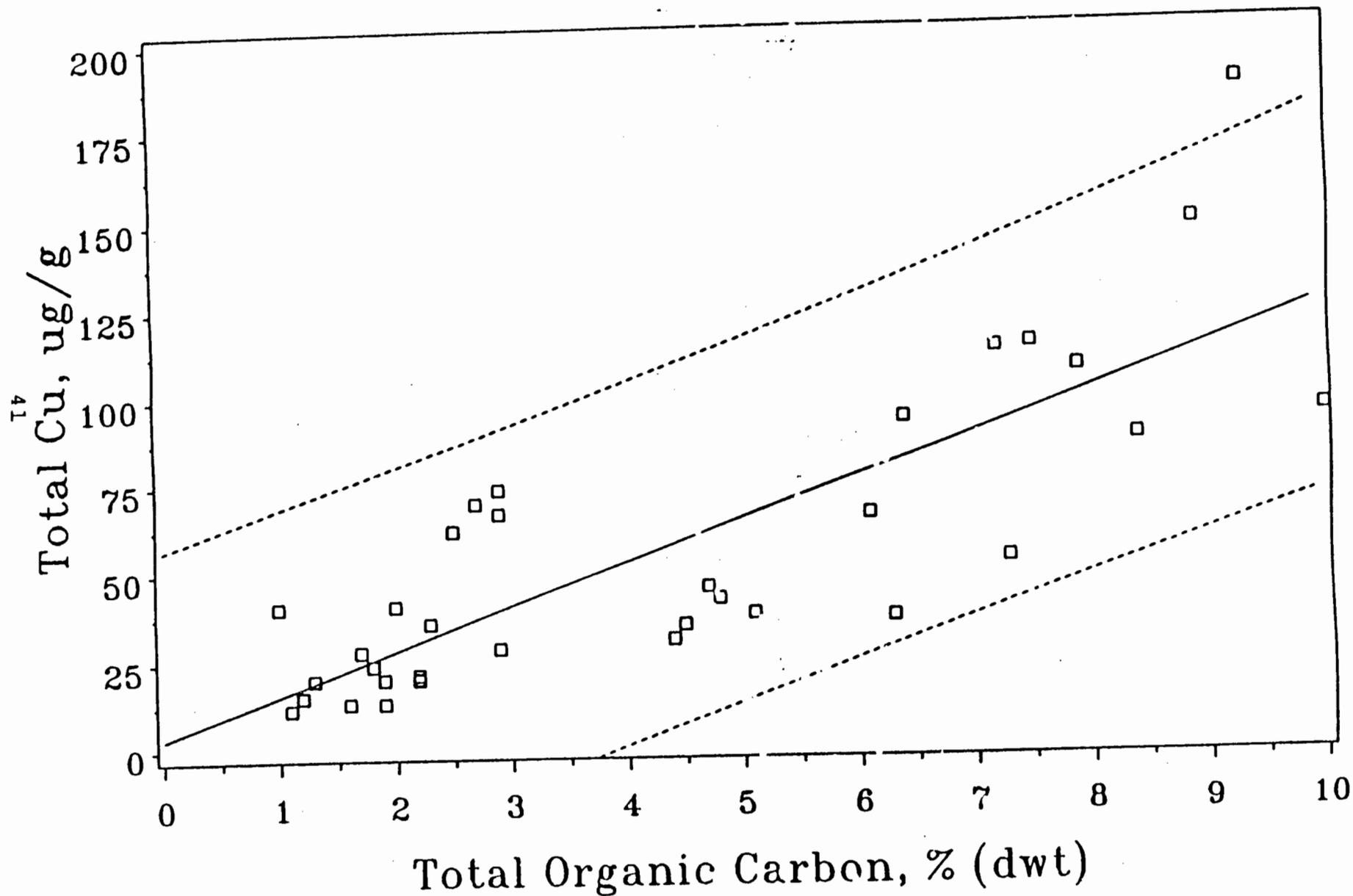


Figure 19. Dependence of total sediment Cu on total organic carbon content

Dependence of Loss on Ignition On Total Organic Carbon Content

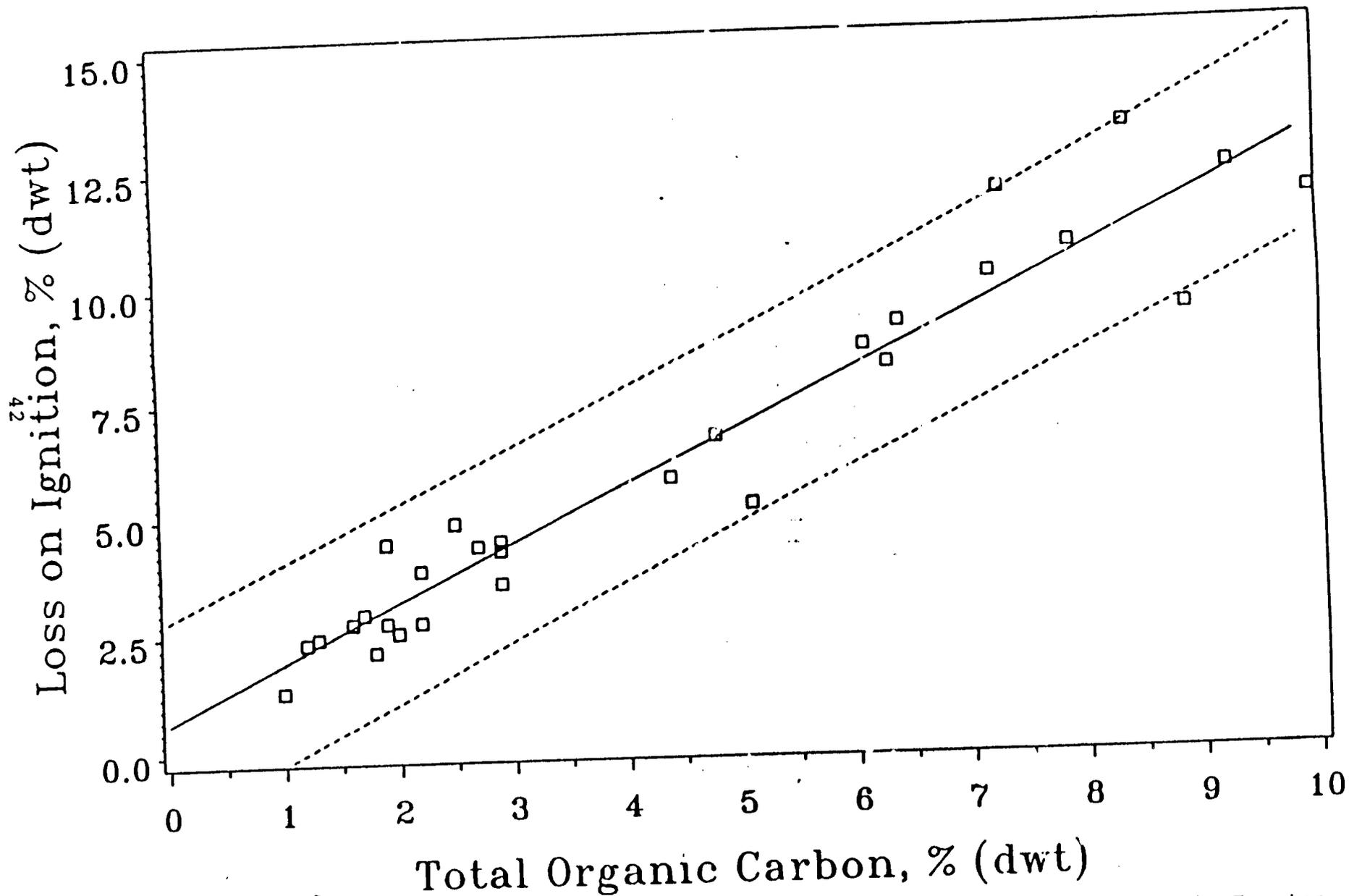


Figure 20. Interdependence of loss-on-ignition (LOI) on total organic carbon (TOC) in Trenton channel sediments.

level of intercorrelation among the metals. It is worth noting parenthetically that loss on ignition would have provided a reasonably accurate and less costly substitute estimate of sediment organic carbon (Figure 20) than the total-inorganic carbon procedure used for this study. In general, variables that correlated with total organic carbon also correlated with loss on ignition and did so with the same level of confidence for statistical tests.

The all-pairwise correlation procedure is often used to examine relationships among variables; however, when the number of variables is large and significant intercorrelation among variables exists, the procedure results in a large number of comparisons which may not be readily interpreted. To reduce the complexity of the data, the correlation matrix was factor analyzed after exclusion of derived quantities. Seven factors were extracted that accounted for 68.2 percent of the total variance. The results of this analysis are presented in Table 3. The first two factors accounted for 38.5 percent of the total variance of the data, and the remaining five factors accounted for a combined total of 29.6 percent of the variance. The latter factors involved mixed associations of porewater metal concentrations with several other variables and were not readily identifiable. On the other hand, interpretation of the components and processes giving rise to the first two factors was possible.

The first factor reflects the earlier observation of an association between total sediment metal levels, sediment organic matter (predominant fraction of total sediment carbon; loss on ignition), and moisture content. Moisture content commonly follows the organic content of sediments, while the ligand-like character of sediments also is a function of sediment organic content. The second factor connotes an association of sediment inorganic carbon with relatively fine grained sediments and elevated cation exchange capacity. The greater surface area for cation exchange of the fine grained samples would explain part of this association. It cannot be ascertained by the method of inorganic carbon determination whether it was present as primary mineral carbonate or occurred as carbonate formed secondarily from bicarbonate and carbon dioxide during sample processing.

FIELD RESUSPENSION EXPERIMENTS

Analysis Methods

A subset of all data collected from field resuspension experiments was analyzed statistically as a means of evaluating important associations among variables. The subset consisted of results from nine separate experiments conducted at three stations (30, 34, 53) which included the data vectors time, pH, frequency of shaking (freq), total suspended solids (TSS), total metal concentration (TMe) and dissolved metal concentration

TABLE 3.

Analysis of Sediment Survey Data -- In Place Pollutants Project
 Untransformed Data, No Derived Characteristics
 Factor Analysis of Relationships Among Sediment Variables

FACTOR PATTERN (VARIMAX ROTATION)							
	FACTOR1	FACTOR2	FACTOR3	FACTOR4	FACTOR5	FACTOR6	FACTOR7
TCD	47	13	58 *	20	6	-3	-14
TCO	30	5	-2	68 *	-2	-29	-10
TCR	80 *	8	17	-6	13	-7	16
TCU	74 *	26	12	10	-12	-13	-13
TNI	74 *	16	-5	23	24	-17	11
TPB	72 *	35	14	13	-7	-7	15
TZN	47	48	20	-9	-5	8	42
PCD	17	-7	1	14	11	4	64 *
PCO	0	9	82	7	12	4	-3
PCR	2	23	37	60 *	17	15	2
PCU	-15	-22	19	5	20	73 *	8
FNI	19	-12	3	64	-26	42	13
PPB	28	-15	18	-23	74 *	0	-18
PZN	21	8	17	27	9	3	-57 *
CEC	23	64 *	19	8	-19	-6	11
TC	82 *	16	-4	10	-11	19	-12
IC	17	52 *	-22	-4	3	52 *	-30
SG	67 *	10	24	10	-3	-23	-9
H2O	49	23	49	4	-16	18	12
LOI	79 *	15	-8	14	-1	24	-5
D710	-21	4	0	16	75 *	18	25
D63	21	83 *	10	13	1	-13	-12
D1	24	85 *	5	-2	7	-4	-10

NOTE: PRINTED VALUES ARE MULTIPLIED BY 100 AND ROUNDED TO THE NEAREST INTEGER
 VALUES GREATER THAN 0.5 HAVE BEEN FLAGGED BY AN '*'

VARIANCE EXPLAINED BY EACH FACTOR

FACTOR1	FACTOR2	FACTOR3	FACTOR4	FACTOR5	FACTOR6	FACTOR7
5.271169	2.827351	1.740595	1.675954	1.451658	1.405464	1.320811

TCD - represents total sediment metal content

PCD - represents particulate metal content

CEC - cation exchange capacity

TC - total carbon content

IC - inorganic carbon content

SG - specific gravity

H₂O - moisture content

LOI - loss-on-ignition

D710 - percent (dry wt.) passing 710 µm mesh

D63 - percent (dry wt.) passing 63 µm mesh

D1 - percent (dry wt.) passing 1 µm mesh

(DMe). Table 4 gives a summary of the control variables for these experiments, while Table 5 gives average dissolved concentrations, along with ranges, observed. Raw data from all field resuspension experiments are provided in data Appendix C.

Both bivariate and multivariate linear regressions were used in analyzing the data. Calculations and graphic depictions were facilitated through the use of the software program STATGRAPHICS (STSC, Inc., Rockville, MD) run on a Zenith 200 microcomputer equipped with a floating point co-processor.

Results and Interpretation

Table 6 summarizes the results of the multiple linear regression analysis for total suspended solids and pH and their dependencies on experimental conditions. As would be expected, TSS shows a high direct correlation with frequency of shaking, with average values of 0.58 and 5.14 g/L for the low and high frequencies, respectively. When the TSS regression against time is performed separately at the two frequencies, the correlation becomes significant ($|p| = .04$) at the lower rate of shaking. This suggests that the sampling time interval may have been too long to observe the rate of TSS increase at the high frequency, where a steady state was reached within approximately five minutes.

Total metal concentrations were found to correlate with TSS and frequency for each station; however, comparison of means tests revealed significant differences in total suspended metals among all three stations reflecting different sediment physical characteristics and historical deposition of pollutants described in the previous subsection.

One of the interesting observations of the experimental system used in the field was a general increase in pH with time yielding the strong positive correlation shown in Table 6. Figure 21 shows the data as a simple linear regression. The cause of this pH increase is not definitively known, although a likely contributor is the release of CO_2 from the column during shaking. Examination of the pH trend during individual experiments (Figures 22 and 23) suggests that this may not be a constant process and that other reactions may exert an influence. In any case the bottom sediments in the core can hardly be thought of as spatially homogeneous and the vigorous action of the shaker undoubtedly uncovers areas of greater or lesser acidity. The variation of pH as shown in Figures 22 and 23 could perhaps be thought of as a response to the flux of acidic material through the column.

The range of pH values observed in the field resuspension apparatus (7.0-8.06) appears to be similar to the historical ranges recorded for the Detroit River as given in Figure 24 (Great Lakes Water Quality Board, 1983). This in itself is not surprising since those factors which control pH in the shaker are

TABLE 4

DATA SUBSET FOR FIELD RESUSPENSION EXPERIMENTS
SUMMARY INFORMATION

Exp. #	Station	Frequency (sec ⁻¹)
1	53	7
2	53	12.5
3	53	7
4	53	12.5
18	30	12.5
19	30	7
22	34	7
23	34	12.5
24	34	12.5

TABLE 5
SUMMARY DATA
FIELD RESUSPENSION EXPERIMENTS

Metal	Avg. Concentration ($\mu\text{g/L}$)	Range ($\mu\text{g/L}$)
Cd	1.45	0.1 - 6.0
Co	.44	<.1 - 1.8
Cr	5.30	0.19 - 54.4
Cu	8.18	0.7 - 40.2
Ni	21.0	3.2 - 206.6
Pb	7.57	0.23 - 56.4
Zn	655.9	24.9 - 4130

TABLE 6

MULTIPLE REGRESSION OF SUSPENDED SOLIDS AND PH
DURING FIELD RESUSPENSION EXPERIMENTS

Dependent Variable	INDEPENDENT VARIABLE				
	TSS	Freq.	pH	Time	exp.
TSS	N/A	*** (+)			
pH			N/A	*** (+)	

*** $|p| \leq .01$

(+) indicates direct correlation

blank = $|p| > .1$

N/A = factor not included in regression

Regression of pH on time

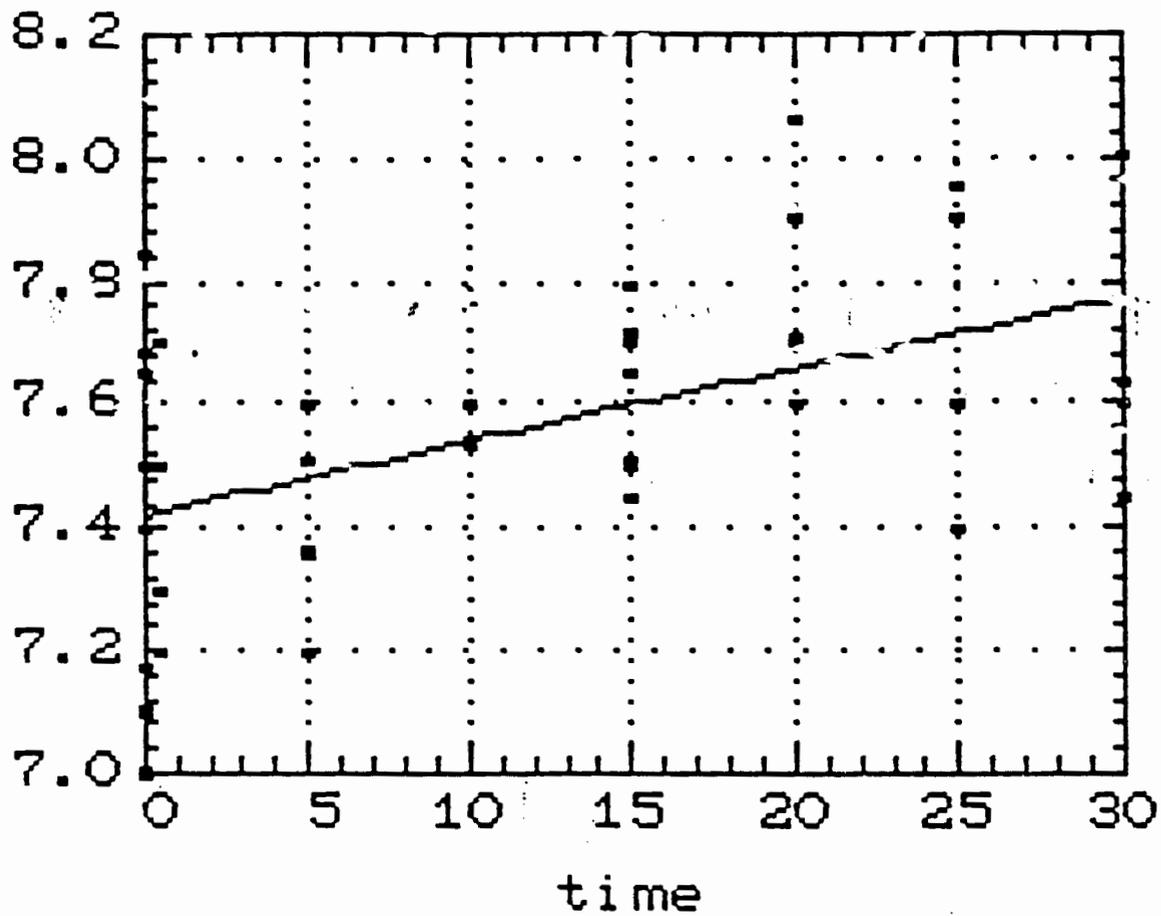


Figure 21. Linear regression of pH on time for field resuspension experiments

Plot of pH vs time (experiment # 5)

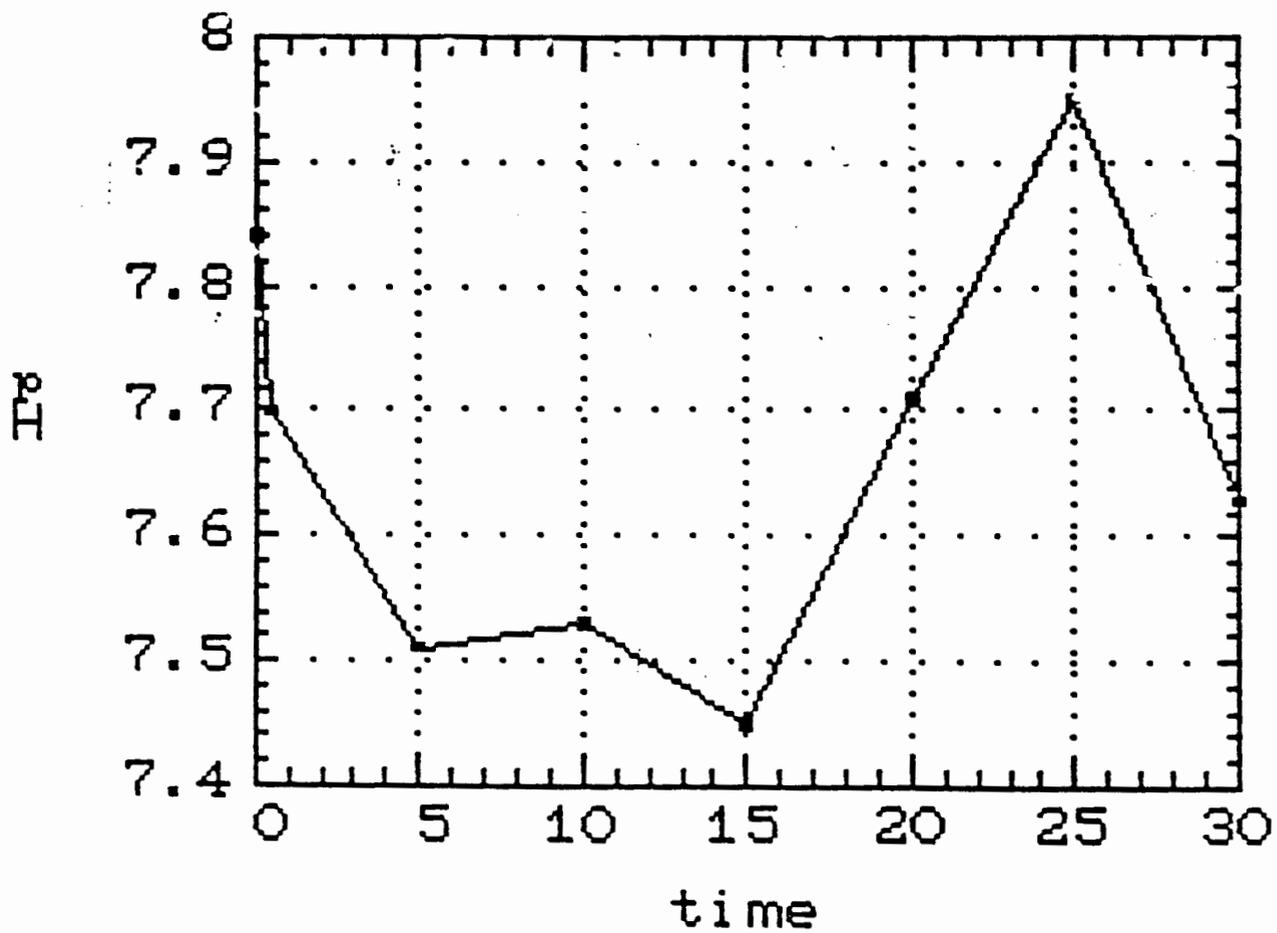


Figure 22. Plot of pH versus time for field resuspension experiment #5

Plot of pH vs time (experiment # 6)

