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NEARSHORE CHEMISTRY IN THE VICINITY

OF THE GRAND RIVER, MICHIGAN

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NEARSHORE CHEMISTRY IN THE VINICITY OF THE GRAND RIVER, MICHIGAN*

Richard L. Chambers and Brian J. Eadie

The impact on nearshore water chemistry and bottom sediments of the input from the Grand River, Mich., is assessed. The Grand River is the largest tributary flowing into Lake Michigan and a major contributor of several noxious substances. During the spring peak flows, as much as 10 percent of the annual total phosphorus and 9 percent of the total suspended matter can be loaded to the lake. Riverine polychlorinated biphenyls (PCB's), zinc, nickel, and lead were found to be above the International Joint Commission recommended levels for aquatic health. Nearshore sediment chemistry reflects the dominance of the longshore component of the river plume, which is generally confined to a $10\text{-}km^2$ area around the river's mouth. Seasonal patterns of phosphorus:carbon and carbon:nitrogen in water and sediment samples are presented. Spatial distributions of the variables examined indicate that there are two significant phases (dissolved and particulate) and three transport regions (surface microlayer, thermocline, and nepheloid) in which the material moves from the river to the open lake.

1. INTRODUCTION

The nearshore zone is the primary region for the introduction of polluting and enriching materials into the Great Lakes. In these lakes, coastally entrained circulation impedes offshore mixing of land-derived contaminants, creating observable gradients of materials in the nearshore zone. The immediate effects of greater concentrations of enriching and polluting substances in the nearshore are poorly understood, but the process surely leads to accelerated eutrophication. Since the vast majority of human contacts through recreation, water requirements, etc., is associated with the nearshore, our understanding of the processes involved in this accelerated enrichment and contamination must be refined in order to numerically simulate the system and evaluate its response to applied stresses.

Given the importance of this zone and the severe stresses to which it has been exposed, it is surprising to find that it is not as well studied and understood as the open lake. If we are to protect these areas from further degradation and, it is to be hoped, reverse the deleterious changes that have already occurred, it is essential that we understand the transfer of material through the nearshore zone and be able to predict the concentration of substances at sites of interest.

In response to the Great Lakes Environmental Research Laboratory's (GLERL's) Priority Great Lakes Environmental Research Initiatives Workshop (Pinsak, 1975) and the Great Lakes Water Quality Research Needs report (Great Lakes Research Advisory Board, 1976) concerning the importance of addressing the question of materials movement in the nearshore zone and

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water quality research needs, a program was conducted in the vicinity of the mouth of the Grand River in 1976. Our investigations were designed to iden- tify the major transport modes of materials being introduced into the lake system and to attempt to determine their dispersion pattern, their interac- tions with the nearshore sediments, and their eventual sinks. Most impor- tantly, this study attempted to estimate the influence of the input of river materials on the nearshore region of Lake Michigan.

Beginning at an elevation of 317 m, the Grand River flows 418 km through a drainage basin of 14,430 km^2, emptying into Lake Michigan at Grand Haven, Mich. (elevation 177 m; figure 1). The harbor at Grand Haven has a minimum draft of 6.4 m and a dredged 2.4-m-deep channel extending 27 km upstream. The river outflow is channeled into Lake Michigan through a breakwater extending approximately 400 m offshore.

The bathymetry of the lake immediately offshore of the river is a gent- ly sloping shelf with only a slightly steeper slope region. The visible or traceable plume is generally confined within an area of 10 km^2 or less, its spatial characteristics highly responsive to the prevailing winds (Eadie *et* al., 1979).

The Grand River is the largest tributary flowing directly into Lake Michigan, and previous studies of its water chemistry have shown it to be the major contributor of several noxious substances. Robbins et *al.* (1972) found the Grand River