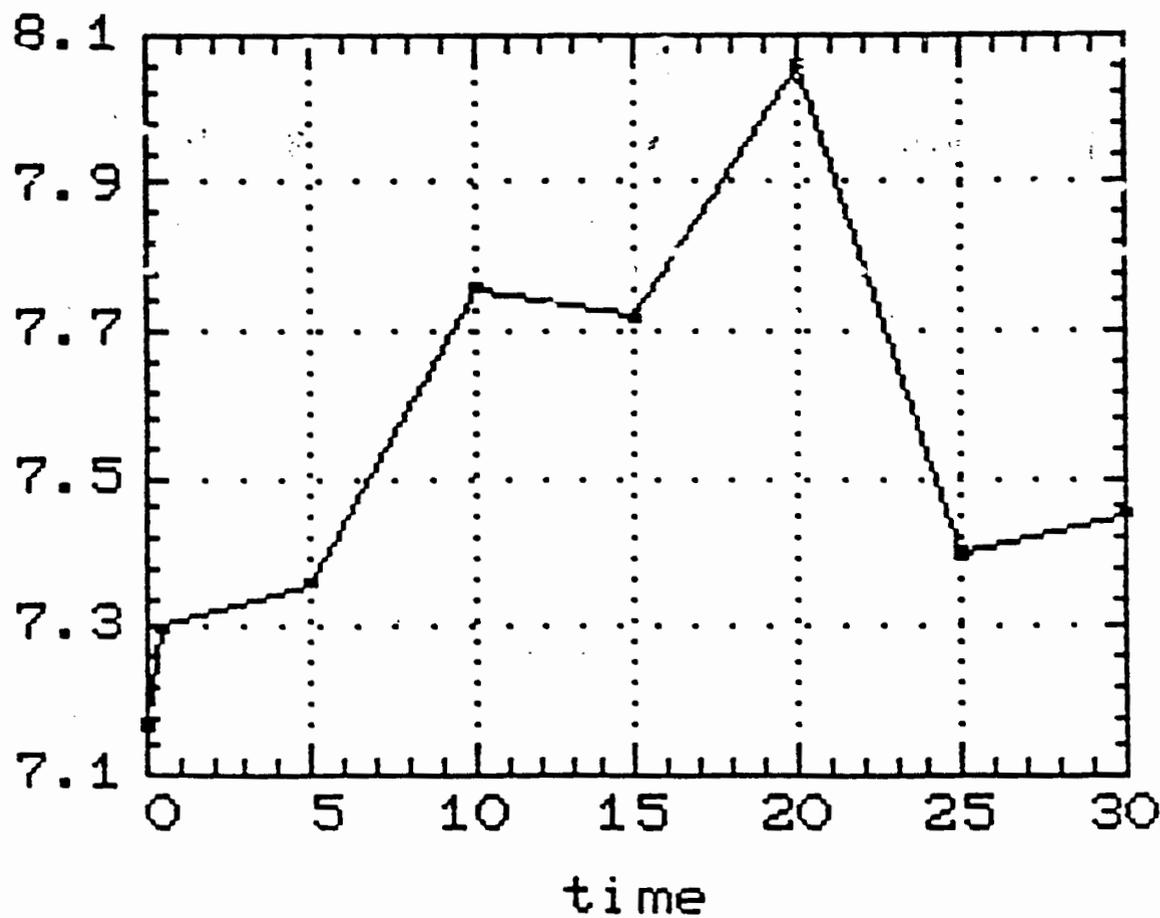


Figure 23. Plot of pH versus time for field resuspension experiment #6

Historical data of pH for Detroit River

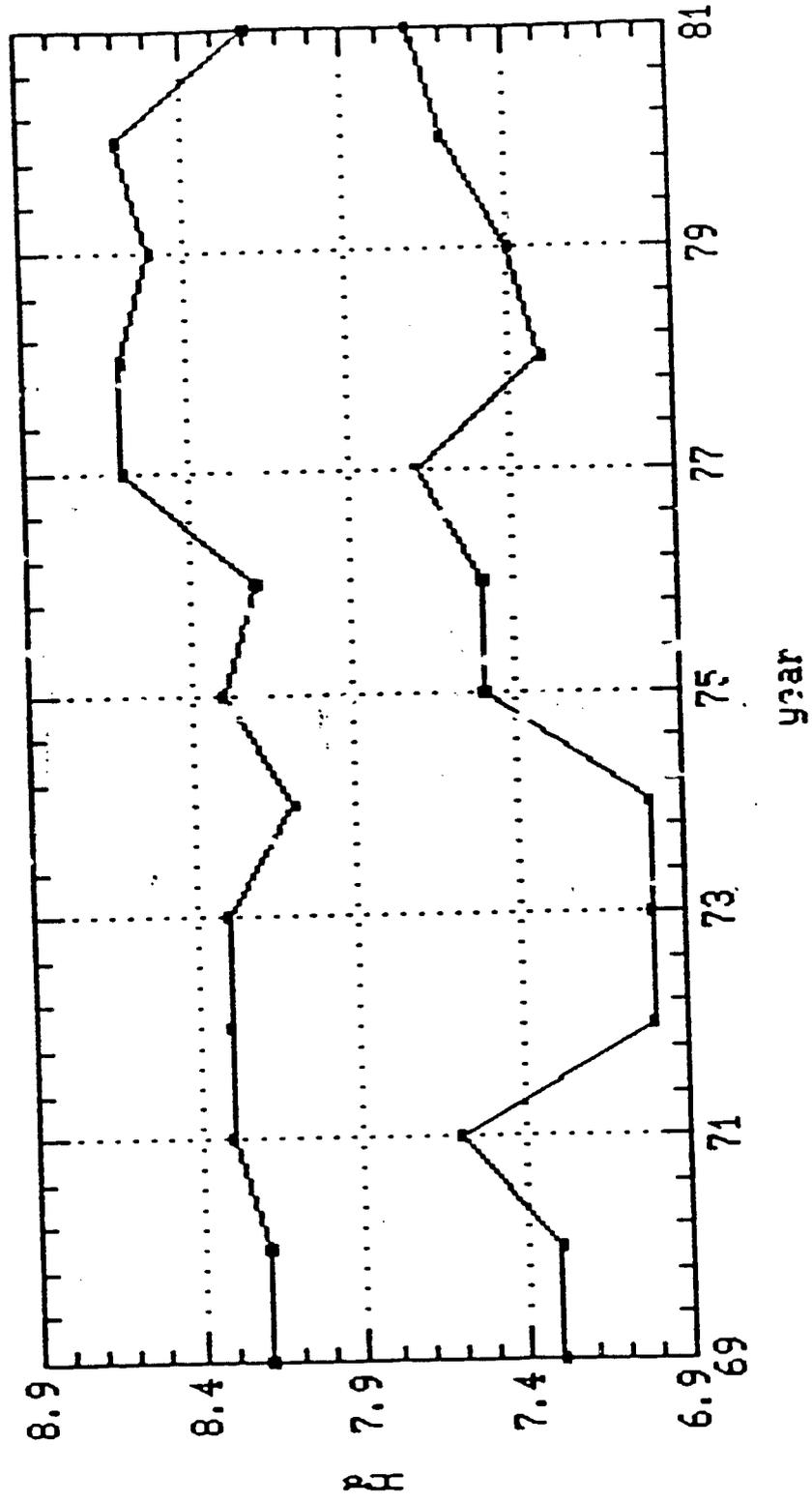


Figure 24. Historical pH data for the Detroit River

the same as in the river as a whole, thus the range over which the pH is buffered should be similar. Of course the magnitudes and rates of change of pH are different for each system. However for the purposes of the study, i.e. to establish the interaction among relevant variables, the concurrence of pH in both systems lends a degree of realism and applicability to the resuspension results.

Table 7 summarizes the results of multiple regression analyses for the dissolved metal concentrations Cd, Co, Cu, Cr, Ni, Pb and Zn on selected factors. Two important features of the data are illustrated, first the inverse relation to pH and second the direct relation to time. The pH-time interaction noted earlier plays a significant role in that time correlates positively for all metals, except Zn, only when the pH is at or below 7.5. Zinc concentrations are correlated with time for all values of pH. Thus the dissolved metal concentrations appear to follow a time-dependent release from the sediments which is arrested as the pH rises above 7.5. This phenomenon is illustrated for selected cases in Figures 25 and 26 for Cd and Zn in experiment #6. Comparison of these trends with the pH data contained in Figure 23 for the same experiment reveal the initial release of metal at low pH which ceases as the pH rises. Subsequent variations in metal concentrations reflect the strong inverse relation to pH. Figure 27 shows the combined effects of pH and time on dissolved Cd for all data. The partitioning of Cd to the sediments can be clearly seen as the pH rises.

The inverse correlation of dissolved metals with pH is suggestive of surface adsorptive controls on solution concentration although the solubility of discrete or mixed phases on the surface of the sediments may also play a role. Chromium shows a somewhat weaker inverse correlation ($p = .13$) which could be due to a mixture of oxidation states, Cr(VI) existing predominantly in anionic form (chromate) while Cr(III) exists as one or more cationic species. These ionic forms would be expected to exhibit inverse behavior with respect to the influence of pH on solution concentration. The direct correlation with time within a restricted range of pH indicates the need for carefully controlled kinetic release and uptake studies in which pH is a control variable.

A surprising feature of the analysis is the lack of significant direct correlations between respective dissolved and total particulate metal concentrations. It is also not obvious why several dissolved metals correlate inversely with frequency, that is as the frequency of shaking increases and suspended solids increase, dissolved metals show a decrease. Further examination of the data provide some explanation. Table 8 contains the results of simple linear regressions of dissolved metals on total metals at both frequencies and at the high frequency only. The correlations go from essentially random to direct, and in two cases, Co and Ni, a significant relation is noted. This effect may be related to the rate at which

TABLE 7

MULTIPLE REGRESSION OF DISSOLVED METAL
CONCENTRATION ON SELECTED FACTORS DURING
FIELD RESUSPENSION EXPERIMENTS

Dependent Variable	INDEPENDENT VARIABLE				
	pH	Time ⁴	TMe ³	Freq.	TSS
DCd ²	*** (-)	*** (+)		* (-)	
nCo	** (-)	*** (+)		** (-)	
DCu	** (-)	*** (+)		* (-)	* (-)
DCr		*** (+)			
DNi	*** (-)	*** (+)		*** (-)	** (+)
DPb	*** (-)	*** (+)	** (-)		** (+)
DZn	** (-)	*** ⁵ (+)			

¹ *** |p| < .01
 ** |p| < .05
 * |p| < .10
 blank = |p| > .10
 (+)(-) indicates direct and inverse correlation,
 respectively

² DMe = Dissolved metal concentration

³ TMe = Total metal concentration corresponding to
 indicated dissolved metal

⁴ Time values for which corresponding pH was less than
 or equal to 7.5

⁵ All pH values included

Plot of DCd vs time (experiment # 5)

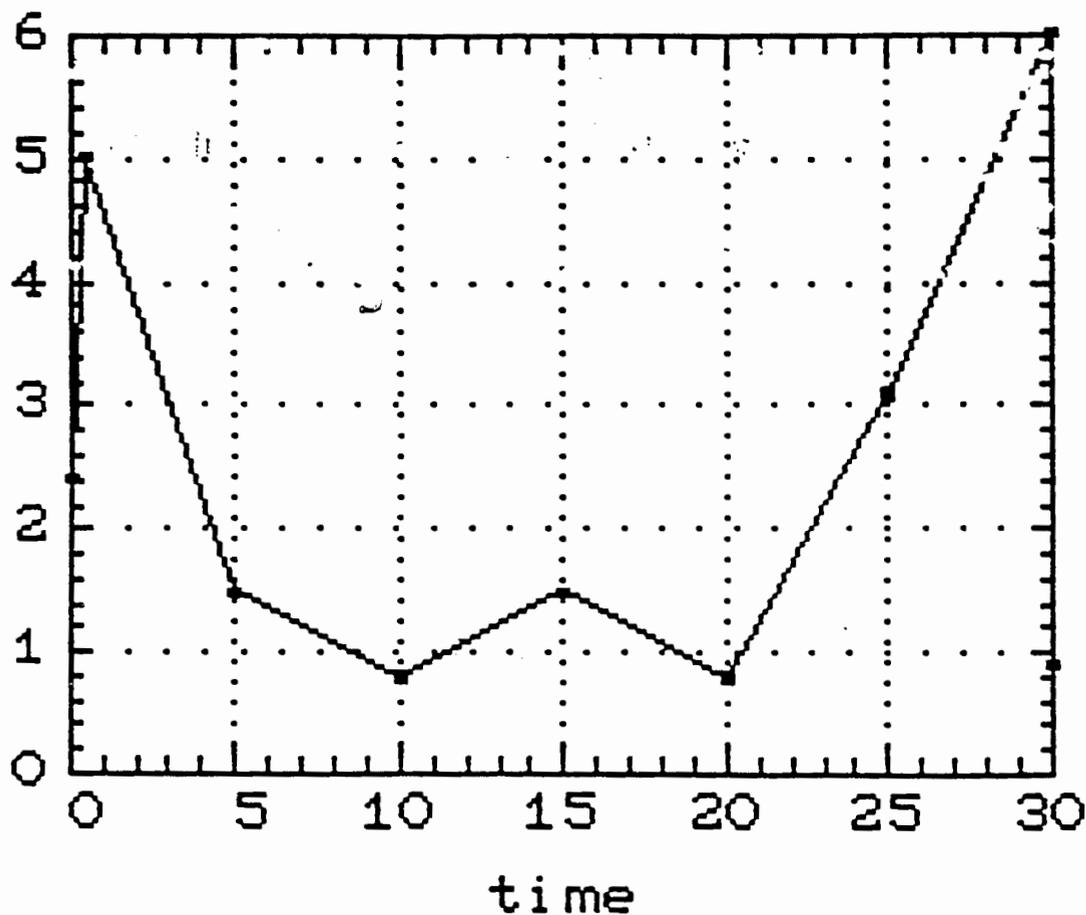


Figure 25. plot of dissolved Cd versus time for field resuspension experiment #6

Plot of DZn vs time (experiment #6)
(X 1000)

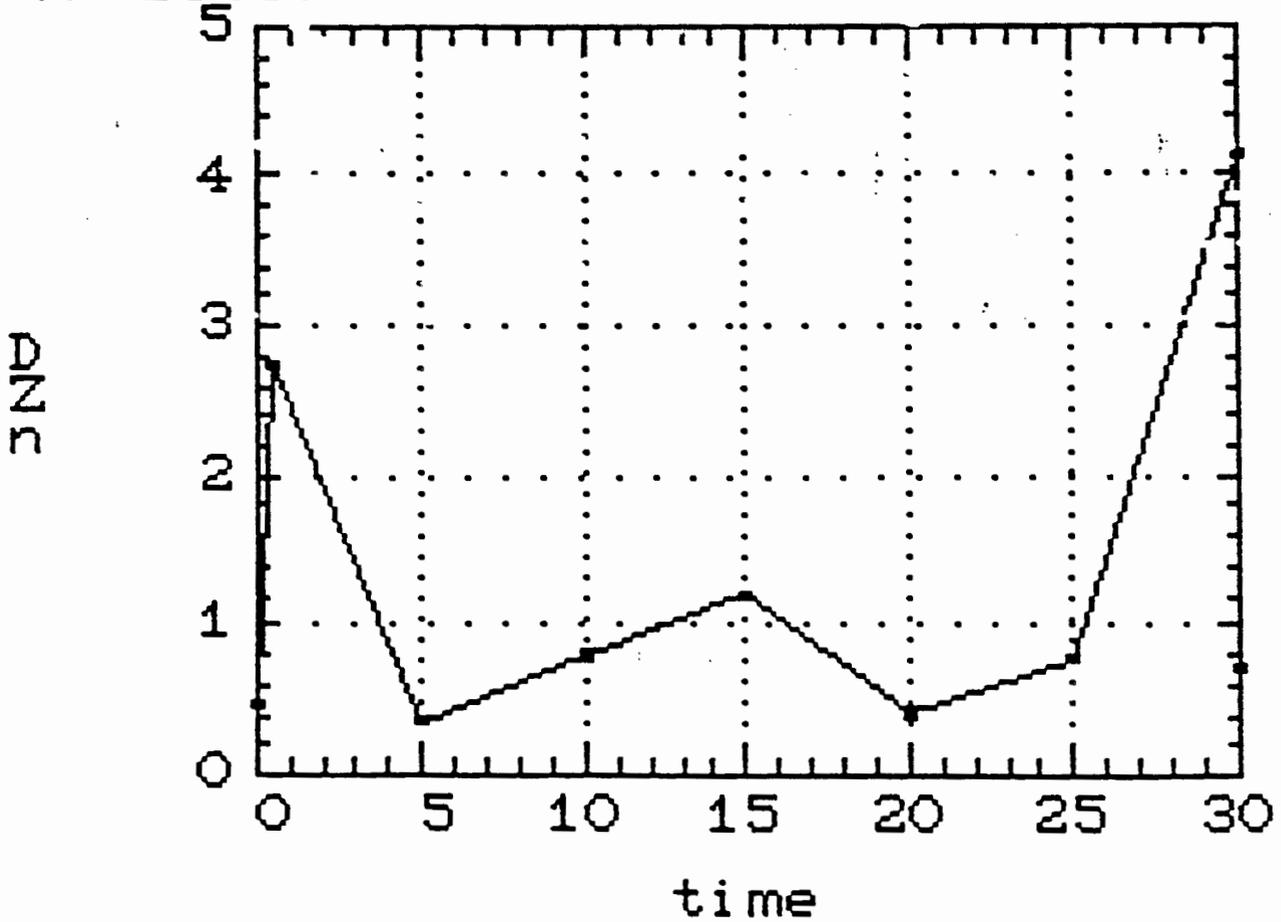


Figure 26. Plot of dissolved Zn versus time for field resuspension experiment #6

Plot of DCd
vs pH and time

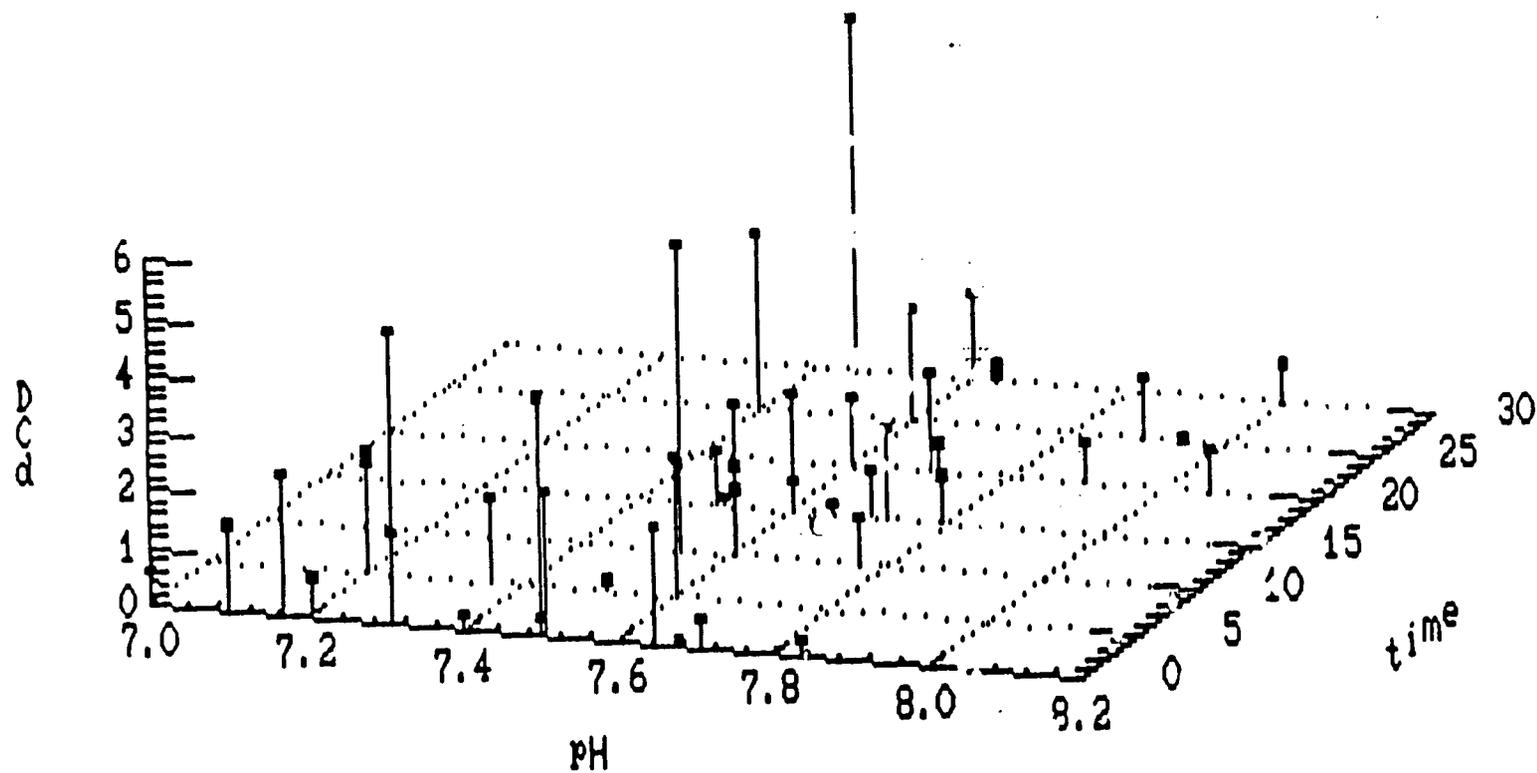


Figure 27. Plot of dissolved Cd versus pH and time for field resuspension experiment #6

TABLE 8

SIMPLE REGRESSION OF DISSOLVED METAL CONCENTRATION
ON TOTAL CONCENTRATION: EFFECT OF MIXING RATE

=====

Metal	PROBABILITY LEVEL	
	12.5 and 7 sec ⁻¹	12.5 sec ⁻¹ only
Cd	.52 (-)	.40 (+)
Co	.27 (-)	.04 (+)
Cr	.59 (+)	.14 (.)
Cu	.17 (-)	.62 (+)
Ni	.33 (-)	.01 (+)
Pb	.66 (-)	.59 (+)
Zn	.32 (-)	.11 (+)

=====

(+)(-) indicate direct and inverse correlation, respectively

equilibrium in these systems is approached. If metal release from sediment particles is wholly or partially limited by mass transfer considerations, the process would be expected to be more rapid at higher particle velocities where surface boundary layer effects are less pronounced. Clearly more research is needed on those factors which affect release kinetics, however the analysis presented strongly indicates major interactions among pH, time, degree of mixing and total metal concentrations.

LABORATORY RESUSPENSION EXPERIMENTS

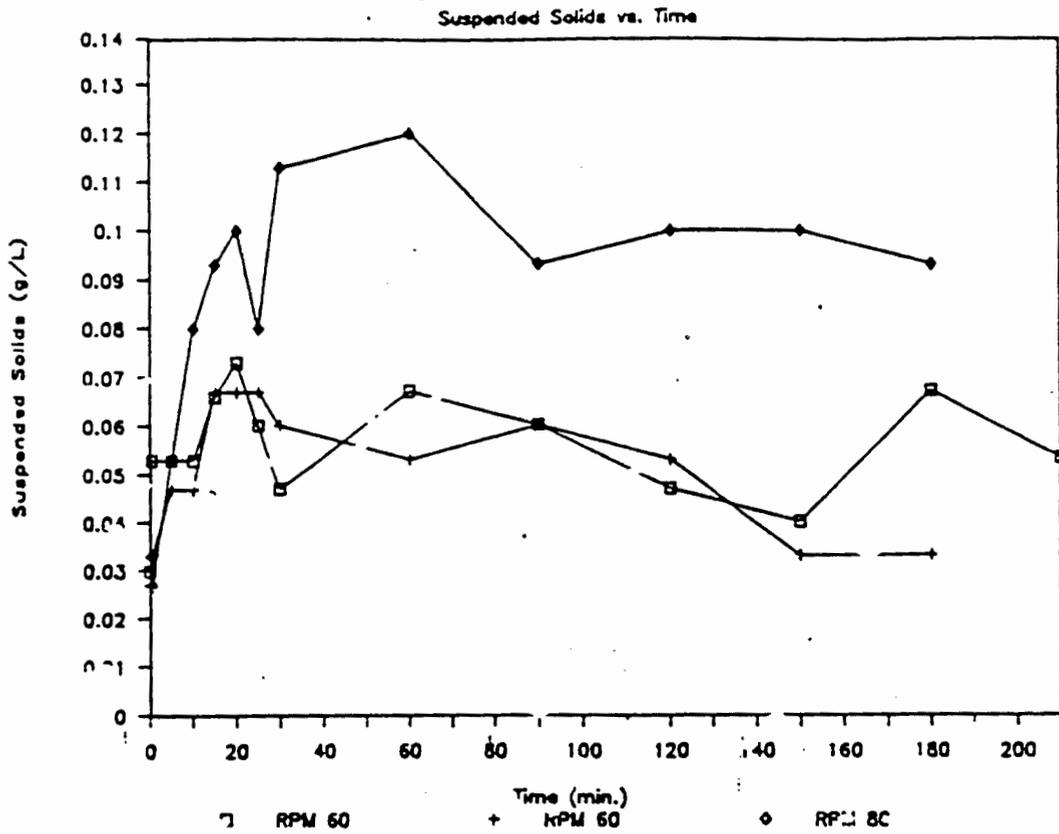
Sixteen laboratory resuspension experiments have been conducted to date (using sediments from station 53); however, the results of these experiments have not yet been fully interpreted or integrated into the overall project. Raw data from these experiments are presented in Appendix D. The experiments were intended to evaluate the effects of bottom shear stress (as controlled by the RPM of the annular ring at the water surface), pH and time on particle and metal resuspension and solid-solution metal partitioning.

The results of experiments 1-5 demonstrated that RPMs between 60 and 105 produced shear stresses (as measured by resuspended solids levels) in the range of those applied in the field resuspension experiments. Also, as expected, resuspended solids tended to reach an approximate steady-state level that was proportional to RPM (Figure 28). The exception was the experiment conducted at 150 RPM, which did not achieve a steady-state suspended solids level during the course of the experiment.

Experiments 6 through 9 (conducted as one run) were designed to investigate the pH effect on dissolved metals levels noted in the field resuspension study. These experiments were all conducted at a constant stirring rate of 105 RPM, with sequential pH adjustments of 7.7, 7.0, 7.5, and 8.0 for experiments 6-9, respectively. Although the interpretation is somewhat confounded by the fact that the suspended solids level gradually rose through the run, the dissolved metal results were consistent with the observations in the pH stat experiment (discussed below), which used the same station sediment (53). That is, there did appear to be an inverse relationship between dissolved Cd in the overlying water and pH; however, Cr and Pb did not appear to respond significantly to pH changes. These results suggest the possibility of some strengthening of Cr and Pb bonding or a species shift during handling and storage of the sediments prior to and between conducting the resuspension experiments.

To better investigate metals partitioning in our study system as a function of pH, experiments 10-16 (conducted as two runs: 10-12 and 13-16) were performed by adding a dissolved metals spike to the reactor overlying water after an initial resuspension equilibration period. In both runs the metals spike

Laboratory Resuspension Reactor



Laboratory Resuspension Reactor

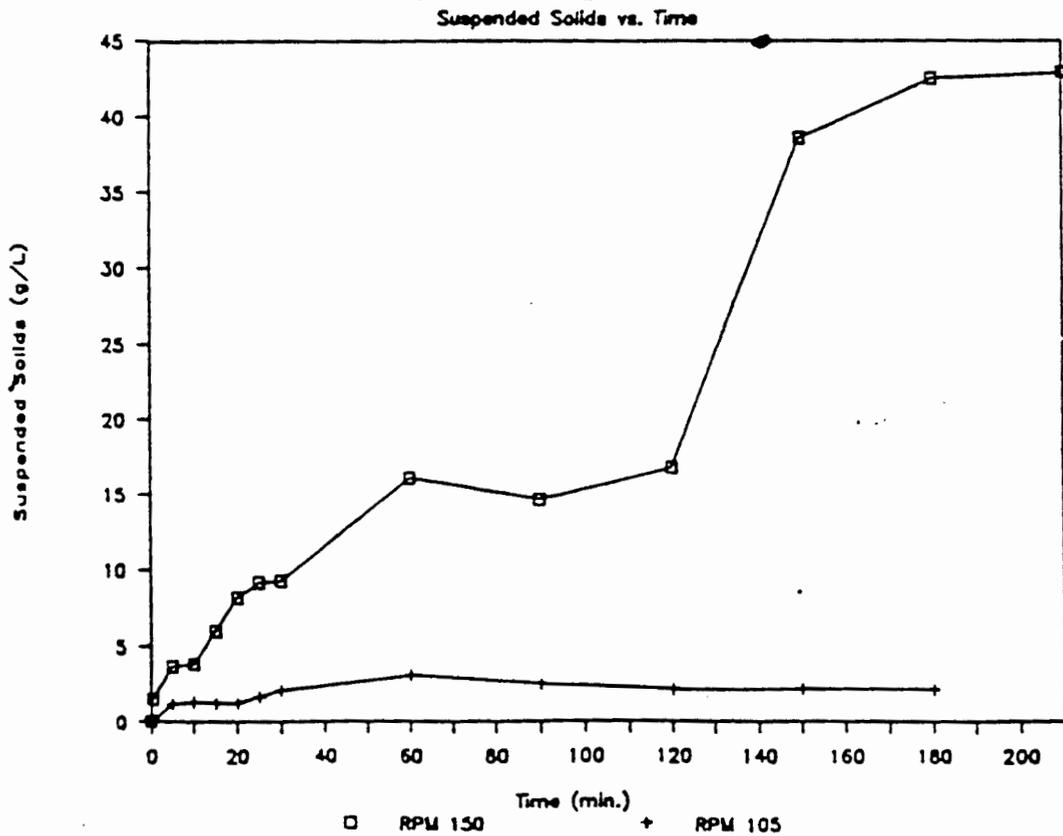


Figure 28. Temporal trend of suspended solids for different RPM (exp. 1-5)

was designed to produce the following dissolved metals concentration increases in the reactor overlying water: 25 ug/L Cd, 50 ug/L Cr, and 100 ug/L Pb.

Experiment 10 was performed to obtain background SS and metals levels at 95 RPM and pH 6.4 prior to the metal spike. At the start of experiment 11 the dissolved metals spike was added to the reactor. The system was run at pH 7.64 for 2 hours (exp. 11) and then the pH was lowered to 7.05 (exp. 12). RPM and the resulting SS were held constant throughout the three experiments; dissolved Cd and Pb results for experiments 11 and 12 are presented in Figure 29. In experiment 11 there was a very rapid (< 0.5 min) uptake of a portion of all three metal spikes, followed by a slower depletion of the remaining dissolved fraction. Lowering the pH for experiment 12 appeared to cause an initial release of all three metals; but, because the system had not yet reached a state of adsorption equilibrium by the time experiment 12 was begun, there continued to be a gradual uptake of all three metals during experiment 12. By the end of experiment 12, it appeared that the pH drop from 7.63 to 7.05 had not produced an increase in dissolved metals as had been noted in the field shaker experiments. Although this appears to be inconsistent with the shaker observations, these results have to be interpreted in view of the dynamic solids exchange between those in the initially unspiked bed and the initially spiked overlying water.

In experiments 13-16, which were also performed using the same metals spike followed by pH adjustment during continuous resuspension at constant rate of 95 RPM, dissolved Cd did increase in response to pH decreases in overlying water (Figure 30). The Cr and Pb results are more difficult to interpret; however, the response of these metals to the pH adjustments (even the decrease from 7 to 5) did not appear to be as evident as Cd. It is our hypothesis that the sediment handling and storage is responsible for quantitatively different response of dissolved metals between the field shaker and laboratory resuspension systems. Further modeling and experimental efforts have been designed to address this question.

METALS ADSORPTION/DESORPTION EXPERIMENTS

Nickel exhibited a linear adsorption isotherm with station 82 sediments at pH 7.2; the partition coefficient was a very low 240 L/Kg. A lead adsorption isotherm conducted with station 30 sediments at pH 7.2 was also linear, with a partition coefficient of 1.35×10^5 L/Kg. The difference in partitioning for these two experiments may be explained in large part by the differences between the two sediment samples. Station 30 has a higher cation exchange capacity, a smaller mean particle size, and, most noticeably, a much larger organic carbon content (7.5% compared to 1.2%) than station 82. The difference in metal solubilities at pH 7.2 also contributes to the observations.

Laboratory Resuspension Reactor

Dissolved Cd and Pb vs. Time

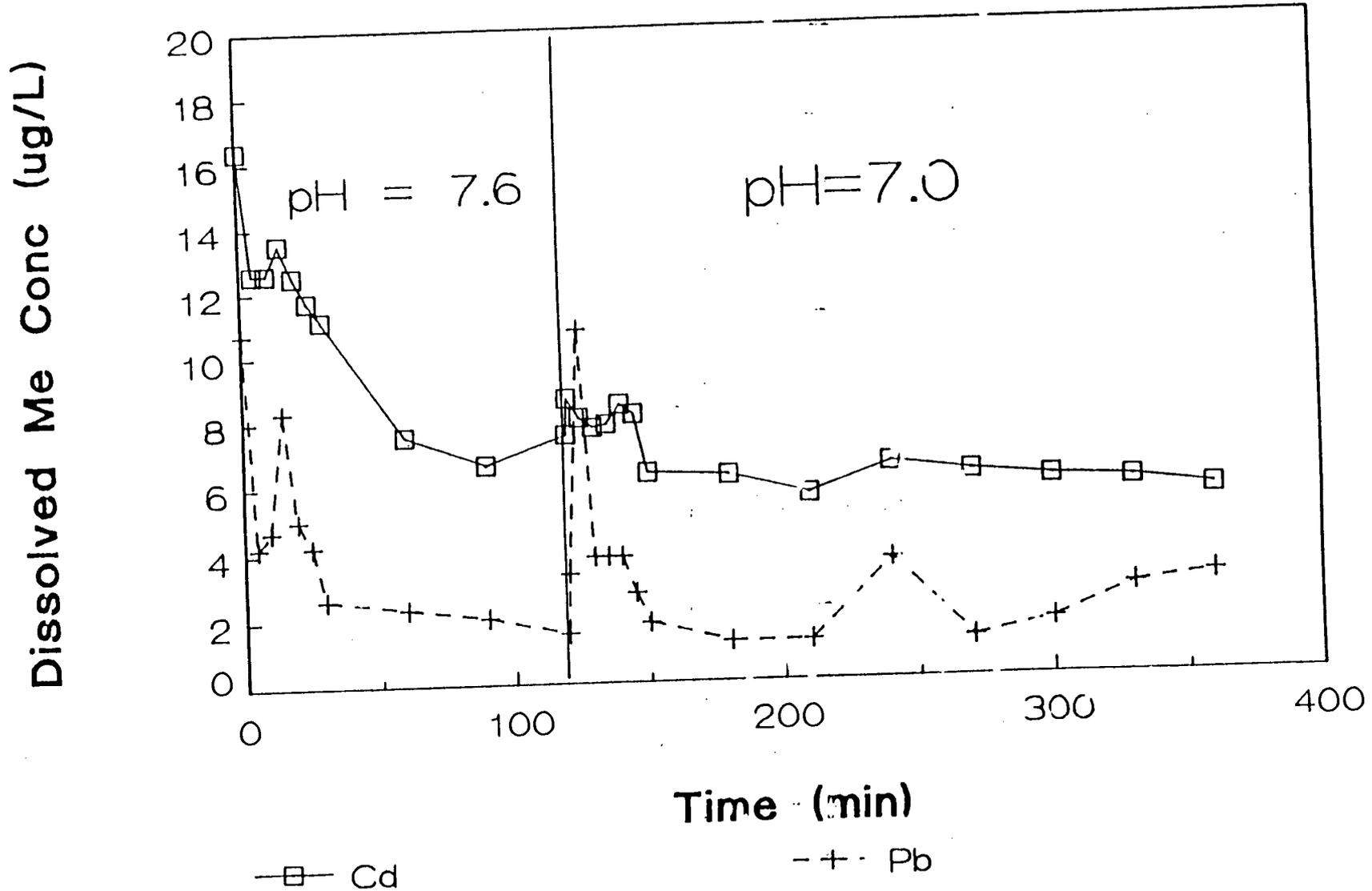


Figure 29. Plot of dissolved Cd and Pb as a function of time for laboratory resuspension reactor experiments 11-12, following metal spikes of 25 $\mu\text{g/L}$ Cd and 100 $\mu\text{g/L}$ Pb

Dissolved Cd vs Time

63

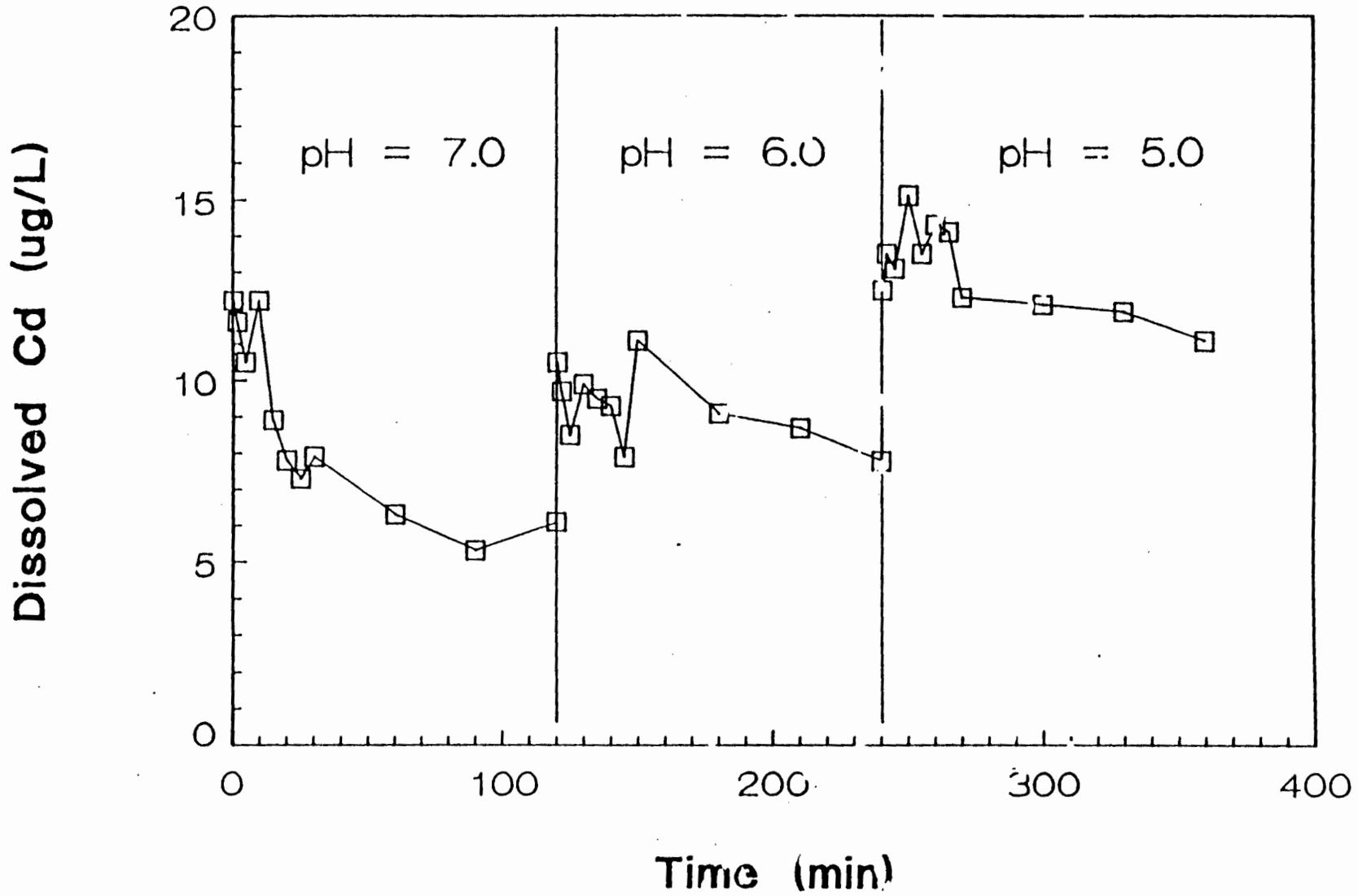


Figure 30. Plot of dissolved Cd as a function of time for laboratory resuspension reactor experiments 13-16, following metal spike of 25 ug/L Cd

In contrast to the above linear behavior, Cadmium displayed a Langmuir-type adsorption isotherm with station 30 sediments at pH 7.2. A standard Langmuir linearization of the cadmium adsorption data is shown in Figure 31; this analysis yields a maximum adsorption density of 0.4 ug Cd/mg SS.

The laboratory pH stat fractional adsorption experiments have been aimed at confirming under controlled conditions the field observations of dissolved metals-pH relationship during a resuspension event. The first experiment used station 53 sediments, with no metal spikes so that only metals originally present in the sediment sample were available for partitioning. The results for Cadmium displayed a marked decrease in fractional adsorption (from 0.95 to 0.35) as pH was decreased from 8 to 5 (Figure 32). In contrast to the Cd results, however, Pb and Cr exhibited negligible changes in their fractional adsorption values over the same pH range. This is consistent with the laboratory resuspension reactor but inconsistent with the field observations. In contrast to the Cd results, Pb and Cr exhibited negligible changes in their fractional adsorption values over the same pH range. It seems that the "native" Pb and Cr on this sediment sample are relatively immobile compared to Cd. This result may also be an artifact of the sediment sample storage or preparation method (freeze-drying). Further study of this phenomenon is warranted.

While we are in the process of investigating the effects of sample handling and storage, the results of an additional pH stat experiment seems to lend credence to the hypothesis that "aging" of sediment-bound metals affects their mobility. This experiment was performed by sequentially adjusting the pH of a metal-spiked suspension (ie., freshly adsorbed Cd and Ni) from 6.5 to 8.0 (with 4 hour equilibration between each step) followed by a decrease in pH back to 6.5 with a 36 hour equilibration after the decrease in pH. The results of this experiment are presented in Figure 33 as plots of the adsorbed fraction of the metal spike as a function of pH. The most striking observations are: 1) significant additional adsorption takes place for both metals as pH is increased over a range similar to that observed in the natural system; and 2) there does not appear to be any hysteresis with respect to the "fresh" metals spike provided enough time is allowed for desorption to occur. These results have provided a basis for our future metals-pH interaction investigations.

MODEL DEVELOPMENT

Conceptual Development

The model developed herein is intended to be used in formulating a mechanistic description of metal ion exchange between the aqueous and solid phases during a bottom sediment resuspension event. It is a dynamic model which takes into account the relative rates of the transport and reaction

Cd Langmuir Isotherm, Stn 30 Sed.

Final pH: 7.16 - 7.20, 1.062 g TSS/L

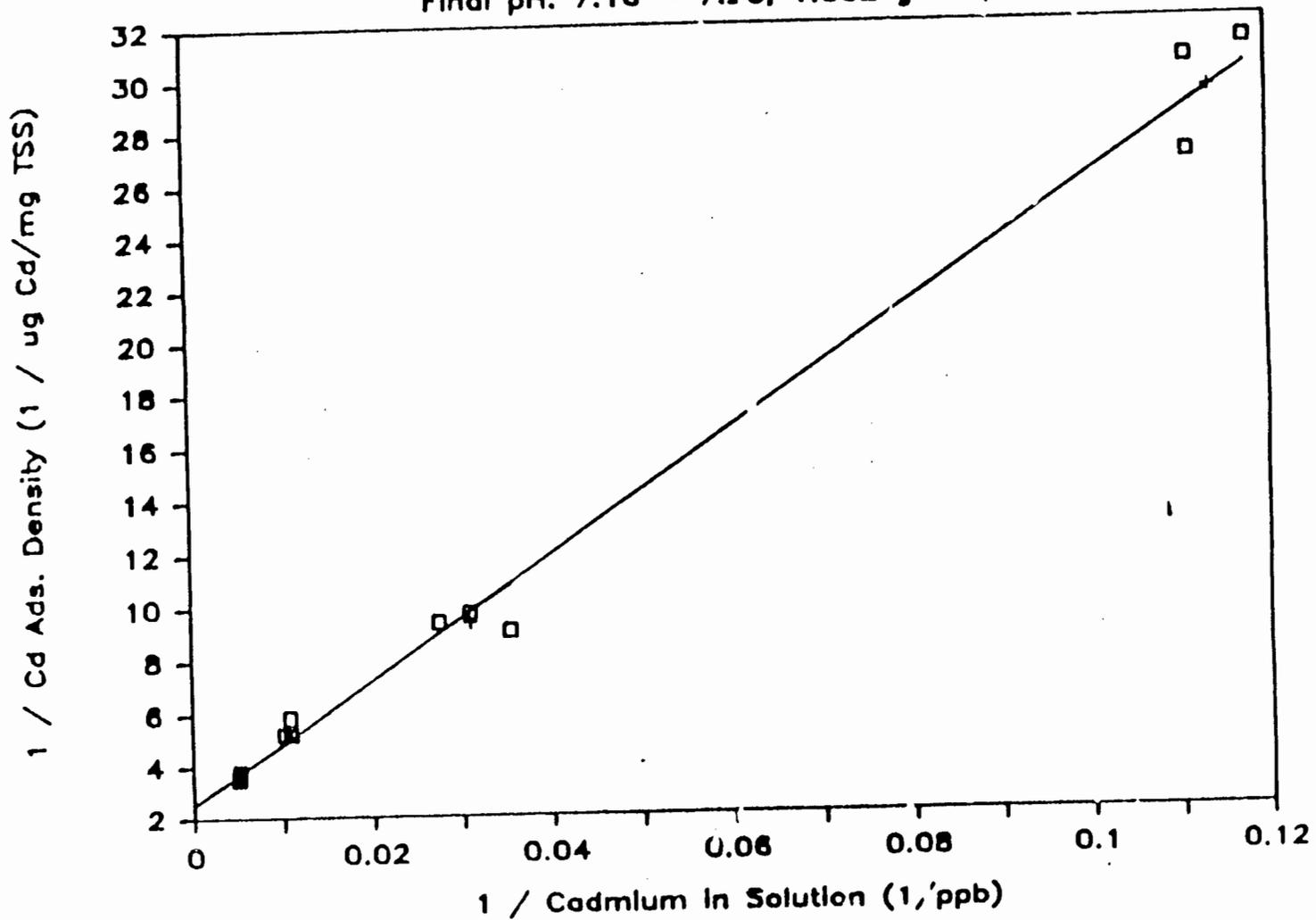


Figure 31. Langmuir isotherm linearization of Cd adsorption on station 30 sediments at pH 7.2

Cadmium, static pH, no spike, stn 53

pH vs. Cd part./Cd total

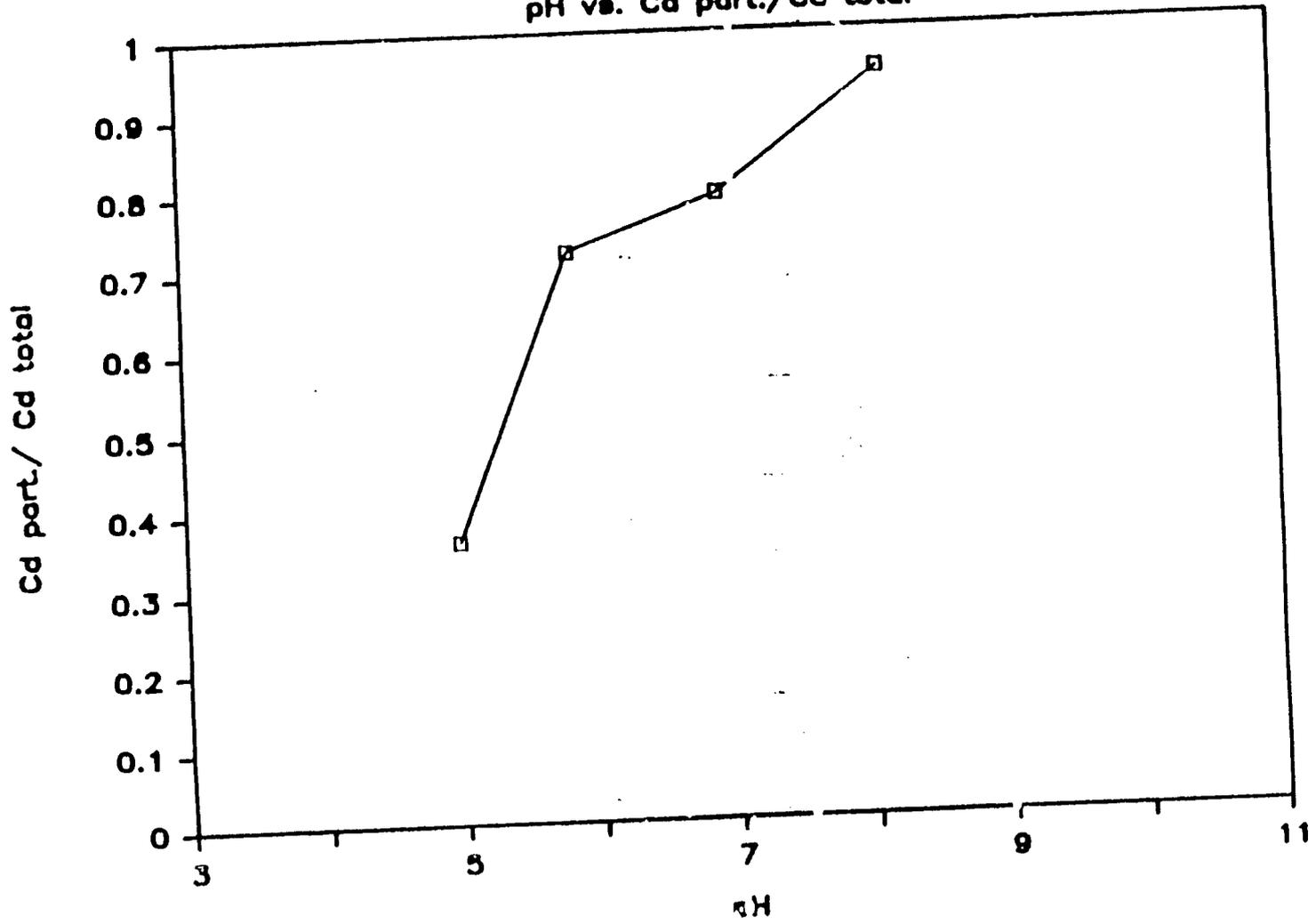
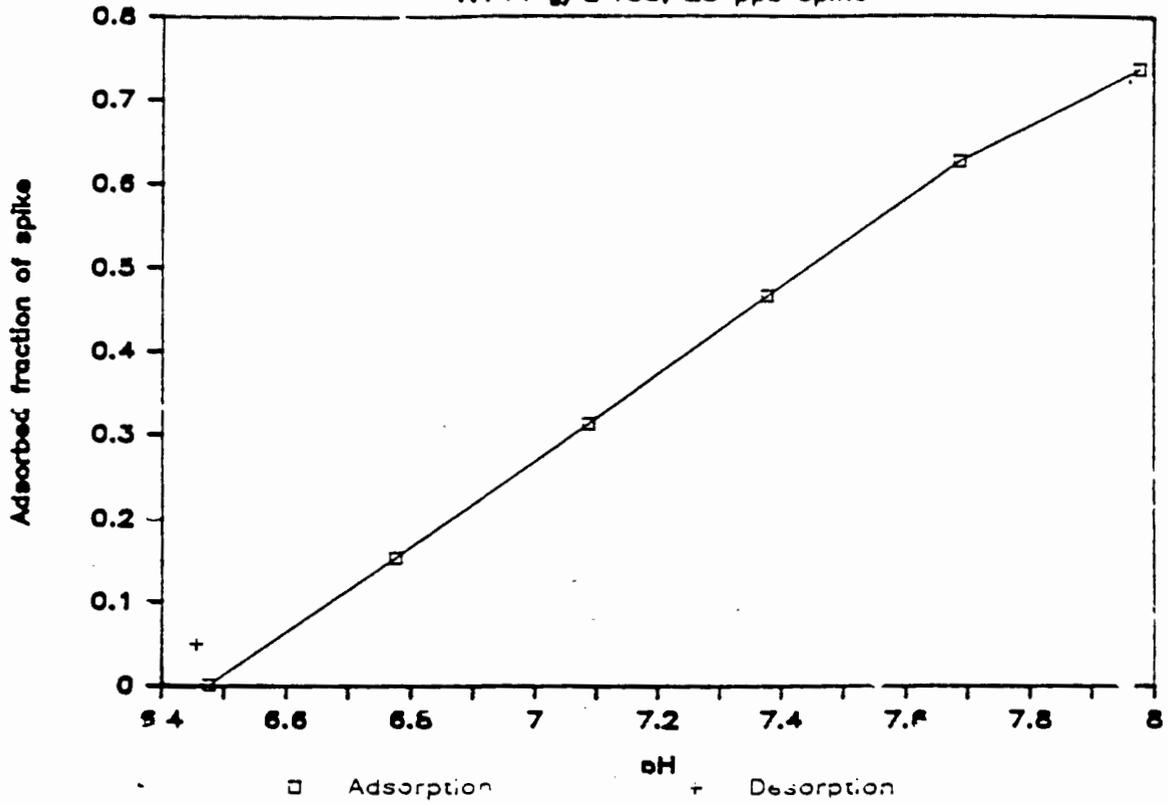


Figure 32. Results of pH stat equilibrium fractional adsorption experiment for Cd on station 53 sediments

Cadmium, Experiment 7, Stn. 53

1.144 g/L TSS, 25 ppb spike



Nickel, Experiment 7, Stn. 53

1.144 g/L TSS, 100 ppb spike

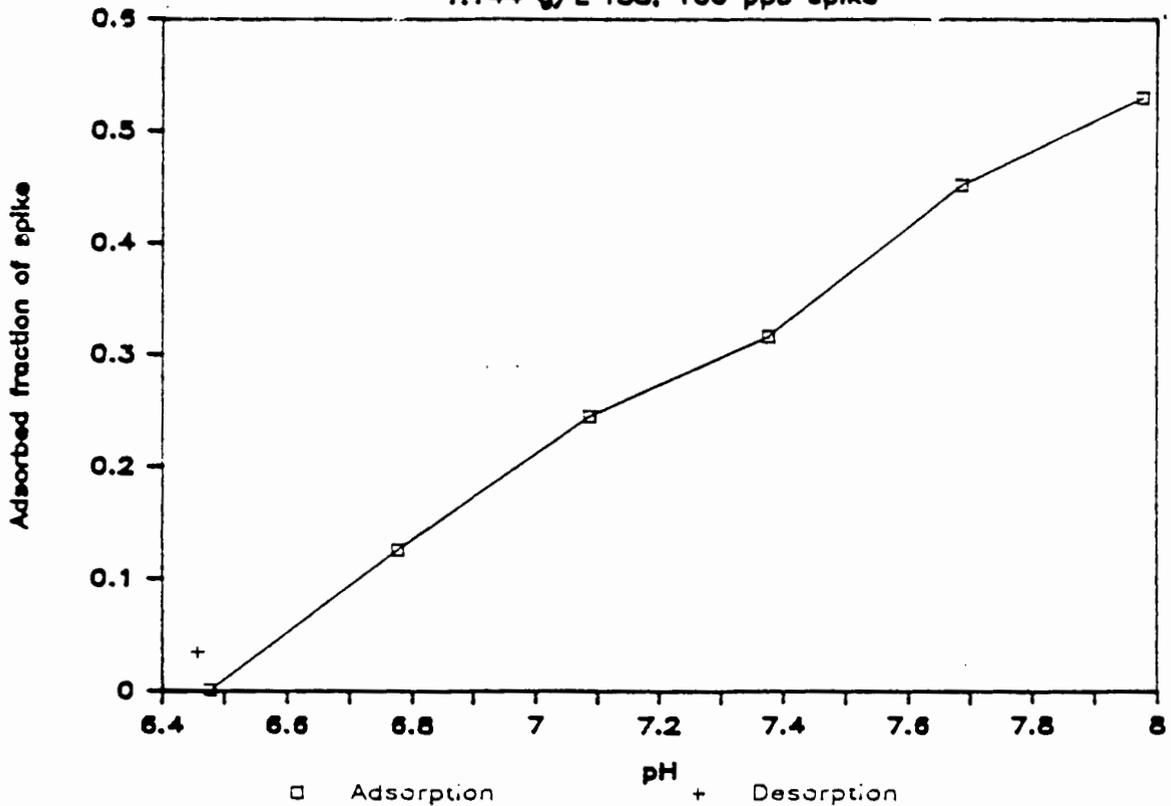


Figure 33. Results of pH stat fractional adsorption-desorption experiment using Cd and Ni spiked station 53 sediments

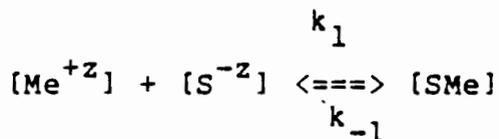
processes involved.

This model will examine five transport and adsorption processes. Selection of these steps as important parameters is based on the characteristics of the adsorbent and knowledge of typical adsorption kinetics. Since the adsorbent is a river sediment, it is composed of a combination of silt, sand and natural organic material. This material is known to be porous, thus the model must include intramolecular diffusion and adsorption as well as the surface phenomena. As model development continues, it may become apparent that the effects of one or more of these steps may be insignificant when compared to the others. The steps include:

- 1.) Bulk transport - transfer of material from liquid bulk solution to the liquid surface film surrounding the particle. In a well mixed solution, this step is normally rapid and not rate limiting.
- 2.) Film transport - transfer of the material through the surface film to the adsorbent particle surface through a layer (film) of quiescent liquid near the particle surface.
- 3.) Surface adsorption - adsorption of material on to the surface of the adsorbent particle.
- 4.) Pore diffusion - transport of the adsorbate from the particle surface to the intramolecular pore spaces. This can be both axial (directly into the pore from the surface) or radial (outward diffusion from the center of the pore to the pore wall)
- 5.) Pore adsorption - adsorption of diffused material on to the walls of the pores.

In order to develop a model to reasonably simulate a natural system, several assumptions must first be made about the system. These are based on knowledge of similar systems and on experimental controls which will simplify the system.

The first assumption is that both the transport and adsorption steps are reversible. In terms of adsorption, this means that there is no hysteresis of the material. Since this is a kinetic model, it must be calibrated for both a forward and reverse rate constant for the adsorption process. The reaction will be treated as a first order reaction based on the following equation:



For the transport processes, the rates will be assumed equal for both the forward and reverse direction.

As stated above, the adsorbent is assumed to be a porous media. In addition, all adsorption sites will be assumed as the same - both internal and external. Therefore, the reaction rate constants are assumed to be the same in the pores as on the particle surface. The model will be developed on a surface area site concentration basis. The concentration of sites on the surface and in the pores will be treated as separate and distinct. Any difference between internal and external adsorption will be controlled by the difference in concentrations due to pore diffusion and the variation in site concentration.

Mathematical Development

This section will present the mathematical formulation of each of the 5 transport and adsorption steps listed above. These will then be incorporated into the differential equations to be solved in the model.

First, both the bulk and film diffusion steps are based on Fick's First Law. For the bulk solution:

$$J = \frac{V_B}{A_B} \frac{dC_B}{dt} = k_B (C_{B0} - C_B) \quad (A)$$

where J =Flux from bulk solution (M/L^2-t)
 V_B =Bulk solution volume (L^3)
 A_B =Cross sectional area (L^2)
 k_B =Bulk mass transfer coefficient (L/t)
 C_{B0} =Initial bulk solution concentration (M/L^3)
 C_B =Bulk solution concentration (M/L^3)

Similarly, for the film solution transfer to the particle surface:

$$J = \frac{V_F}{A_F} \frac{dC_F}{dt} = k_F (C_B - C_F) \quad (B)$$

where J =Flux from film solution (M/L^2-t)

V_F = Film solution volume (L^3)

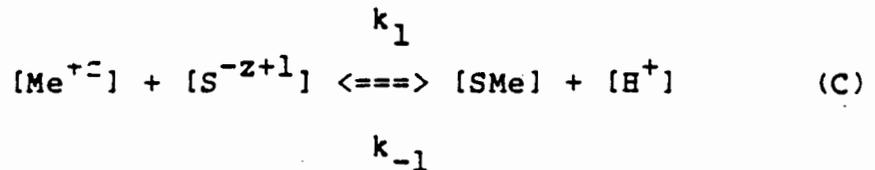
A_F = Film cross sectional area (L^2)

k_F = Film mass transfer coefficient (L/t)

C_B = Film solution concentration (M/L^3)

C_F = Surface solution concentration (M/L^3)

Next is the formulation of the equation for the adsorption process. This is based on the previously discussed equation for adsorption. However, from the initial experimental data it has been shown that the pH of the system may be a governing factor, so a hydrogen ion term is included in the equation.



where $[Me^{+z}]$ = Metal concentration
 $[S^{-z+1}]$ = Site concentration
 $[SMe]$ = Adsorbed concentration
 $[H^+]$ = Hydrogen ion concentration
 k_1 = Forward rate constant
 k_{-1} = Reverse rate constant

The rate mechanism for this process can be expressed as

$$\frac{d[Me^{+z}]}{dt} = -k_1 [Me^{+z}] [S^{-z+1}] + k_{-1} [SMe] [H^+] \quad (D)$$

Finally, the diffusion of metal ions into the pore spaces must be accounted for. This is based on the equation for a solute diffusing into a sphere (Crank, 1975).

$$\frac{dC_p}{dt} = \frac{D}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_p}{dr} \right) \quad (E)$$

Combining these equations, a system of differential equations is developed which will be used in the computer model. The differential equations are as follows:

$$V_B \frac{dC_B(t)}{dt} = V_T \left\{ \frac{A_S}{V_S} k_M [C_F(t) - C_B(t)] \right\} \quad (1)$$

$$V_F \frac{dC_F(t)}{dt} = V_T \left\{ \frac{A_S}{V_S} [k_M (C_B(t) - C_F(t)) - k_1 C_F(t) S_S + k_{-1} C_{AS}(t) [H^+]] \right\} \quad (2)$$

$$A_S \frac{dC_{AS}(t)}{dt} = V_T \left\{ \frac{A_S}{V_S} [k_1 C_F(t) S_S - k_{-1} C_{AS}(t) [H^+]] \right\} \quad (3)$$

$$V_P \frac{dC_P(r,t)}{dt} = V_T \left\{ \frac{D}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_P(r,t)}{dr} \right) + \frac{A_P}{V_P} [-k_1 C_P(r,t) S_P + k_{-1} C_{AP}(r,t) [H^+]] \right\} \quad (4)$$

$$A_P \frac{dC_{AP}(r,t)}{dt} = V_T \left\{ \frac{A_P}{V_P} [k_1 C_P(r,t) S_P - k_{-1} C_{AP}(r,t) [H^+]] \right\} \quad (5)$$

where $C_B(t)$ = Bulk concentration (M/L^3)

$C_F(t)$ = Film concentration (M/L^3)

k_F = Film mass transfer coefficient (L/t)

$C_P(r,t)$ = Pore concentration (M/L^3)

D = Pore diffusion coefficient (L^2/t)

R = Particle radius (L)

k_1 = Forward rate constant ($L^3/M-t$)

k_{-1} = Reverse rate constant ($L^3/M-t$)

$S_S(t)$ = Site density at the surface (Sites/L²)

S_{ST} = Total site density at the surface (Sites/L²)

$S_P(r,t)$ = Site density in the pore (Sites/L³)

S_{PT} = Total site density in the pore (Sites/L³)

$C_{AS}(t)$ = Concentration of material adsorbed at surface
(M/L²)

$C_{AP}(r,t)$ = Concentration of material adsorbed in the pore
(M/L²)

V_F = Volume of the film layer (L³)

A_S = Surface area of the solid (L²)

V_P = Volume of the pores (L³)

A_P = Surface area of the pores (L²)

V_T = Total volume (L³)

$$\text{and } S_S(t) = S_{ST} \cdot C_{AS}(t)$$

$$S_P(r,t) = S_{PT} - C_{AP}(r,t)$$

The initial conditions for the equations are:

$$C_B(0) = C_{B0}$$

$$V_F C_F(0) + A_S C_{AS}(0) + \frac{3}{R^3} \frac{d}{dt} \int_0^R \{C_P(r,0) + (A_P/V_P) C_{AP}(r,0)\} r^2 dr = \text{Const}$$

$$C_P(r,0) = C_{AP}(r,0) = 0$$

The boundary conditions are:

$$\frac{3}{R^3} \frac{d}{dt} \int_0^R \{C_P(r,t) + (A_P/V_P) C_{AP}(r,t)\} r^2 dr = \frac{A_F}{V_F} \{k_F [C_B - C_F(t)]\}$$

$$\frac{dC_p(0,t)}{dr} = \frac{dC_{AP}(0,t)}{dr} = 0$$

$$C_p(R,t) = C_F(t)$$

For the purposes of this model, it will be assumed that the bulk solution is well mixed and that C_B is a constant throughout the bulk solution. Equation (1) is a simple expression of the mass transfer term. Equation (2) describes the reactions in the Film layer. Material is diffusing across the film layer and subsequently adsorbing at the particle surface. The next equation (3) represents the mass balance on adsorption at the particle surface, while Equation (4) takes into account pore diffusion and adsorption onto the wall of the pore. The final equation (5) is a mass balance on the activity at the pore wall surface.

Since Equation (4) is parabolic, the system of equations will be solved using the Crank-Nicholson technique. This is an implicit finite difference technique and has been proven to be unconditionally stable for parabolic partial differential equations. Also, the error is relatively small, $O(\kappa^2 : h^2)$. (Budden and Faires, 1985)

Some assumptions must be made to solve this system of equations. As indicated in the boundary conditions, it is assumed that the Film concentration is the same as the pore concentration at $r=R$. Also, the initial concentrations of both dissolved (C_p) and adsorbed (C_{AP}) material in the pores is negligible compared to the surface adsorbed concentration (C_{AS}) and the bulk concentration (C_B). Finally, the adsorption site densities of the previous time step will be used to simplify the solution.

REFERENCES

1. Black, C.A. 1965. Methods of soil analysis. American Society of Agronomy. Madison, WI.
2. Bonner, J.S. 1983. The vertical transport and aggregation tendency of freshwater phytoplankton. PhD. dissertation. Clarkson University, Potsdam, NY.
3. Crank, J. 1975. The Mathematics of Diffusion. Second Edition, Oxford University Press, Oxford, England. 414 pp.
4. DePinto, J.V., T.C. Young, R.L. Autenrieth, and T.W. Kipp. 1986. Interactions of heavy metals and organics with particulate matter from the lower Raisin River, Michigan. Final report for project No. CR810776, Large Lakes Research Station, ERL-Duluth, Grosse Ile, MI.
5. Fukuda, M.K. and W. Lick. 1980. The entrainment of cohesive sediments in freshwater. J. Geophysical Res. 85:J(C5): 2813-2824.
6. Great Lakes Water Quality Board. 1981. 1981 Report on Great Lakes Water Quality. Report to the International Joint Commission, Windsor, Ontario. 74 pp.
7. Great Lakes Water Quality Board. 1981a. 1981 Report on Great Lakes Water Quality. Appendix: Great Lakes Surveillance. Report to International Joint Commission, Windsor, Ontario. 174 pp.
8. Great Lakes Water Quality Board. 1982. Annual Report on Great Lakes Water Quality. Report to International Joint Commission, Windsor, Ontario. 153 pp.
9. Great Lakes Water Quality Board. 1983. Annual Report on Great Lakes water Quality. Report to International Joint Commission, Windsor, Ontario.
10. Great Lakes Human Health Effects Committee. 1982. Annual Report on Assessment of Human Health Effects of Great Lakes Water Quality. Report to Great Lakes Water Quality Board/Science Advisory Board, IJC, Windsor, Ontario. 88 pp.
11. McCann, M.J. 1986. Sorption kinetics of hydrophobic compounds on Gamma Aluminum Oxide. M.S. Thesis. Clarkson University, Potsdam, NY.
12. Nriagu, J.O. and M.S. Simmons (eds.). 1984. Toxic contaminants in the Great Lakes. John Wiley & Sons, New York.

13. Polemio, M. and J.D. Rhoades. 1977. Determining cation exchange capacity: a new procedure for calcareous and gypsiferous soils. Soil Sci. Soc. Am. Jour. 41: 524-528.
14. Toxic Substances Committee. 1981. Toxic Substances Control Programs in the Great Lakes Basin. Report to the Great Lakes Water Quality Board, IJC, Windsor, Ontario. 94 pp.
15. Tsai, C-H and W. Lick. 1986. A portable device for measuring sediment resuspension. J. Great Lakes Res. 12(4): 314-321.

APPENDIX A

Appendix A. Sediment Survey Analyses

serv. No.	Non-Metals			Phys. Variables				Percent With Diameter Less Than (um):											
	CEC (meq/g)	TC (%)	IC (%)	TOC (%)	Sp.Gr.	H2O (%)	LOI (%)	710	500	355	250	180	125	90	63	20	10	5	1
1	0.623	2.9	0.7	2.2	2.29	35.97	3.8	90.27	83.05	72.62	59.50	37.94	18.33	14.53	12.30	9.92	8.50	8.00	7.15
2																			
3	0.583	2.2	0.4	1.8	2.31	25.92	2.1	92.17	82.10	69.38	55.29	34.20	29.89	16.69	14.73	12.98	11.66	11.15	10.17
4																			
5	0.623	5.3	0.2	5.1	2.41	10.70	5.1	96.21	94.55	92.99	88.82	86.94	30.92	29.48	26.04	21.53	20.15	19.14	18.13
6																			
7	2.05	9.9	0.6	9.3	2.75	58.34	12.2												
8	0.885	7.5	1.1	6.4	2.65	51.11	9.0	96.53	96.01	93.85	91.74	89.43	74.60	73.20	71.12	68.90	64.00	56.64	55.51
9	0.975	8.6	1.4	7.2	2.63	54.20	10.0	99.77	99.64	99.67	99.33	98.97	98.03	95.66	95.57	88.31	84.53	82.93	83.21
10		8.9	1.4	7.5															
11	1.11	9.1	1.2	7.9	2.70	61.07	10.6	99.35	99.30	99.20	97.95	97.64	96.85	96.84	92.21	92.19	92.10	88.32	85.52
12	0.815	7.9	1.8	6.1	2.46	26.33	8.5	99.86	99.59	99.54	98.56	90.63	83.73	79.19	78.59	77.37	75.63	73.50	72.13
13																			
14																			
15	1.671	10.6	0.6	10.0	2.79	55.31	11.6	99.36	99.29	99.13	98.80	98.40	98.31	97.00	96.91	91.12	83.76	82.73	81.93
16																			
17																			
18	0.555	2.2	0.5	1.7	2.49	16.73	2.9	99.93	99.35	91.21	61.17	61.00	60.07	57.86	57.72	52.14	51.06	50.44	50.02
19	0.363	2.5	0.6	1.9	2.32	30.28	2.7	99.97	97.04	97.81	93.24	91.56	85.57	84.51	74.49	79.32	69.04	67.15	52.44
20	1.118	3.9	1.0	2.5	2.43	33.61	4.1	99.95	99.81	98.80	98.00	96.41	95.84	93.84	90.11	83.11	69.09	62.28	59.08
21	0.333	5.1	0.7	4.4	2.60	43.81	5.7	99.96	94.05	98.09	28.06	27.97	19.50	11.15	11.77	10.65	10.23	9.86	9.56
22		2.9	0.4	4.5															
23	0.523	2.0	0.7	1.3	2.37	34.43	2.4	99.99	99.92	99.37	99.62	98.90	91.70	88.20	52.85	46.47	41.26	36.99	36.19
24																			
25																			
26	0.983	4.0	1.1	2.9	2.29	35.56	3.5	99.50	99.85	99.63	98.94	96.44	86.00	80.87	76.55	62.40	53.47	47.56	43.76
27	0.623	2.7	0.8	1.9	2.31	27.56	4.4	99.98	99.95	99.80	99.01	99.12	73.26	47.77	47.25	46.00	46.52	46.12	45.28
28	0.788	3.2	1.0	2.2	2.47	29.70	2.7	99.85	99.75	99.45	98.69	97.87	83.84	74.43	64.71	59.04	53.18	44.46	41.33
29	0.733	6.5	0.5	6.3	2.43	53.21	8.1	99.98	99.87	99.78	99.44	98.51	97.77	87.05	65.99	59.07	52.93	48.22	45.33
30																			
31	0.798	5.7	0.9	4.8	2.41	51.81	6.6	99.81	99.00	97.11	96.02	93.17	92.87	92.54	83.11	76.24	68.91	68.02	67.04
32		5.5	0.8	4.7															
33	0.888	3.6	0.9	2.7	2.45	33.17	4.3	99.98	99.05	98.83	98.86	98.75	98.48	85.71	80.11	79.92	77.07	77.14	75.90
34	0.708	2.9	0.9	2.0	2.48	30.87	2.5	99.79	98.48	98.34	98.27	97.86	97.79	96.76	94.97	93.73	89.19	87.68	85.96
35		3.0	0.7	2.3															
36	1.628	1.7	0.7	1.0	2.45	36.88	1.3	99.90	98.16	95.46	95.22	93.89	91.30	91.04	88.96	81.12	76.98	76.05	73.40
37																			
38	1.04	2.3	1.1	1.2	2.28	27.87	2.3	99.90	99.34	98.00	96.93	96.28	92.72	79.76	78.52	77.97	77.38	75.80	74.04
39																			
40	0.878	2.6	1.0	1.6	2.21	35.94	2.7	99.95	99.54	99.08	98.03	95.45	93.23	89.80	81.36	78.27	76.55	74.75	71.22
41		2.3	1.2	1.1															
42	0.518	4.4	1.9	2.5	2.40	34.86	4.8	99.89	99.77	98.84	96.52	80.02	79.94	79.28	78.04	71.89	69.08	66.76	66.09
43																			
44	0.555	4.6	1.7	2.9	2.42	33.39	4.4	99.85	99.64	98.57	94.37	77.50	77.33	77.09	76.41	75.73	72.77	71.04	70.18
45																			
46	1.128	10.3	1.9	8.4	2.65	76.01	13.1	99.94	99.86	99.73	99.45	99.21	98.69	98.17	97.42	95.98	93.39	90.94	89.30
47	0.905	9.8	2.5	7.3	2.35	33.16	11.8	99.94	99.82	99.78	99.73	99.40	97.67	86.78	84.56	84.24	80.64	80.54	79.98
48	0.908	10.7	1.8	8.9	2.77	51.08	9.2	99.02	97.40	95.53	95.28	95.03	93.45	92.41	91.54	90.99	89.42	81.77	75.93
49																			

Appendix A. Sediment Survey Analyses

Observ. No.	Sample Site	Sample Repl.	Analyt. Repl.	Total Metals (mg/kg)							Pore Water Metals (ug/L)						
				Cd	Co	Cr	Cu	Ni	Pb	Zn	Cd	Co	Cr	Cu	Ni	Pb	Zn
1	25	1	1	2.1	12.0	25	19.7	20.0	15	71	1.9	0.0	0.4	3.3	8.4	1.0	11.3
2	25	1	2	2.2	0.0	0.4	3.3	8.2	2.1	12.3
3	25A	1	1	2.1	11.6	39	23.5	21.3	29	140	2.6	1.5	0.3	3.7	3.7	3.4	9.0
4	29	1	1	14.9	3.4	2.0	28.2	32.3	1.0	24.8
5	30AC	1	1	3.6	17.3	49	37.1	34.7	56	188	2.2	0.0	0.7	2.5	10.9	1.0	13.9
6	30CR	1	2	17.1	1.1	1.9	4.7	42.9	1.3	14.3
7	30CR	1	1	18.6	11.2	389	186.1	112.2	440	4080	15.4	0.7	1.3	4.5	43.5	1.8	13.5
8	30UP	1	1	10.3	24.5	111	93.1	100.2	148	594	17.0	1.3	1.1	3.7	7.6	5.3	13.7
9	30	1	1	25.7	30.2	87	112.8	62.2	176	596	1.2	8.5	2.5	6.1	48.4	1.0	26.0
10	30	1	2	24.7	29.0	88	114.0	64.6	174	560
11	30	2	1	23.7	19.2	93	107.0	67.0	182	532	1.6	14.0	2.2	5.3	42.5	1.0	27.7
12	32	1	1	4.6	16.2	81	65.1	56.6	73	246	6.3	1.5	1.0	4.7	4.6	8.5	29.8
13	32	1	2	5.9	1.7	1.1	4.1	5.9	8.5	31.2
14	33	1	1	17.3	0.3	0.0	10.9	11.5	3.7	10.5
15	34	1	1	27.8	16.6	213	94.4	62.2	248	3920	16.5	14.2	2.2	0.9	6.0	13.7	16.7
16	34	1	2	14.6	12.2	2.1	1.5	4.8	16.1	18.5
17	41	1	2	1.0	1.3	1.3	17.2	6.4	6.4	5.7
18	41	1	1	2.6	17.2	28	27.4	30.9	10	72	0.9	0.1	1.0	17.4	5.8	6.9	5.3
19	42	1	1	8.2	16.3	44	19.7	71.3	58	330	3.4	0.7	1.1	3.1	8.4	1.0	12.2
20	43	1	1	6.7	16.6	107	72.8	64.5	110	172	4.2	0.0	1.8	0.7	11.1	4.2	11.3
21	44A	1	1	9.0	17.9	146	30.0	98.8	110	645	14.3	0.7	1.7	5.5	14.6	7.7	11.7
22	44A	1	2	7.3	16.3	158	34.1	107.1	114	660
23	45	1	1	26.3	17.8	36	19.7	25.1	15	121	1.2	1.1	2.3	22.6	19.2	9.9	39.0
24	45	1	2	1.1	1.5	2.3	24.2	20.1	13.7	42.3
25	47	1	2	1.1	1.5	1.1	20.7	13.5	7.8	9.3
26	47	1	1	41.0	13.6	55	27.8	33.8	30	177	5.0	1.1	1.1	19.6	13.3	4.8	11.1
27	49	1	1	1.6	7.7	23	13.0	33.8	36	180	13.3	0.9	0.9	3.5	6.7	5.3	15.3
28	51	1	1	6.2	10.6	32	20.7	25.1	15	104	2.3	0.5	0.8	6.7	10.5	1.5	13.3
29	52	1	1	9.3	16.0	155	50.1	60.0	96	372	1.6	1.5	0.8	58.7	8.0	25.6	12.3
30	52	1	2	2.0	1.5	0.9	57.9	7.0	27.5	10.5
31	53	1	1	6.2	11.7	105	41.4	43.2	52	384	4.1	0.3	1.6	5.5	6.2	3.1	10.5
32	53	1	2	6.2	11.7	103	44.7	43.2	50	372
33	54	1	1	9.3	16.0	102	68.9	68.5	97	564	27.2	0.9	0.7	4.3	6.0	3.1	2.6
34	59A	1	1	7.7	11.3	71	40.0	27.6	78	272	1.3	0.5	0.8	3.1	7.0	6.4	11.3
35	59A	1	2	6.7	12.9	70	35.0	25.4	72	266
36	77	1	1	11.3	15.1	67	40.0	35.9	49	222	6.8	1.3	1.0	1.7	5.4	5.3	25.9
37	77	1	2	5.3	2.0	1.1	2.1	7.4	1.0	22.7
38	82	1	1	2.1	9.4	25	14.9	21.6	57	720	0.8	0.9	0.8	4.1	5.2	1.0	11.1
39	82	1	2	1.2	0.7	0.8	3.7	5.0	1.0	11.9
40	82	2	1	1.6	13.0	25	13.0	20.4	55	688	10.3	0.9	1.3	10.9	9.7	1.5	7.3
41	82	2	2	1.0	11.7	26	11.4	19.6	52	676	9.4	0.7	1.7	10.5	8.6	1.8	7.6
42	83	1	1	8.2	4.5	104	61.2	41.9	83	351	2.2	0.5	0.7	4.5	4.6	6.9	17.5
43	83	1	2	2.5	0.5	0.8	3.7	5.2	6.9	16.3
44	83	2	1	9.3	5.2	114	66.0	48.0	93	386	14.3	0.9	0.9	28.0	35.6	5.3	13.7
45	83	2	2	17.7	0.7	1.1	28.6	22.9	6.9	13.6
46	104	1	1	19.6	12.3	205	87.3	175.0	172	1200	1.0	0.9	0.7	2.1	2.1	11.0	14.6
47	105	1	1	6.0	24.3	95	52.5	93.2	83	318	5.1	0.0	1.8	5.7	11.5	6.7	25.7
48	107	1	1	13.4	30.1	201	147.6	83.8	448	1136	1.5	0.1	0.9	0.9	17.0	3.1	20.7
49	107	1	2	2.0	0.3	0.8	1.1	17.8	3.7	22.7

(Continued)

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 QUALITATIVE SEDIMENT SURVEY
 SAMPLING DATE, MAY 13 -17, 1986

STATION NO.	DESCRIPTION
25	SANDY WITH PEBBLES, GRAY-BROWN
25A	NO SAMPLE COLLECTED (SOME PEBBLES)
29	
10AC	SAND WITH SILT AND PEBBLES, SEPTIC ODOR
10CR	SILTY, GRAY-BLACK, VERY STRONG OILY ODOR
10UP	TWO STRATIFIED LAYERS OF SAND AND SILTY CLAY, SOME PEBBLES PRESENT, GRAY, VERY OILY SMELL
10	GELATINOUS GRAY SANDY-SILT, OILY ODOR
12	BROWN-GREY SAND WITH SOME SILT, STONES AND PEBBLES, SHELLS PRESENT
13	
14	GELATINOUS SILT, OILY SLICKS AND SMELL, LARGE AMOUNTS OF ENTRAPPED GAS
18	NO SAMPLE COLLECTED (SMALL AMOUNT SAND AND PEBBLES)
41	CLAY AND SAND WITH SOME PEBBLES, MOLLUSK AND SNAIL SHELLS PRESENT, INSECT LARVAE PRESENT
42	SILTY-SAND WITH PEBBLES, OILY SLICKS AND SMELL, ENTRAPPED GASES PRESENT
43	SANDY WITH PEBBLES, SOME OILY SLICKS, EARTHY SMELL
44A	SILTY-SAND WITH CLAY, VEGETATION PRESENT
45	SANDY WITH LARGE PEBBLES AND SOME CLAY, EARTHY SMELL
47	SILT AND CLAY WITH SOME SAND, LARGE AMOUNTS OF VEGETATION
49	SILTY SAND, EARTHY SMELL, LARGE AMOUNTS OF VEGETATIVE DETRITUS, SOME NEW VEGETATION PRESENT
49A	NO SAMPLE COLLECTED (SOME PEBBLES)
51	SANDY SILT, EARTHY SMELL, LIVING AND DEAD VEGETATION
52	SILTY CLAY, SLIGHT OILY SMELL, SHELLS PRESENT
52A	NO SAMPLE COLLECTED
53	SILTY, GRAY-BROWN, OILY MALODOROUS SMELL, SHELLS PRESENT
54	SANDY, GRAY-BROWN, OILY SMELL, SHELLS PRESENT
54A	NO SAMPLE COLLECTED
59A	SANDY, GRAY, MILD OILY SMELL, SHELLS PRESENT
77	BROWN SILTY SAND, VEGETATION PRESENT, EARTHY SMELL
82	SANDY-CLAY, SHELLS AND VEGETATION PRESENT
83	SANDY-CLAY, WORMS AND VEGETATION PRESENT
104	BLACK SILT, OIL SLICKS AND OILY SMELL
105	DARK BROWN CLAY (IN GLOBULAR MASSES), OILY SMELL
107	CLAY WITH SILT, OILY SLICKS AND SMELL

APPENDIX B

APPENDIX B

KENDALL TAU B CORRELATION COEFFICIENTS
 / PROB > |R| UNDER H0:RHO=0 / NUMBER OF OBSERVATIONS

	TCD	TCO	TCR	TCU	TNI	TPB	TZN
TCD	1.00000 0.0000 34	0.25522 0.0362 34	0.46017 0.0002 34	0.50093 0.0000 34	0.41163 0.0007 34	0.48321 0.0001 34	0.29323 0.0161 34
TCO	0.25522 0.0362 34	1.00000 0.0000 34	0.18979 0.1159 34	0.32646 0.0069 34	0.36738 0.0024 34	0.33932 0.0050 34	0.09481 0.4318 34
TCR	0.46017 0.0002 34	0.18979 0.1159 34	1.00000 0.0000 34	0.59426 0.0000 34	0.42122 0.0000 34	0.61456 0.0000 34	0.47628 0.0001 34
TCU	0.50093 0.0000 34	0.32646 0.0069 34	0.59426 0.0000 34	1.00000 0.0000 34	0.56421 0.0000 34	0.63186 0.0000 34	0.35157 0.0036 34
TNI	0.41163 0.0007 34	0.36738 0.0024 34	0.62422 0.0000 34	0.56421 0.0000 34	1.00000 0.0000 34	0.58273 0.0000 34	0.41756 0.0005 34
TPB	0.48321 0.0001 34	0.33932 0.0050 34	0.61456 0.0000 34	0.63186 0.0000 34	0.58273 0.0000 34	1.00000 0.0000 34	0.61580 0.0000 34
TZN	0.29323 0.0161 34	0.09481 0.4318 34	0.47628 0.0001 34	0.35157 0.0036 34	0.41756 0.0005 34	0.61580 0.0000 34	1.00000 0.0000 34
PCD	-0.00467 0.9715 30	-0.01387 0.9147 30	0.16222 0.2112 30	0.09756 0.4530 30	0.15759 0.2245 30	0.16047 0.2175 30	0.17110 0.1864 30
PCO	0.36277 0.0071 30	0.10855 0.4170 30	0.10638 0.4272 30	0.12117 0.3668 30	0.06528 0.6262 30	0.15528 0.2479 30	0.18574 0.1649 30
PCR	0.24646 0.0643 30	0.30581 0.0207 30	0.09742 0.4619 30	0.14052 0.2896 30	0.17821 0.1784 30	0.18121 0.1725 30	0.16357 0.2159 30
PCU	-0.01636 0.9004 30	-0.12269 0.3439 30	-0.12297 0.3437 30	-0.19767 0.1287 30	-0.16009 0.2177 30	-0.20489 0.1157 30	-0.05324 0.6813 30
PNI	0.25409 0.0513 30	0.24711 0.0561 30	0.13657 0.2920 30	0.14385 0.2680 30	0.14120 0.2760 30	0.19512 0.1334 30	0.07621 0.5558 30
PPB	0.17270 0.1951 30	-0.02139 0.8715 30	0.30965 0.0194 30	0.10027 0.4501 30	0.17864 0.1776 30	0.05259 0.6924 30	-0.01188 0.9284 30

KENDALL TAU B CORRELATION COEFFICIENTS
 / PROB > |R| UNDER H0:RHO=0 / NUMBER OF OBSERVATIONS

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	TCD	TCO	TCR	TCU	TNI	TPB	TZN
PZN	0.36215 0.0056 30	0.14583 0.2605 30	0.16937 0.1921 30	0.30465 0.0192 30	0.22970 0.0769 30	0.23283 0.0738 30	0.02546 0.8443 30
CEC	0.29428 0.0266 29	0.14815 0.2602 29	0.26733 0.0426 29	0.39206 0.0030 29	0.21287 0.1065 29	0.38214 0.0038 29	0.38025 0.0039 29
TC	0.36053 0.0031 34	0.29364 0.0150 34	0.54301 0.0000 34	0.60144 0.0000 34	0.53812 0.0000 34	0.60378 0.0000 34	0.37959 0.0017 34
IC	0.06506	-0.00367	0.09010	0.23211	0.09		

KENDALL TAU B CORRELATION COEFFICIENTS
/ PROB > |R| UNDER H0:RHO=0 / NUMBER OF OBSERVATIONS

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	TCD	TCO	TCR	TCU	TNI	TPB	TZN
PZN	0.36215 0.0056 30	0.14583 0.2605 30	0.16937 0.1921 30	0.30465 0.0192 30	0.22970 0.0769 30	0.23283 0.0738 30	0.02546 0.8443 30
CEC	0.29428 0.0266 29	0.14815 0.2602 29	0.26733 0.0426 29	0.39206 0.0030 29	0.21287 0.1065 29	0.38214 0.0038 29	0.38025 0.0039 29
TC	0.36053 0.0031 34	0.29364 0.0150 34	0.54501 0.0000 34	0.60144 0.0000 34	0.53812 0.0000 34	0.60378 0.0000 34	0.37959 0.0017 34
IC	0.06506 0.6014 34	-0.00367 0.9762 34	0.09010 0.4653 34	0.23211 0.0604 34	0.09939 0.4210 34	0.22679 0.0662 34	0.18005 0.1443 34
SG	0.45421 0.0007 29	0.30560 0.0209 29	0.51557 0.0001 29	0.60175 0.0000 29	0.50561 0.0001 29	0.54182 0.0000 29	0.35529 0.0072 29
H2O	0.51560 0.0001 29	0.14550 0.2663 29	0.48702 0.0002 29	0.39902 0.0025 29	0.34364 0.0091 29	0.47832 0.0003 29	0.44143 0.0008 29
LOI	0.31290 0.0187 29	0.28501 0.0308 29	0.50932 0.0001 29	0.52055 0.0001 29	0.58385 0.0000 29	0.53549 0.0001 29	0.41984 0.0015 29
D710	0.05413 0.6917 28	-0.10710 0.4285 28	-0.06175 0.6488 28	-0.26649 0.0498 28	0.04027 0.7665 28	-0.12113 0.3726 28	-0.01874 0.8898 28
D63	0.34541 0.0107 28	0.19868 0.1383 28	0.29482 0.0282 28	0.43410 0.0013 28	0.32138 0.0168 28	0.42344 0.0017 28	0.37881 0.0047 28
D1	0.25437 0.0600 28	0.13510 0.3136 28	0.23639 0.0785 28	0.41279 0.0022 28	0.33201 0.0135 28	0.43410 0.0013 28	0.48477 0.0003 28

KENDALL TAU B CORRELATION COEFFICIENTS
 / PROB > |R| UNDER H0:RHO=0 / NUMBER OF OBSERVATIONS

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	PCD	PCO	PCR	PCU	PNI	PPB	PZN
TCD	-0.00467	0.36277	0.24646	-0.01636	0.25409	0.17270	0.36215
	0.9715	0.0071	0.0643	0.9004	0.0513	0.1951	0.0056
	30	30	30	30	30	30	30
TCO	-0.01387	0.10855	0.30581	-0.12269	0.24711	-0.02139	0.14583
	0.9147	0.4170	0.0207	0.3439	0.0561	0.8715	0.2605
	30	30	30	30	30	30	30

KENDALL TAU B CORRELATION COEFFICIENTS
 / PROB > |R| UNDER H0:RHO=0 / NUMBER OF OBSERVATIONS

	PCD	PCO	PCR	PCU	PNI	PPB	PZN
TCR	0.16222 0.2112 30	0.10638 0.4272 30	0.09742 0.4619 30	-0.12297 0.3437 30	0.13657 0.2920 30	0.30965 0.0194 30	0.16937 0.1921 30
TCU	0.09756 0.4530 30	0.12117 0.3668 30	0.14052 0.2896 30	-0.19767 0.1287 30	0.14385 0.2680 30	0.10027 0.4501 30	0.30465 0.0192 30
TNI	0.15759 0.2245 30	0.06528 0.6262 30	0.17821 0.1784 30	-0.16009 0.2177 30	0.24120 0.2750 30	0.17864 0.1776 30	0.22970 0.0769 30
TPB	0.16047 0.2175 30	0.15528 0.2479 30	0.18121 0.1725 30	-0.20489 0.2157 30	0.19512 0.1324 30	0.05259 0.6924 30	0.23283 0.0758 30
TZN	0.17110 0.1864 30	0.18574 0.1649 30	0.16357 0.2159 30	-0.05324 0.6813 30	0.07621 0.5558 30	-0.01188 0.9284 30	0.02546 0.8443 30
PCD	1.00000 0.0000 45	0.09910 0.3546 45	0.13864 0.1938 45	0.02148 0.8370 45	0.11202 0.2815 45	0.02197 0.8352 45	-0.03064 0.7689 45
PCO	0.09910 0.3546 45	1.00000 0.0000 45	0.34835 0.0015 45	0.16066 0.1343 45	-0.02315 0.8285 45	0.16757 0.1250 45	0.18575 0.0830 45
PCR	0.13864 0.1938 45	0.34835 0.0015 45	1.00000 0.0000 45	0.15163 0.1562 45	0.32284 0.0024 45	0.05924 0.5863 45	0.24707 0.0207 45
PCU	0.02148 0.8370 45	0.16066 0.1343 45	0.15163 0.1562 45	1.00000 0.0000 45	0.24400 0.0193 45	0.13952 0.1903 45	-0.15054 0.1498 45
PNI	0.11202 0.2815 45	-0.02315 0.8285 45	0.32284 0.0024 45	0.24400 0.0193 45	1.00000 0.0000 45	-0.20571 0.0525 45	0.12232 0.2400 45
PPB	0.02197 0.8362 45	0.16757 0.1250 45	0.05924 0.5863 45	0.13952 0.1903 45	-0.20571 0.0525 45	1.00000 0.0000 45	0.12150 0.2534 45
PZN	-0.03064 0.7689 45	0.18575 0.0830 45	0.24707 0.0207 45	-0.15054 0.1498 45	0.12232 0.2400 45	0.12150 0.2534 45	1.00000 0.0000 45
CEC	0.09665 0.4640 29	0.17073 0.2104 29	0.20593 0.1265 29	-0.22829 0.0841 29	0.06436 0.6255 29	-0.09432 0.4843 29	0.12407 0.3477 29

KENDALL TAU B CORRELATION COEFFICIENTS
/ PROB > |R| UNDER H0:RHO=0 / NUMBER OF OBSERVATIONS

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	PCD	PCO	PCR	PCU	PNI	PPB	PZN
TC	0.08806 0.4973 30	0.07011 0.6008 30	0.13544 0.3065 30	-0.10441 0.4215 30	0.22454 0.0832 30	0.13101 0.3229 30	0.33411 0.0101 30
IC	-0.04514 0.7332 30	-0.01239 0.9278 30	0.08770 0.5165 30	0.09515 0.4729 30	0.07120 0.5905 30	0.01954 0.8852 30	0.20695 0.1184 30
SG	0.03990 0.7637 29	0.15357 0.2625 29	0.19442 0.1513 29	-0.15231 0.2516 29	0.11208 0.3979 29	0.18468 0.1731 29	0.23221 0.0805 29
H2O	0.03941 0.6523 29	0.25578 0.0603 29	0.27932 0.0390 29	-0.01239 0.9252 29	0.22003 0.0949 29	0.06110 0.6501 29	0.16605 0.2084 29
LJI	0.11443 0.3875 29	0.05193 0.7047 29	0.20670 0.1263 29	-0.01245 0.3251 29	0.19627 0.1370 29	0.13304 0.3252 29	0.31133 0.0188 29
D710	0.09140 0.5007 28	0.04779 0.7334 28	0.10520 0.3292 28	0.24732 0.0664 28	0.01879 0.8898 28	0.26601 0.0554 28	-0.04576 0.7363 28
D63	-0.10107 0.4525 28	0.09456 0.4964 28	0.28664 0.0359 28	-0.23405 0.0819 28	0.01328 0.9213 28	-0.02193 0.8734 28	0.17843 0.1851 28
D1	-0.05851 0.6636 28	0.14463 0.2982 28	0.16106 0.2410 28	-0.14894 0.2682 28	-0.07171 0.5935 28	0.02741 0.8421 28	0.17843 0.1851 28

KENDALL TAU B CORRELATION COEFFICIENTS
 / PROB > |R| UNDER H0:RHO=0 / NUMBER OF OBSERVATIONS

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	CEC	TC	IC	SG	H2O	LOI	D710
TCD	0.29428 0.0266 29	0.36053 0.0031 34	0.06506 0.6014 34	0.45421 0.0007 29	0.51560 0.0001 29	0.31290 0.0187 29	0.05413 0.6917 28
TCO	0.14815 0.2602 29	0.29364 0.0150 34	-0.00367 0.9762 34	0.30560 0.0209 29	0.14550 0.2683 29	0.28501 0.0308 29	-0.10710 0.4285 28
TCR	0.26733 0.0426 29	0.54301 0.0000 34	0.09010 0.4653 34	0.51557 0.0001 29	0.48702 0.0002 29	0.50932 0.0001 29	-0.06175 0.6483 28
TCU	0.39206 0.0030 29	0.60144 0.0000 34	0.23211 0.0604 34	0.60175 0.0000 29	0.39902 0.0025 29	0.52055 0.0001 29	-0.26645 0.0198 28

KENDALL TAU B CORRELATION COEFFICIENTS
/ PROB > |R| UNDER H0:RHO=0 / NUMBER OF OBSERVATIONS

	CEC	TC	IC	SG	H2O	LOI	D710
TNI	0.21287 0.1065 29	0.53812 0.0000 34	0.09939 0.4210 34	0.50561 0.0001 29	0.34364 0.0091 29	0.58385 0.0000 29	0.04027 0.7665 28
TPB	0.38214 0.0038 29	0.60378 0.0000 34	0.22679 0.0668 34	0.54182 0.0000 29	0.47832 0.0003 29	0.53549 0.0001 29	-0.12113 0.3726 28
TZN	0.38025 0.0039 29	0.37959 0.0017 34	0.18005 0.1443 34	0.35529 0.0072 29	0.44143 0.0008 29	0.41884 0.0015 29	-0.01874 0.8890 28
PCD	0.09665 0.4640 29	0.08806 0.4973 30	-0.04514 0.7332 30	0.03990 0.7637 29	0.05941 0.6573 29	0.11443 0.3875 29	0.09140 0.5007 28
PCO	0.17073 0.2104 29	0.07011 0.6008 30	-0.01239 0.9278 30	0.15357 0.2625 29	0.25578 0.0603 29	0.05193 0.7041 29	0.04779 0.7334 28
PCR	0.20593 0.1255 29	0.13544 0.3065 30	0.08770 0.5165 30	0.19442 0.1513 29	0.27932 0.0380 29	0.20670 0.1263 29	0.13520 0.3293 28
PCU	-0.22829 0.0841 29	-0.10441 0.4215 30	0.09515 0.4729 30	-0.15231 0.2516 29	-0.01239 0.9252 29	-0.01245 0.9251 29	0.24732 0.0684 28
PNI	0.06436 0.6255 29	0.22454 0.0832 30	0.07120 0.5905 30	0.11208 0.3979 29	0.22003 0.0949 29	0.19627 0.1378 29	0.01879 0.8898 28
PPB	-0.09432 0.4843 29	0.13101 0.3229 30	0.01954 0.8852 30	0.18468 0.1731 29	0.06110 0.6501 29	0.13304 0.3253 29	0.26601 0.0554 28
PZN	0.12407 0.3477 29	0.33411 0.0101 30	0.20695 0.1184 30	0.23221 0.0805 29	0.16605 0.2084 29	0.31133 0.0188 29	-0.04576 0.7363 28
CEC	1.00000 0.0000 29	0.36836 0.0052 29	0.21836 0.1048 29	0.24100 0.0685 29	0.35265 0.0073 29	0.30483 0.0209 29	-0.08836 0.5136 28
TC	0.36836 0.0052 29	1.00000 0.0000 34	0.28134 0.0226 34	0.45772 0.0005 29	0.44938 0.0006 29	0.83375 0.0001 29	-0.20912 0.1225 28
IC	0.21836 0.1048 29	0.28134 0.0226 34	1.00000 0.0000 34	0.05365 0.6918 29	0.12426 0.3554 29	0.25995 0.0542 29	-0.02748 0.8424 28

KENDALL TAU B CORRELATION COEFFICIENTS
 / PROB > |R| UNDER H0:RHO=0 / NUMBER OF OBSERVATIONS

	CEC	TC	IC	SG	H2O	LOI	D710
SG	0.24100 0.0685 29	0.45772 0.0005 29	0.05365 0.6918 29	1.00000 0.0000 29	0.33748 0.0107 29	0.44888 0.0007 29	-0.22103 0.1042 28
H2O	0.35265 0.0073 29	0.44938 0.0006 29	0.12426 0.3554 29	0.33748 0.0107 29	1.00000 0.0000 29	0.44060 0.0008 29	-0.05348 0.6923 28
LOI	0.30483 0.0209 29	0.83375 0.0001 29	0.25995 0.0542 29	0.44888 0.0007 29	0.44060 0.0008 29	1.00000 0.0000 29	-0.10753 0.4282 28
D710	-0.08036 0.5136 28	-0.20912 0.1225 28	-0.02748 0.8424 28	-0.22103 0.1042 28	-0.05343 0.6923 28	-0.10753 0.4282 28	1.00000 0.0000 28
D63	0.52185 0.0001 28	0.30239 0.0243 28	0.32621 0.0172 28	0.30401 0.0242 28	0.34921 0.0091 28	0.25532 0.0576 28	-0.06417 0.6348 28
D1	0.46887 0.0005 28	0.31300 0.0197 28	0.39145 0.0042 28	0.30001 0.0176 28	0.25455 0.0482 28	0.30220 0.0242 28	0.05883 0.6633 28
	D63	D1					
TCD	0.34541 0.0107 28	0.25437 0.0600 28					
TCO	0.19868 0.1383 28	0.13510 0.3136 28					
TCR	0.29482 0.0282 28	0.23639 0.0785 28					
TCU	0.43410 0.0013 28	0.41279 0.0022 28					
TNI	0.32138 0.0168 28	0.33201 0.0135 28					
TPB	0.42344 0.0017 28	0.43410 0.0013 28					

KENDALL TAU B CORRELATION COEFFICIENTS
 / PROB > |R| UNDER H0:RHO=0 / NUMBER OF OBSERVATIONS

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	D63	D1
TZN	0.37881 0.0047 28	0.48477 0.0003 28
PCD	-0.10107 0.4525 28	-0.05851 0.6636 28
PCO	0.09456 0.4964 28	0.14463 0.2982 28
PCR	0.23664 0.0369 28	0.16106 0.2410 28
PCU	-0.23405 0.0812 28	-0.14894 0.2682 28
PNI	0.01328 0.9213 28	-0.07171 0.5935 28
PPB	-0.02193 0.8734 28	0.02741 0.8421 28
PZN	0.17843 0.1851 28	0.17843 0.1851 28
CEC	0.52185 0.0001 28	0.46887 0.0005 28
TC	0.30239 0.0243 28	0.31300 0.0197 28
IC	0.32621 0.0172 28	0.39145 0.0042 28
SG	0.30401 0.0241 28	0.32001 0.0176 28
H2O	0.34921 0.0091 28	0.26455 0.0482 28

KENDALL TAU B CORRELATION COEFFICIENTS
 / PROB > |R| UNDER H0:RHO=0 / NUMBER OF OBSERVATIONS

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	D63	D1
LOI	0.25532	0.30320
	0.0576	0.0242
	28	28
D710	-0.06417	-0.05883
	0.6348	0.6633
	28	28
D63	1.00000	0.75661
	0.0000	0.0000
	28	28
D1	0.75661	1.00000
	0.0000	0.0000
	28	28

APPENDIX C

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 5/13/86- 5/17/86

OBS	STATION	EXPER. #	SECONDS/ STROKE	TIME OF SAMPLE min.	SUSPEN. SOLIDS g/L	pH
1	53	1	0.14	0.00	0.06	7.4
2	53	1	0.14	15	0.38	7.6
3	53	2	0.08	0.00	0.16	7.5
4	53	2	0.08	0.5	1.31	.
5	53	2	0.08	7	4.26	.
6	53	2	0.08	15	4.6	7.51
7	53	3	0.14	0.0	0.06	7.5
8	53	3	0.14	15	0.47	7.65
9	53	4	0.08	0.0	0.11	7.68
10	53	4	0.08	15	1.93	7.79
11	83	5	0.14	0.0	0.46	.
12	83	5	0.14	15	0.55	.
13	83	6	0.08	0.0	0.58	.
14	83	6	0.08	15	0.76	.
15	83	7	0.14	0.0	0.60	.
16	83	7	0.14	15	0.66	.
17	83	8	0.08	0.0	0.51	.
18	83	8	0.08	15	0.90	.
19	30	9	0.14	0.0	1.5	.
20	30	9	0.14	5	2.9	.
21	30	9	0.14	10	2.9	.
22	30	9	0.14	20	2.7	.
23	30	10	0.08	0.0	1.3	.
24	30	10	0.08	0.5	4.6	.
25	30	10	0.08	5	10.7	.
26	30	10	0.08	10	9.65	.
27	30	10	0.08	20	10.8	.
28	34	11	0.14	0.0	0.8	.
29	34	11	0.14	0.5	1.9	.
30	34	11	0.14	5	2.4	.
31	34	11	0.14	10	2.2	.
32	34	11	0.14	20	1.9	.
33	34	12	0.08	0.0	0.9	.
34	34	12	0.08	0.5	4.0	.
35	34	12	0.08	5	7.4	.
36	34	12	0.08	10	7.6	.
37	34	12	0.08	20	7.8	.

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 5/13/86- 5/17/86

OBS	TOTAL METALS CONCENTRATION ug/L						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
1	10.7	7.75	56.5	96.0	147.50	50.5	2025
2	13.4	9.48	174.7	95.0	174.00	95.5	4656
3	30.1	6.12	87.6	132.2	212.40	67.6	4680
4	23.9	18.90	167.0	167.7	190.40	191.4	5866
5	54.6	28.80	330.6	339.4	314.00	411.6	7480
6	77.3	45.80	525.7	566.8	345.00	646.5	7383
7	5.1	5.13	29.4	37.6	95.70	34.8	3056
8	26.2	11.60	37.4	362.0	133.00	206.3	5570
9	10.0	7.50	34.2	46.8	226.70	71.0	3866
10	61.6	30.64	304.2	373.8	246.40	303.0	5064
11	2.50	0.00	31.6	22.2	31.00	12.3	450
12	18.9	5.40	38.3	147.1	79.20	114.8	888
13	4.80	2.10	16.9	51.5	31.00	29.2	910
14	38.9	5.90	35.99	160.1	134.00	128.4	1090
15	9.90	0.00	17.0	39.0	78.00	66.9	1210
16	4.40	1.00	12.7	33.0	33.00	31.1	300
17	5.30	0.20	41.7	44.0	135.00	52.9	1330
18	3.50	4.60	26.0	52.8	45.00	39.9	1020
19	15.3	13.00	96	84	94.00	142	2090
20	46.8	34.50	283	240	306.00	368	4890
21	54.2	48.50	322	444	352.00	498	4940
22	50.6	39.90	292	376	608.00	910	5710
23	11.2	11.40	36	97.6	139.20	108	2016
24	97.8	48.72	553	494	445.20	740	6600
25	236.5	127.30	1292	1249	1852.20	2198	22860
26	233.5	113.70	1580	1256	1241.80	1869	15848
27	256.8	112.70	1646	1333	1005.60	2057	12816
28	6.49	1.10	48.4	59.4	104.50	59.4	1782
29	37.3	14.70	479	264	461.00	456	4080
30	45.2	17.90	653	281	324.00	702	5800
31	47.7	20.30	669	356	375.00	720	8640
32	51.5	19.90	682	344	429.00	744	8310
33	13.4	7.80	205	109	126.00	166	3420
34	78.8	32.40	1035	502	576.00	1139	10970
35	141.2	71.70	2092	857	964.00	2050	15460
36	150.4	75.90	2386	889	1090.00	2176	17680
37	166.6	82.90	2770	1088	1180.00	2328	20660

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 5/13/86- 5/17/86

OBS	DISSOLVED METALS CONCENTRATION ug/L						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
1	0.23	0.00	0.30	2.82	4.70	0.79	917.0
2	0.48	0.00	0.26	7.23	7.32	0.77	843.0
3	4.11	0.04	0.42	18.9	15.49	21.3	96.0
4	0.39	0.00	1.14	3.24	3.21	4.11	256.0
5	0.34	0.00	0.19	7.47	6.07	0.41	2357.0
6	0.10	0.00	0.29	1.99	4.13	0.57	123.0
7	0.32	0.13	0.49	3.40	4.55	0.81	465.0
8	0.18	0.00	0.20	1.54	3.74	0.23	199.0
9	0.18	0.08	0.27	2.68	5.17	0.62	323.0
10	0.78	0.32	0.50	4.16	7.86	2.27	76.0
11	2.03	0.00	0.44	8.72	3.78	2.31	419.0
12	0.22	0.01	0.26	3.44	1.54	0.47	344.0
13	1.24	0.14	0.41	5.20	5.98	2.03	678.0
14	0.29	0.07	0.19	1.47	1.39	0.25	297.0
15	1.53	0.15	0.61	5.10	12.69	1.78	1880.0
16	0.15	0.01	0.26	0.96	0.90	0.07	24.0
17	0.44	0.14	0.29	2.01	2.33	0.44	247.0
18	0.14	0.01	0.36	1.02	1.53	0.22	159.0
19	0.98	5.27	3.4	3.51	17.35	2.66	1648.0
20	0.43	5.00	3.22	1.74	15.06	1.4	655.0
21	0.21	4.84	3.36	2.36	13.15	0.72	62.0
22	0.12	5.00	2.09	0.79	14.16	0.10	330.0
23	0.34	4.77	4.56	2.89	11.67	0.51	1225.0
24	0.43	5.24	3.66	2.65	12.50	2.50	183.0
25	0.28	4.69	2.87	2.26	13.49	0.95	56.0
26	0.18	4.18	3.51	2.44	14.05	0.95	62.0
27	0.26	4.52	2.94	5.36	18.93	1.52	83.0
28	0.59	0.48	1.05	2.3	9.98	1.53	482.0
29	0.08	0.40	1.56	0.96	4.94	0.15	11.0
30	0.29	0.31	1.72	1.95	6.93	1.88	187.0
31	0.08	0.52	0.57	0.91	6.60	0.26	14.0
32	0.08	0.53	0.45	0.43	8.94	0.49	10.0
33	0.08	0.46	0.77	0.61	2.72	0.36	35.0
34	0.20	0.25	2.20	0.57	3.75	1.00	106.0
35	0.32	0.57	0.75	1.67	5.80	1.12	12.0
36	0.13	0.29	0.46	1.14	4.09	0.59	50.0
37	0.12	0.34	0.43	1.44	5.98	0.77	169.0

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 5/13/86- 5/17/86

OBS	INTERSTITIAL WATER METALS CONCENTRATION ug/L						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
1
2	2.38	0.57	2.58	16.4	10.88	5.99	694.0
3
4
5
6	2.81	1.12	2.36	19.4	16.90	5.17	500.0
7
8	2.35	0.89	2.92	12.1	17.84	3.80	442.0
9
10	2.08	0.40	2.14	12.1	14.37	2.20	635.0
11
12	3.04	0.65	4.89	10.8	21.25	2.69	590.0
13
14	1.69	0.49	2.15	4.70	8.16	2.03	308.0
15
16	1.34	0.81	4.43	7.95	10.12	3.99	117.0
17
18	2.08	0.45	4.81	5.47	6.19	0.60	168.0
19
20
21
22	2.04	3.81	4.45	9.98	19.25	3.9	583.0
23
24
25
26
27	1.90	5.42	3.49	27.2	20.63	1.5	868.0
28
29
30
31
32	1.38	0.46	2.04	19.9	12.95	1.0	287.0
33
34
35
36
37	1.44	0.63	1.31	8.94	24.11	1.0	321.0

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 5/13/86- 5/17/86

OBS	SEDIMENT METALS CONCENTRATION ug/g						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
1
2	11.00	6.50	79.00	79.00	71.80	115.30	645.00
3
4
5
6	10.00	6.70	90.00	78.00	79.90	125.10	620.00
7
8	11.00	6.50	85.00	189.00	79.40	115.00	658.00
9
10	11.00	6.40	73.00	81.00	72.90	123.00	753.00
11
12	0.60	5.10	10.00	10.00	14.00	21.30	62.00
13
14	0.30	4.00	11.00	14.00	10.00	18.60	241.00
15
16	0.40	4.40	8.00	10.00	12.00	19.00	62.00
17
18	0.40	5.10	8.00	12.00	20.40	19.20	90.00
19
20
21
22	23.00	9.10	113.00	116.00	102.10	206.00	581.00
23
24
25
26
27	22.00	9.20	112.00	112.00	101.20	194.00	577.00
28
29
30
31
32	20.00	8.70	264.00	159.00	177.40	347.00	1880.00
33
34
35
36
37	21.00	8.60	221.00	148.00	161.00	324.00	2040.00

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 9/3/86-9/5/86

OBSER- VATION #	STATION	EXPER. #	SECONDS/ STROKE	TIME OF SAMPLE min.	SUSPEN. SOLIDS g/L	pH
1	53	13	0.14	0.0	0.02	.
2	53	13	0.14	0.5	0.33	.
3	53	13	0.14	5	0.56	.
4	53	13	0.14	10	0.46	.
5	53	13	0.14	15	0.32	.
6	53	13	0.14	20	0.25	.
7	53	13	0.14	25	0.19	.
8	53	13	0.14	30	0.2	.
9	53	13	0.14	30	0.21	.
10	53	14	0.08	0.0	0.01	.
11	53	14	0.08	0.5	2.58	.
12	53	14	0.08	5	4.81	.
13	53	14	0.08	10	4.67	.
14	53	14	0.08	15	4.36	.
15	53	14	0.08	20	4.24	.
16	53	14	0.08	25	4.38	.
17	53	14	0.08	30	4.17	.
18	53	14	0.08	30	4.18	.
19	53	15	0.14	0.0	0.01	.
20	53	15	0.14	0.5	0.33	.
21	53	15	0.14	5	0.56	.
22	53	15	0.14	10	0.51	.
23	53	15	0.14	15	0.48	.
24	53	15	0.14	20	0.42	.
25	53	15	0.14	25	0.41	.
26	53	15	0.14	30	0.4	.
27	53	15	0.14	30	0.39	.
28	83	16	0.08	0.0	0.05	.
29	83	16	0.08	0.5	1.11	.
30	83	16	0.08	5	1.9	.
31	83	16	0.08	10	1.64	.
32	83	16	0.08	15	1.56	.
33	83	16	0.08	20	1.42	.
34	83	16	0.08	25	1.4	.
35	83	16	0.08	30	1.35	.
36	83	16	0.08	30	1.33	.
37	83	17	0.14	0.0	0.02	.
38	83	17	0.14	0.5	0.24	.
39	83	17	0.14	5	0.37	.
40	83	17	0.14	10	0.43	.
41	83	17	0.14	15	0.36	.
42	83	17	0.14	20	0.39	.
43	83	17	0.14	25	0.32	.
44	83	17	0.14	30	0.34	.
45	83	17	0.14	30	0.33	.

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 9/3/86-9/5/86

OBSER- VATION #	STATION	EXPER. #	SECONDS/ STROKE	TIME OF SAMPLE min.	SUSPEN. SOLIDS g/L	pH
46	30	18	0.08	0.0	0.01	7.84
47	30	18	0.08	0.5	0.68	7.7
48	30	18	0.08	5	2.34	7.51
49	30	18	0.08	10	2.97	7.53
50	30	18	0.08	15	3.58	7.45
51	30	18	0.08	20	3.48	7.71
52	30	18	0.08	25	3.29	7.95
53	30	18	0.08	30	2.8	7.63
54	30	18	0.08	30	2.83	7.63
55	30	19	0.14	0.0	0.06	7.17
56	30	19	0.14	0.5	0.3	7.3
57	30	19	0.14	5	0.37	7.36
58	30	19	0.14	10	0.29	7.76
59	30	19	0.14	15	0.43	7.72
60	30	19	0.14	20	0.42	8.06
61	30	19	0.14	25	0.42	7.4
62	30	19	0.14	30	0.4	7.43
63	30	19	0.14	30	0.43	.
64	30	20	0.08	0.0	0.01	.
65	30	20	0.08	0.5	2.35	.
66	30	20	0.08	5	4.4	.
67	30	20	0.08	10	5.13	.
68	30	20	0.08	15	5.54	.
69	30	20	0.08	20	5.42	.
70	30	20	0.08	25	5.26	.
71	30	20	0.08	30	4.88	.
72	30	20	0.08	30	5.39	.
73	30	21	0.14	0.0	0.005	.
74	30	21	0.14	0.5	0.19	.
75	30	21	0.14	5	0.26	.
76	30	21	0.14	10	0.26	.
77	30	21	0.14	15	0.25	.
78	30	21	0.14	20	0.23	.
79	30	21	0.14	25	0.25	.
80	30	21	0.14	30	0.24	.
81	30	21	0.14	30	0.23	.
82	34	22	0.14	0.0	0.005	7.65
83	34	22	0.14	0.5	0.14	7.5
84	34	22	0.14	5	0.52	7.6
85	34	22	0.14	10	0.57	7.6
86	34	22	0.14	15	0.55	7.6
87	34	22	0.14	20	0.54	7.6
88	34	22	0.14	25	0.6	7.6
89	34	22	0.14	30	0.53	7.6

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 9/3/86-9/5/86

OBSER- VATION #	STATION	EXPER. #	SECONDS/ STROKE	TIME OF SAMPLE min.	SUSPEN. SOLIDS g/L	pH
90	34	22	0.14	30	0.55	.
91	34	23	0.08	0.0	0.001	7.1
92	34	23	0.08	0.5	1.94	7.2
93	34	23	0.08	5	5.31	7.2
94	34	23	0.08	10	5.49	7.6
95	34	23	0.08	15	5.46	7.5
96	34	23	0.08	20	4.77	7.9
97	34	23	0.08	25	4.51	7.9
98	34	23	0.08	30	4.15	8.0
99	34	23	0.03	30	4.31	.
100	34	24	0.08	0.0	0.01	7.0
101	34	24	0.08	0.5	1.25	7.3
102	34	24	0.08	5	4.2	7.2
103	34	24	0.08	10	4.66	7.6
104	34	24	0.08	15	4.97	7.7
105	34	24	0.08	20	4.61	7.7
106	34	24	0.08	25	4.33	.
107	34	24	0.08	30	4.39	.
108	34	24	0.08	30	4.28	.

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 9/3/86-9/5/86

OBSER- VATION #	TOTAL METALS CONCENTRATION ug/L						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
1	4.3	1.3	13.0	72.0	93.5	51.5	4500
2	18.5	5.7	72.0	126.0	121.5	136.5	3750
3	23.3	8.2	126.0	174.5	179.0	214.0	3900
4	15.2	6.5	103.0	143.0	169.5	157.1	3016
5	16.3	4.4	77.5	136.0	99.0	126.0	1600
6	17.3	4.6	69.0	128.5	151.5	136.5	2700
7	10.7	3.0	57.5	110.0	107.0	193.0	2250
8	17.7	3.6	48.5	134.0	97.0	108.0	1750
9	10.4	4.1	49.0	118.0	112.0	84.5	1950
10	14.5	1.5	13.0	61.0	66.5	304.0	800
11	56.4	24.2	316.5	347.5	266.5	458.5	5000
12	113.6	55.2	804.0	740.8	551.6	1069.6	7200
13	133.7	59.9	941.0	951.0	562.0	947.5	7900
14	125.3	57.5	921.0	971.0	615.0	1198.0	8100
15	130.6	58.3	952.5	1066.0	589.0	1063.5	7600
16	124.0	55.1	917.5	1183.5	570.5	986.0	7350
17	125.4	48.9	963.5	1178.5	558.5	985.0	8000
18	168.1	53.6	1009.5	1252.0	712.0	593.5	7600
19	3.1	1.1	5.0	58.0	26.5	57.0	500
20	10.9	5.8	71.5	114.5	50.0	116.5	1100
21	21.7	8.8	117.5	159.0	88.5	212.0	1400
22	23.0	9.0	107.5	144.5	129.5	172.5	1500
23	18.1	6.8	102.5	158.5	95.0	175.0	1700
24	21.5	6.7	93.5	151.5	107.5	133.0	1500
25	44.0	6.3	92.0	155.5	111.0	235.0	1450
26	15.6	6.4	94.5	137.0	86.5	153.0	1250
27	19.9	7.8	96.5	139.0	71.0	195.5	1700
28	3.6	1.4	13.0	82.5	479.5	58.5	1000
29	19.3	15.4	56.0	177.0	324.5	134.5	1000
30	18.2	26.2	96.0	147.5	476.5	176.0	1600
31	13.8	23.8	101.0	137.0	365.0	207.5	1150
32	7.5	22.1	90.0	134.5	282.5	167.0	1750
33	4.1	23.8	99.5	147.5	514.0	134.5	1300
34	4.7	19.9	99.0	134.5	400.0	143.5	1750
35	11.6	25.0	90.0	132.0	243.0	138.0	900
36	3.6	22.8	96.5	120.0	263.0	121.0	1600
37	9.0	7.6	5.0	98.5	181.0	84.5	2400
38	1.7	4.8	16.5	49.0	75.0	35.0	1100
39	3.4	8.2	27.0	65.5	62.5	55.0	1900
40	15.9	8.1	29.0	89.0	125.0	101.5	1850
41	21.0	8.5	30.5	80.5	114.0	170.5	1650
42	1.5	7.7	31.5	71.0	79.5	45.5	2550
43	8.7	6.8	28.0	88.0	95.5	76.0	3050
44	6.5	7.5	24.4	89.5	105.5	107.6	1910
45	24.0	8.8	38.5	112.5	169.0	109.0	1250

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 9/3/86-9/5/86

OBSER- VATION #	TOTAL METALS CONCENTRATION ug/L						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
46	12.3	1.3	19.0	68.0	60.0	55.5	750
47	18.7	11.9	367.0	260.0	218.0	360.0	2100
48	65.8	38.8	1745.0	741.0	761.0	1142.0	4300
49	91.1	61.1	2330.0	999.0	1185.0	1634.0	6100
50	108.2	66.2	2760.0	1142.0	1210.0	1723.0	6600
51	129.6	71.8	2885.0	1202.0	1110.0	1799.0	7100
52	118.8	68.9	2865.0	1179.0	1050.0	1877.0	7000
53	94.1	56.1	2425.0	981.0	1048.0	1319.0	6100
54	48.9	57.0	2310.0	985.0	905.0	1236.0	6100
55	6.3	1.4	23.5	64.5	48.0	55.5	600
56	9.5	5.5	105.6	110.8	76.4	107.0	1190
57	11.3	6.1	132.5	136.5	81.0	162.0	950
58	11.3	1.4	152.0	176.5	109.0	172.0	950
59	12.2	0.1	141.5	125.0	92.0	203.5	1150
60	11.6	0.1	142.5	120.5	79.0	126.0	1050
61	12.5	8.1	152.0	135.0	95.0	118.5	1100
62	11.8	10.2	149.0	134.0	103.5	137.0	1100
63	12.8	8.0	144.5	131.0	88.0	110.0	1350
64	7.5	1.2	11.0	104.5	63.5	24.5	1150
65	50.1	35.3	725.0	486.0	477.0	499.0	3700
66	91.2	75.9	1535.0	882.0	840.0	1171.0	6300
67	146.2	94.9	1085.0	1095.0	990.0	1536.0	7900
68	138.6	92.2	2130.0	1068.0	1010.0	1644.0	7900
69	150.3	95.6	2030.0	1083.0	1065.0	1391.0	7700
70	145.9	89.2	2090.0	1083.0	1080.0	2304.0	7300
71	159.6	44.2	1085.0	1324.0	1500.0	1496.0	9200
72	157.0	92.2	2170.0	1151.0	1065.0	2595.0	8000
73	2.2	2.2	8.5	52.0	42.5	19.0	1100
74	7.8	5.0	63.0	102.5	157.0	63.5	950
75	25.2	6.9	110.5	115.0	108.0	133.5	1350
76	12.4	8.7	151.0	124.0	101.0	147.5	1250
77	14.5	6.7	120.6	114.4	160.2	140.0	1300
78	11.0	6.2	117.5	115.5	80.5	90.5	950
79	11.1	6.9	121.0	129.5	99.5	76.5	1400
80	14.9	6.6	117.0	134.0	172.5	75.0	1400
81	16.3	7.2	117.5	121.0	182.5	79.5	1100
82	4.9	1.5	8.0	81.5	101.0	27.0	1100
83	13.9	6.0	64.5	103.0	154.5	202.0	3450
84	35.3	11.0	159.0	192.0	215.0	310.0	7150
85	40.5	10.2	167.5	176.5	169.6	384.3	7526
86	79.9	11.0	179.0	200.0	194.5	358.5	7650
87	42.0	13.3	184.0	171.5	132.0	334.0	8100
88	39.1	12.1	180.0	184.1	143.3	351.4	7650
89	38.7	10.4	177.0	182.5	164.5	334.0	8150

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 9/3/86-9/5/86

OBSER- VATION #	TOTAL METALS CONCENTRATION ug/L						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
90	40.5	11.0	175.5	194.5	153.5	286.0	7450
91	7.7	0.3	10.0	81.5	64.0	31.5	1200
92	113.3	33.1	513.0	374.0	272.0	673.0	17700
93	283.7	83.3	1372.0	895.0	680.0	2307.0	47500
94	312.2	86.0	1468.0	923.0	774.0	2530.0	49500
95	349.1	79.8	1472.0	960.0	708.0	2546.0	51000
96	270.5	78.2	1280.0	898.0	710.0	2288.0	46100
97	253.6	69.4	1120.0	847.0	659.0	2072.0	43400
98	266.0	69.2	1179.0	779.0	597.0	1977.0	41400
99	267.7	68.2	1101.0	820.0	649.0	2172.0	44500
100	4.8	0.4	2.5	75.0	151.5	37.5	1300
101	63.6	21.7	315.0	256.0	193.0	430.0	12500
102	273.2	69.0	1110.0	790.0	613.0	2034.0	44500
103	282.3	77.1	1451.0	853.0	654.0	2344.0	51000
104	302.0	80.5	1545.0	918.0	762.0	2447.0	52600
105	293.1	77.3	1540.0	855.0	650.0	2266.0	50600
106	274.8	72.5	1389.0	843.0	533.0	2257.0	48900
107	280.6	72.5	1299.0	834.0	622.0	2219.0	47900
108	238.8	70.5	1390.0	799.0	602.0	2056.0	48900

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 9/3/86-9/5/86

OBSER- VATION #	DISSOLVED METALS CONCENTRATION ug/L						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
1	1.6	0.3	3.4	15.4	13.2	10.1	711.0
2	4.3	0.6	6.8	30.1	29.5	23.1	974.0
3	2.7	0.9	9.0	21.7	35.7	18.9	1120.0
4	5.3	1.3	9.4	25.4	55.7	14.4	1642.0
5	2.9	1.0	18.0	33.6	74.7	7.4	1302.0
6	3.2	0.5	5.6	21.7	47.2	7.5	1378.0
7	1.4	0.7	2.8	15.3	28.2	3.9	1156.0
8	2.3	0.7	7.7	19.9	45.5	12.3	1447.0
9	5.3	2.1	59.2	33.8	92.2	21.7	2154.0
10	1.2	0.3	4.1	7.0	8.7	6.9	212.0
11	2.8	0.4	6.5	11.3	19.8	8.1	316.0
12	17.7	3.0	18.7	26.9	64.7	52.4	1677.0
13	3.2	0.6	9.3	20.0	30.7	9.6	1324.0
14	2.1	0.6	4.8	12.6	26.2	3.5	487.0
15	6.0	0.9	6.1	18.8	33.5	10.9	3344.0
16	7.7	0.3	1.5	8.0	7.5	2.1	335.0
17	10.3	7.0	19.0	34.7	32.1	37.9	1485.0
18	2.3	0.7	13.2	29.1	26.1	5.9	431.0
19	2.3	0.5	4.6	24.3	10.1	11.8	240.0
20	2.0	0.5	3.8	24.2	21.3	6.7	182.0
21	0.7	0.4	2.0	5.6	6.7	2.9	213.0
22	4.6	0.5	5.4	65.1	19.6	18.1	816.0
23	1.1	0.4	5.2	8.3	14.2	3.2	541.0
24	1.4	0.4	2.3	8.9	8.7	4.4	1207.0
25	1.0	0.3	2.7	10.6	8.9	4.2	760.0
26	0.7	0.1	3.5	10.9	9.8	3.5	386.0
27	1.3	0.9	6.0	16.2	24.6	5.0	640.0
28	1.3	1.0	3.5	10.0	8.6	6.4	300.0
29	1.3	0.5	3.4	8.3	7.7	3.9	227.0
30	2.1	0.2	2.7	10.9	6.1	8.8	210.0
31	1.6	0.1	1.9	8.6	6.2	4.0	309.0
32	1.3	0.3	1.7	9.0	9.2	7.0	237.0
33	1.1	0.2	0.8	6.4	5.4	1.6	377.0
34	3.8	.0	4.1	15.4	15.5	23.4	352.0
35	2.8	0.7	2.4	11.3	13.0	1.9	277.0
36	1.4	0.2	2.2	9.8	8.8	9.0	220.0
37	1.4	0.0	2.0	8.3	4.5	3.5	153.0
38	1.0	0.1	1.5	6.8	4.2	2.6	135.0
39	0.8	0.2	1.8	7.5	5.4	3.1	383.0
40	1.2	0.1	1.8	7.9	11.0	5.3	236.0
41	0.8	0.1	1.6	6.8	7.3	2.4	110.0
42	1.2	0.1	1.4	6.6	6.7	4.6	379.0
43	0.9	0.3	1.6	6.6	5.4	2.3	508.0
44	0.9	0.4	1.8	6.7	18.8	1.8	442.0
45	1.8	0.4	2.2	9.5	7.6	4.2	755.0

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 9/3/86-9/5/86

OBSER- VATION #	DISSOLVED METALS CONCENTRATION ug/L						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
46	0.3	0.0	0.9	3.0	4.2	0.3	24.9
47	0.4	0.1	0.8	4.5	6.0	1.1	62.7
48	0.2	0.1	0.9	4.0	9.7	0.6	65.1
49	5.3	1.7	54.4	40.2	41.9	56.4	127.3
50	0.7	0.4	2.3	11.7	16.6	2.0	62.7
51	0.5	0.3	1.8	5.2	12.5	4.9	46.9
52	0.1	0.2	1.1	3.6	11.0	1.1	25.0
53	0.1	0.2	1.2	4.9	12.2	1.5	38.0
54	0.3	0.2	0.8	2.9	13.4	2.4	45.0
55	2.4	0.6	5.1	7.5	20.3	10.2	466.0
56	5.0	1.8	16.0	11.2	206.6	12.9	2756.0
57	1.5	0.5	5.6	12.0	18.4	12.1	357.0
58	0.8	0.4	4.8	10.9	11.8	8.6	802.0
59	1.5	0.4	5.7	13.5	18.0	16.2	1213.0
60	0.8	0.5	3.5	3.7	11.8	5.8	418.0
61	3.1	0.2	4.3	8.0	36.4	6.0	779.0
62	6.0	1.7	26.9	30.1	48.8	47.4	4170.0
63	0.9	0.3	6.0	15.1	19.0	8.6	707.0
64	3.0	1.0	10.9	23.2	97.5	11.5	1367.0
65	2.6	0.5	6.1	9.1	42.1	6.5	1183.0
66	3.6	1.1	8.1	11.7	79.9	17.4	4923.0
67	3.0	1.3	9.0	8.3	69.8	9.0	2034.0
68	0.5	0.2	2.8	6.2	16.8	12.3	428.0
69	2.5	0.7	9.6	7.7	37.7	11.8	6591.0
70	11.2	1.6	36.5	23.5	34.2	46.9	1746.0
71	10.0	3.2	59.1	23.0	97.6	83.8	2064.0
72	9.1	5.7	69.9	15.5	143.1	92.9	2297.0
73	1.3	.0	4.1	9.5	22.3	5.9	309.0
74	2.0	0.3	10.4	26.5	19.3	5.7	341.0
75	3.3	0.2	5.4	11.7	32.4	13.4	135.0
76	1.9	0.4	4.0	8.1	38.7	4.3	829.0
77	1.5	0.3	6.2	12.8	15.9	11.7	818.0
78	0.8	0.5	2.9	7.6	29.7	2.3	2060.0
79	0.4	0.3	2.4	9.7	15.2	4.9	446.0
80	1.3	0.6	6.3	15.5	25.2	12.4	446.0
81	0.7	0.7	6.3	12.8	58.3	5.8	610.0
82	2.0	0.6	4.9	12.3	14.0	10.6	915.0
83	2.4	1.0	8.4	16.4	36.5	10.7	1124.0
84	2.4	0.8	5.7	11.9	34.0	7.1	1139.0
85	2.6	1.5	20.0	9.2	47.5	11.7	1204.0
86	2.0	1.3	14.5	5.4	40.1	13.7	866.0
87	1.2	0.8	4.7	21.6	13.3	7.6	1484.0
88	2.0	1.1	12.2	1.1	25.6	7.1	1104.0
89	1.5	0.8	4.1	11.2	22.3	5.2	932.0

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 9/3/86-9/5/86

OBSER- VATION #	DISSOLVED METALS CONCENTRATION ug/L						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
90	2.9	0.6	2.4	27.5	29.2	7.4	472.0
91	1.5	.0	4.5	3.6	17.0	6.2	693.0
92	0.6	0.1	4.4	0.8	19.3	3.0	422.0
93	1.9	0.9	13.1	1.2	33.0	4.9	925.0
94	1.1	0.3	7.8	2.9	16.2	8.0	501.0
95	0.9	0.5	3.5	2.7	14.1	4.0	629.0
96	0.7	0.4	2.1	0.7	10.7	6.0	728.0
97	1.1	0.4	2.5	1.4	24.4	2.9	286.0
98	0.7	0.3	2.1	4.0	15.9	2.1	218.0
99	1.3	0.5	2.6	6.0	14.3	3.9	321.0
100	0.6	0.4	1.1	7.6	8.1	2.7	357.0
101	1.5	0.3	1.8	7.1	12.6	5.7	375.0
102	2.1	0.4	2.7	4.3	24.9	7.1	715.0
103	1.5	0.4	2.5	10.2	24.2	4.5	383.0
104	0.8	0.1	1.9	5.8	11.4	2.6	408.0
105	1.7	.0	1.8	4.8	10.7	10.1	800.0
106	1.0	0.0	1.3	4.6	10.3	4.1	570.0
107	1.3	0.1	3.3	9.0	15.4	3.8	367.0
108	3.5	0.5	8.3	6.2	14.5	19.0	554.0

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 9/3/86-9/5/86

OBSER- VATION #	INTERSTITIAL WATER METALS CONCENTRATION ug/L						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
1
2
3
4
5
6
7
8
9	1.6	0.8	8.2	14.9	41.2	6.2	151.0
10
11
12
13
14
15
16
17
18	0.9	1.3	3.0	8.1	68.7	2.9	93.0
19
20
21
22
23
24
25
26
27	1.5	0.8	2.7	13.2	17.8	5.2	150.0
28
29
30
31
32
33
34
35
36	1.3	1.0	3.9	21.2	14.6	7.7	251.0
37
38
39
40
41
42
43
44
45	1.1	1.1	2.6	20.4	10.0	2.2	364.0

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 9/3/86-9/5/86

OBSER- VATION #	INTERSTITIAL WATER METALS CONCENTRATION ug/L						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
46
47
48
49
50
51
52
53
54	26.2	12.5	92.5	80.7	368.4	91.6	132.0
55
56
57
58
59
60
61
62
63	1.2	4.2	14.0	14.0	41.2	17.1	66.1
64
65
66
67
68
69
70
71
72	1.8	4.5	12.5	16.7	53.9	12.9	85.7
73
74
75
76
77
78
79
80
81	2.8	4.8	16.2	31.9	55.3	25.8	409.0
82
83
84
85
86
87
88
89

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 9/3/86-9/5/86

OBSER- VATION #	INTERSTITIAL WATER METALS CONCENTRATION ug/L						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
90	0.3	0.8	3.2	2.5	5.8	0.8	134.0
91
92
93
94
95
96
97
98
99	0.3	0.7	3.5	2.9	5.1	0.5	60.0
100
101
102
103
104
105
106
107
108	0.6	1.0	5.4	9.3	13.5	3.3	178.0

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 9/3/86-9/5/86

OBSER- VATION #	SEDIMENT METALS CONCENTRATION ug/g						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
1
2
3
4
5
6
7
8
9	13.0	5.1	79.0	90.0	66.8	126.0	799.0
10
11
12
13
14
15
16
17
18	14.0	5.5	85.0	97.0	73.0	132.0	804.0
19
20
21
22
23
24
25
26
27	16.0	5.8	96.0	105.0	73.8	136.0	881.0
28
29
30
31
32
33
34
35
36	0.6	6.0	18.0	23.0	24.0	13.8	229.0
37
38
39
40
41
42
43
44
45	0.4	5.2	16.0	17.0	37.1	40.4	115.0

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 9/3/86-9/5/86

BSER- VATION #	SEDIMENT METALS CONCENTRATION ug/g						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
46
47
48
49
50
51
52
53
54	13.0	8.1	281.0	194.0	215.5	342.0	1005.0
55
56
57
58
59
60
61
62
63	14.0	7.1	224.0	125.0	131.7	211.0	663.0
64
65
66
67
68
69
70
71
72	19.0	9.9	249.0	190.0	192.8	303.0	892.0
73
74
75
76
77
78
79
80
81	17.0	8.9	165.0	143.0	134.4	256.0	783.0
82
83
84
85
86
87
88
89

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 FIELD SEDIMENT/METALS RESUSPENSION EXPERIMENTS
 FIELD SAMPLING DATE 9/3/86-9/5/86

OBSER- VATION #	SEDIMENT METALS CONCENTRATION ug/g						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
90	47.0	7.1	118.0	130.0	93.0	363.0	6930.0
91
92
93
94
95
96
97
98
99	48.0	7.2	108.0	133.0	90.4	354.0	6400.0
100
101
102
103
104
105
106
107
108	50.0	7.4	112.0	133.0	92.0	392.0	7360.0

APPENDIX D

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 LABORATORY SEDIMENT/ METALS RESUSPENSION EXPERIMENTS

RPM DATA

DATE 1/22/87

INITIAL CONDITIONS: AVERAGE SEDIMENT DEPTH 4.6 cm
 DEPTH OF OVERLYING WATER 12 cm
 pH CONTROL none
 METALS SPIKE none

EXP. NO.	RPM	TIME OF SAMPLE min.	pH	S.S. g/L	TOTAL METALS ug/L			SOLUBLE METALS ug/L		
					Cd	Cr	Pb	Cd	Cr	Pb
1	0	0	7.62	0.03	6.15	8.8	9.5	5.4	1.74	1.5
1	60	0.5	7.67	0.053	6.5	12.3	10	9.48	4.96	1.9
1	60	5	7.68	0.053	6.3	9.9	13	4.99	0.8	1
1	60	10	7.65	0.053	7.85	20.2	14	5.69	5.82	1.4
1	60	15	7.64	0.066	7	17.1	14.5	4.67	1.02	1.5
1	60	20	7.71	0.073	14.3	42.1	24	6.64	6.59	2.6
1	60	25	7.51	0.06	7.25	27.9	19	6.39	1.97	5.9
1	60	30	7.71	0.047	6.75	23.65	18.5	4.51	1.68	2.5
1	60	60	7.7	0.067	8.9	9.3	14.5	5.22	1.28	1.4
1	60	90	7.71	0.06	6.15	11.85	11	5.1	2.74	1.4
1	60	120	7.7	0.047	4.85	38.05	11.5	4.6	4.41	1.9
1	60	150	7.71	0.04	5.85	8.5	11	10.89	33.71	4.4
1	60	180	7.8	0.067	6.85	19.3	17.5	5.94	13.2	3.2
1	60	210	7.81	0.053	4.6	27.7	10	4.34	9.66	1.4
2	150	0.5	7.72	1.527	56	259	323	2.18	2.18	1
2	150	5	7.67	3.633	109	594	642	4.86	6.25	2.8
2	150	10	7.64	3.82	135	771	816	1.32	1.96	1.1
2	150	15	7.55	5.98	169	1029	1066	1.87	7.03	1
2	150	20	7.54	8.22	250	1460	2090	13.09	40.64	11.2
2	150	25	7.47	9.233	270	1600	2130	4.19	27.51	2.3
2	150	30	7.53	9.36	280	1660	2300	2.02	4.47	0.7
2	150	60	7.48	16.08	360	2300	2830	3.74	4.4	1.8
2	150	90	7.45	14.66	390	2550	3070	3.37	1.05	1.3
2	150	120	7.51	16.81	410	2780	3220	2.35	1.33	1
2	150	150	7.39	38.6	530	3760	4190	1.83	0.61	1.1
2	150	180	7.32	42.5	660	4550	4990	3.38	1.93	1.7
2	150	210	7.3	42.9	840	6040	6580	1.89	1.63	1.4
2	0	1440	7.53	0.506	16	1090	132	0.24	0.23	0.2

Cd Cr Pb

SEDIMENT METALS CONCENTRATION ug/g
 INTERSTITIAL METALS CONCENTRATION ug/g

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 LABORATORY SEDIMENT/ METALS RESUSPENSION EXPERIMENTS

RPM DATA

DATE 1/29/87

INITIAL CONDITIONS: AVERAGE SEDIMENT DEPTH 5.5 cm
 DEPTH OF OVERLYING WATER 11.5 cm
 pH CONTROL none
 METALS SPIKE none

EXP. NO.	RPM	TIME OF SAMPLE min.	pH	S.S. g/L	TOTAL METALS ug/L			SOLUBLE METALS ug/L		
					Cd	Cr	Pb	Cd	Cr	Pb
3	0	0	7.6	0.027	0.45	12.25	6	0	0.2	3.2
3	60	0.5	7.61	0.033	1.3	10.6	9	0	0.1	0
3	60	5	7.63	0.047	1.5	21.4	11.5	0	0.1	0
3	60	10	7.65	0.047	2.15	20	16	0.1	12.3	3.9
3	60	15	7.66	0.067	4.8	32.5	28	0	0.9	0
3	60	20	7.67	0.067	5.7	34.3	27.5	0.5	28.8	0
3	60	25	7.67	0.067	4.2	28.05	29	0	1.4	0.4
3	60	30	7.68	0.06	2.65	26.95	48	0.1	4.1	0.3
3	60	60	7.71	0.053	2.95	21.35	18.5	0.1	0.8	0.6
3	60	90	7.72	0.06	2.6	25.6	23	0.7	20.2	1.2
3	60	120	7.75	0.053	3.2	21.05	19	0	1.5	0
3	60	150	7.77	0.033	2.25	16.0	16	0.1	1.2	0
3	60	180	7.78	0.033	4.95	17.8	59.5	0.1	1.2	0
4	80	0.5	7.78	0.027	3	17	20	1.8	26	0
4	80	5	7.79	0.053	7.8	21.5	19	0	1.5	0.5
4	80	10	7.79	0.08	3.8	27.3	23.5	0.1	0.8	0.1
4	80	15	7.79	0.093	5.1	30.5	30	0	1.1	0.3
4	80	20	7.8	0.1	7	31	26	0.2	15.6	0.9
4	80	25	7.8	0.08	6.6	35.5	46	0.1	0.8	0.7
4	80	30	7.81	0.113	5.5	36.7	31	1.5	21.5	0.4
4	80	60	7.81	0.12	5.9	35.8	33	0.5	5.9	0.8
4	80	90	7.82	0.093	5.8	32.9	33.5	0.2	4.9	0
4	80	120	7.83	0.1	6.1	37.5		0.4	4.1	1
4	80	150	7.83	0.1	6	33.35	32.5	5.5		0.5
4	80	180	7.84	0.093	8	38.8		0.1	6.2	0
5	105	0.5	7.84	0.167	25	77	97	0	4	0
5	105	5	7.79	1.207	42	198	275	0.04	3.5	0.4
5	105	10	7.76	1.327	44	205	276	0.58	25.8	0.4
5	105	15	7.74	1.247	40	238	294	0.25	6.9	1.1
5	105	20	7.72	1.267	41	227	267	0.21	3.9	0.1
5	105	25	7.67	1.7	52	290	340	0.12	3.5	0.8
5	105	30	7.63	2.133	64	362	423	0.23	6.7	0.7
5	105	60	7.48	3.08	106	574	626	0.02	4.2	0.5
5	105	90	7.5	2.473	94	490	557	3.93	9.4	10.5
5	105	120	7.53	2.087	89	432	533	0.01	17.8	0.3
5	105	150	7.56	2.173	86	445	362	0.02	4.1	0.3
5	105	180	7.58	2.133	87	427	546	0.25	0.9	11.5
5	0	720	7.55	0.113	9	51	12	0	1.8	2.7

Cd Cr Pb

SEDIMENT METALS CONCENTRATION ug/g

INTERSTITIAL METALS CONCENTRATION ug/g

LABORATORY SEDIMENT/ METALS RESUSPENSION EXPERIMENTS

PH DATA

DATE 2/19/87
INITIAL CONDITIONS:

AVERAGE SEDIMENT DEPTH
DEPTH OF OVERLYING WATER
PH CONTROL
METALS SPIKE

5.12 cm

11.9 cm

0.01 M

none

BES (titration w/ 1 M NaOH or 10% HNO₃)

EXP. NO.	RPM	TIME OF SAMPLE min.	pH	S.S. g/L	TOTAL METALS ug/L			SOLUBLE METALS ug/L		
					Cd	Cr	Pb	Cd	Cr	Pb
6	0	0	7.68	0.04	3	43	95.5	0.15	6.3	1.65
6	105	0.5	7.69	0.09	3	53.5	29	0	6.9	1.3
6	105	5	7.69	0.32	9	109	82.5	2.1	11.8	4.8
6	105	10	7.68	0.97	22	221	213	1.65	7.5	2.1
6	105	15	7.68	1.07	29	317	269	0	5.1	1.5
6	105	20	7.68	1.23	34	381	312	0	4.6	1.6
6	105	25	7.68	1.42	38	403	368	0.15	4.5	1.8
6	105	30	7.68	1.53	40	407	357	1.05	5.7	1.6
7	105	0.5	7.03	1.37	41	407	371	0.45	3.9	0.25
7	105	5	7.02	1.36	44	440	410	0.3	4.6	0.45
7	105	15	7.03	1.45	43	416	396	0.9	5.8	0.6
7	105	20	7.04	1.52	45	428	414	1.65	6	1.2
7	105	25	7.05	1.61	47	466	465	8.1	37.3	9.3
7	105	30	7.05	1.57	52	516	468	1.05	5.4	0.45
7	105	60	7.06	2.27	70	728	643	0.3	5.5	0.15
7	105	90	7.05	2.79	85	949	734	0.3	3.7	0.15
7	105	120	7.04	3.54	104	1122	964	2.25	17.7	1.6
7	105	150	7.06	3.33	138	1337	1034	0.75	15.1	0.45
7	105	180	7.07	3.76	104	1110	933	0.15	1.6	0.6
7	105	210	7.08	4.3	109	1163	1026	0.15	2.1	0.45
8	105	0.5	7.51	3.9	118	1157	1175	0.15	2.1	0.75
8	105	5	7.5	3.75	109	1151	1054	0.3	5.8	2.25
8	105	10	7.5	3.87	105	1261	1100	0.75	12.9	1.05
8	105	15	7.5	3.54	118	1216	1128	0.15	1.9	0.15
8	105	20	7.49	3.83	123	1239	1172	0	2.5	0.454
8	105	25	7.48	3.68	121	1223	1088	0	1.9	0.6
8	105	30	7.5	4.08	106	1053	1019	0.45	3.3	0.6
8	105	60	7.49	4.12	118	1185	1114	0	2.5	0.45
8	105	90	7.5	4.18	123	1456	1250	0	5.1	0.3
8	105	120	7.49	4.51	125	1454	1240	0.15	2.1	0.45
8	105	150	7.49	3.93	123	1456	1297	0.15	2.2	0.9
8	105	180	7.48	4.57	136	1528	1179	0.3	5.2	1.5
9	105	0.5	7.99	4.96	141	1624	1298	0	5.2	0.45
9	105	5	7.99	4.97	144	1642	1244	0	3.6	0.15
9	105	10	8.01	4.9	137	1500	1181	0	3.3	0.15
9	105	15	8	4.55	133	1496	1217	0	2.4	0.15
9	105	20	8.02	4.76	130	1624	1082	0	3.7	0.15
9	105	25	8.01	4.49	134	1370	1200	0	2.4	0.15
9	105	30	8.01	4.17	137	1636	1261	0	5.7	0.15
9	105	60	7.99	4.3	136	1568	1275	0	1.9	0.15
9	105	90	8.03	4.47	140	1640	1246	0	2.2	0.15
9	105	120	8.01	4.63	141	1704	1339	0	1.8	0.15
9	105	150	8	5.39	142	1624	1281	0	5.4	0.4
9	105	180	7.98	5.2	139	1676	1299	0	1.9	0.4
9	0	1440	7.93							

SEDIMENT METALS CONCENTRATION ug/g
INTERSTITIAL METALS CONCENTRATION ug/L

Cd 12.2
Cr 71.4
Pb 160.7
1.9 1.5 0.7

TROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 LABORATORY SEDIMENT/ METALS RESUSPENSION EXPERIMENTS

TOTAL SPIKE DATA
 DATE 3/13/87
 INITIAL CONDITIONS:

AVERAGE SEDIMENT DEPTH 4.73 cm
 DEPTH OF OVERLYING WATER 12 cm
 pH CONTROL 0.01 M BES (titration w/ 1 M NaOH or 10% HNO₃)
 METALS SPIKE 25 ug/L Cd, 50 ug/L Cr, 100 ug/L Pb

EXP. NO.	RPM	TIME CP SAMPLE min.	pH	S.S. g/L	TOTAL METALS ug/L			SOLUBLE METALS ug/L		
					Cd	Cr	Pb	Cd	Cr	Pb
10	0	0	7.64	0.01	0.5	18	21	0.2	4.2	0.5
10	95	0.5	7.63	0.01	9.5	19	8	0.1	4.5	0.2
10	95	5	7.63	0.02	2.5	24	27	7.2	26.7	6.6
10	95	10	7.6	0.1	2.5	26.5	25	0	4.65	0
10	95	15	7.63	0.03	2.5	28	25.5	0	5.7	1.7
10	95	20	7.64	0.14	4	67.5	38			
10	95	25	7.64	0.12	4	55.5	43			
10	95	30	7.64	0.17	4	59.5	49			
10	95	60	7.64	0.16	4	46	41			
11	95	0.5	7.63	0.16	30	101.5	140.5	26.4	37.2	10.7
11	95	5	7.63	0.13	28.5	99	129	12.0	19.8	4.2
11	95	10	7.63	0.14	27.5	99	133.5	12.6	39.5	4.7
11	95	15	7.63	0.13	26.5	94.5	122.5	13.5	41.6	8.3
11	95	20	7.63	0.15	25.5	102	126	12.5	28.4	5
11	95	25	7.63	0.14	23.5	90.5	112.5	11.7	37.2	4.2
11	95	30	7.63	0.14	23.5	89	123	11.1	20.7	2.6
11	95	60	7.64	0.11	23	95	123	7.5	16.8	2.3
11	95	90	7.64	0.14	21	94	116.5	6.6	33.3	2
11	95	120	7.64	0.11	17	79.5	99	7.5	15	1.5
12	95	0.5	7.04	0.14	21.5	93.5	111	8.6	19.4	3.3
12	95	5	7.03	0.15	20	86	105.5	8	21	10.7
12	95	10	7.03	0.13	19.5	78	104	7.7	18.6	3.8
12	95	15	7.04	0.12	21	87.5	106.5	7.8	19.2	3.8
12	95	20	7.04	0.12	20	85	104	8.4	34.5	3.8
12	95	25	7.04	0.12	19.5	83	101.5	8.1	16.5	2.7
12	95	30	7.04	0.11	19	86	103	6.3	16.8	1.8
12	95	60	7.05	0.11	17.5	74	93.5	6.2	14.4	1.2
12	95	90	7.05	0.12	16.5	76	94	5.6	11.4	1.2
12	95	120	7.05	0.12	18	85	104.5	6.5	12.9	3.6
12	95	150	7.05	0.12	17.5	79.5	97	6.2	10.2	1.3
12	95	180	7.04	0.12	17	76.5	94.5	6	12.9	1.7
12	95	210	7.05	0.11	15	76.5	93	5.9	14.3	2.7
12	95	240	7.08	0.14	18	78.5	111.5	5.6	17.9	3

SEDIMENT METALS CONCENTRATION ug/g
 INTERSTITIAL METALS CONCENTRATION ug/L

Cd 11.4
 Cr 72.8
 Pb 155
 0.9 1.8 1.2

DETROIT RIVER CONNECTING CHANNELS, IN PLACE POLLUTANTS STUDY
 LABORATORY SEDIMENT/ METALS RESUSPENSION EXPERIMENTS

METAL SPIKE DATA #2
 DATE 4/6/87
 INITIAL CONDITIONS:

AVERAGE SEDIMENT DEPTH 4.73 cm
 DEPTH OF OVERLYING WATER 12 cm
 pH CONTROL 0.01 M BES (titration w/ 1 M NaOH or 10% ENO)
 METALS SPIKE 25 ug/L Cd, 50 ug/L Cr, 100 ug/L Pb

EXP. NO.	RPM	TIME OF SAMPLER min.	pH	S.C. g/L	TOTAL METALS ug/L			SOLUBLE METALS ug/L		
					Cd	Cr	Pb	Cd	Cr	Pb
13	95	0	7.68	0.32	7	30.5	5	0.7	9	0
13	95	0.5	7.06	0.27	6.5	93	65	0.5	7.5	0.1
13	95	2	7.04	0.38	11	127	78.5	1.4	9.2	3
13	95	5	7.04	0.45	11.5	116.5	85	0.6	9	0.1
13	95	10	7.05	0.49	11	123.5	90	1.4	29.4	3.7
13	95	15	7.02	0.42	10	130	85	1.2	8.1	5.1
13	95	20	7.03	0.42	10.5	106.5	100.5	0.9	23.5	0
13	95	25	7.03	0.1	11.5	112	95	0.6	10.3	0
13	95	30	7.04	0.78	14	125	89.5	0.3	28.9	1.5
13	95	60	7.03	0.3	12	120	85	1.4	12.7	8.5
14	95	0.5	7	0.38	36	140.5	143	12.2	14.3	2.9
14	95	2	7.01	0.36	34	144.5	155	11.6	10.3	2.1
14	95	5	7.01	0.35	31.5	178.5	155	10.5	16.1	1.2
14	95	10	7.02	0.51	35	136.5	161.5	12.2	25.7	3.3
14	95	15	7.03	0.36	31	132	147.5	8.9	27.6	3.5
14	95	20	7.03	0.34	31	124.5	150	7.8	18	4.2
14	95	25	7.04	0.35	33	131.5	150	7.3	11.1	2.4
14	95	30	7.01	0.42	30.5	119	152.5	7.9	12.1	4.8
14	95	60	7.02	0.34	26.5	129	141	6.3	11.4	1.1
14	95	90	7.05	0.3	27.5	128.5	144	5.3	8.3	0.9
14	95	120	7.03	0.27	24.5	119	188	6.1	8.1	1.1
15	95	0.5	5.97	0.31	24	122.5	122.5	10.5	9.1	1.2
15	95	2	5.97	0.31	25.5	124	146.5	9.7	8.7	1.1
15	95	5	5.98	0.3	23	118.5	134	8.5	7.8	1.1
15	95	10	6	0.29	27	113	108.5	9.9	8.1	1.9
15	95	15	5.98	0.28	23.5	112.5	140	9.5	8.5	1.8
15	95	20	6	0.27	24	116	120	9.3	7.5	1.9
15	95	25	5.97	0.38	22.5	113	142	7.9	6.5	0
15	95	30	5.99	0.29	24.5	108.5	119.5	11.1	7.8	18.9
15	95	60	6.01	0.25	23	123	128	9.1	7.1	1.1
15	95	90	5.99	0.3	22	114.5	116.5	8.7	6.9	1.8
15	95	120	5.98	0.3	21	101	120.5	7.8	6.45	1.1
16	95	0.5	4.9	0.3	21.5	103	114	12.5	9.5	3
16	95	2	5	0.29	21.5	105.5	117	13.5	9	2.3
16	95	5	5.05	0.31	21	98	120.5	13.1	7.9	9.7
16	95	10	4.9	0.29	22	109	123	15.1	9	2.1
16	95	15	5.02	0.29	24.5	101.5	158.5	13.5	9.3	1.9
16	95	20	5	0.29	20	102	110.5	14.3	8.9	0.7
16	95	25	4.96	0.29	20.5	100.5	115	14.1	7.8	4.7
16	95	30	4.99	0.23	19.5	107	112.5	12.3	6.7	4.8
16	95	60	4.96	0.24	20.5	102.5	172	12.1	7.1	1.7
16	95	90	5	0.24	18.5	97.5	131	11.9	6.9	1.2
16	95	120	5.01	0.24	20.5	103	119	11.1	6.3	1.1

SEDIMENT METALS CONCENTRATION ug/g
 INTERSTITIAL METALS CONCENTRATION ug/L

Cd 11.4
 Cr 72.5
 Pb 148
 Cd 4.5
 Cr 4.3
 Pb 11.9

APPENDIX E

METHOD 3050

ACID DIGESTION OF SLUDGES

1.0 Scope and Application

1.1 Method 3050 is an acid digestion procedure used to prepare sludge-type and soil samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3050 may be analyzed by AAS or ICP for the following metals:

Antimony	Lead
Arsenic	Nickel
Barium	Selenium
Beryllium	Silver
Cadmium	Thallium
Chromium	Zinc
Copper	

1.2 Method 3050 may also be applicable to the analysis of other metals in sludge-type samples. However, prior to using this method for other metals, it must be evaluated using the specific metal and matrix.

2.0 Summary of Method

2.1 A dried and pulverized sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace analysis of Sb or the flame analysis of Sb, Be, Cd, Cr, Cu, Pb, Ni, and Zn. Nitric acid is employed as the final reflux acid for the furnace analysis of As, Be, Cd, Cr, Cu, Pb, Ni, Se, Ag, Tl, and Zn or the flame analysis of Ag and Tl.

3.0 Interferences

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste. Nondestructive techniques such as neutron activation analysis may also be helpful in evaluating the applicability of this digestion method.

4.0 Apparatus and Materials

4.1 125-ml conical Phillips' beakers.

4.2 Watch glasses.

2 / WORKUP TECHNIQUES - Inorganic

- 4.3 Drying ovens that can be maintained at 30° C.
- 4.4 Thermometer that covers range of 0° to 200° C.
- 4.5 Whatman No. 42 filter paper or equivalent.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

5.3 Concentrated hydrochloric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

5.4 Hydrogen peroxide (30%): Oxidant should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and distilled deionized water. Plastic and glass containers are both suitable.

6.3 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Weigh and transfer to a 250-ml conical Phillips® beaker a 1.0-g portion of sample which has been dried at 60° C, pulverized, and thoroughly mixed.

7.2 Add 10 ml of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample at 95° C and reflux for 10 min. Allow the sample to cool, add 5 ml of conc. HNO_3 , replace the watch glass, and reflux for 30 min. Do not allow the volume to be reduced to less than 5 ml while maintaining a covering of solution over the bottom of the beaker.

7.3 After the second reflux step has been completed and the sample has cooled, add 2 ml of Type II water and 3 ml of 30% hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.

7.4 Continue to add 30% H_2O_2 in 1-ml aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 ml 30% H_2O_2 .)

7.5 If the sample is being prepared for the furnace analysis of Ag and Sb or direct aspiration analysis of Ag, Sb, Be, Cd, Cr, Cu, Pb, Ni, Tl, and Zn, add 5 ml of 1:1 HCl and 10 ml of Type II water, return the covered beaker to the hot plate, and heat for an additional 10 min. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3 and is now ready for analysis.

7.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Cu, Pb, Ni, Se, Tl, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 ml, and 10 ml of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted digestate solution contains approximately 2% (v/v) HNO_3 . For analysis, withdraw aliquots of appropriate volume, add any required reagent or matrix modifier, and analyze by method of standard additions.

8.0 Quality Control

8.1 For each group of samples processed, procedural blanks (Type II water and reagents) should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 10% is recommended.

8.3 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.4 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and whenever a new sample matrix is being analyzed.

METHOD 3020

ACID DIGESTION PROCEDURE FOR FURNACE ATOMIC ABSORPTION SPECTROSCOPY

1.0 Scope and Application

1.1 This digestion procedure is approved for the preparation of aqueous samples, mobility procedure extracts, and certain nonaqueous wastes for analysis, by furnace atomic absorption spectroscopy (AAS), for the metals listed below. The procedure is to be used when one is to determine the total amount of the metal in the sample.

1.2 Metals for which Method 3020 is the approved furnace AAS procedure are:

Aluminum	Lead
Barium	Manganese
Beryllium	Molybdenum
Cadmium	Nickel
Chromium	Silver
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc

1.3 If a nonaqueous sample is not completely digested by this method and determination as to the total concentration of a metal in the entire sample is required, then the digestion methods described in Method 3030, 3040, or 3050 should be tried. Some wastes will require fusion techniques to completely release metals from inorganic matrices. The appropriate fusion method should be chosen from the literature and its applicability to the sample of interest proven by analyzing spiked samples and relevant standard reference materials.

2.0 Summary of Method

2.1 A mixture of nitric acid and the material to be analyzed is heated to near dryness in a Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to near dryness, it is cooled and brought up in dilute nitric acid such that the final dilution contains 0.5% (v/v) HNO_3 .

3.0 Interferences

3.1 Interferences are discussed in the referring analytical method.

2 / MURKUP TECHNIQUES - Inorganic

4.0 Apparatus and Materials

4.1 Griffin beakers of assorted sizes.

4.2 Qualitative filter paper or centrifugation equipment.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and distilled deionized water. Plastic and glass containers are both suitable.

6.3 Aqueous wastewaters must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 ml of conc. HNO_3 . Cover the beaker with a watch glass. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. (DO NOT BAKE.) Cool the beaker and add another 3-ml portion of conc. HNO_3 . Re-cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. It should be noted that if a sample is allowed to go to dryness, low recoveries may result for tin and antimony.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of HNO_3 so that the final dilution contains 0.5% (v/v) HNO_3 , and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.3 Wash down the beaker walls and watch glass with distilled water and when necessary filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute nitric acid. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

8.0 Quality Control

8.1 For each group of samples processed, procedural blanks (Type II water and reagents) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 10% is recommended.

8.3 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.4 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and whenever a new sample matrix is being analyzed.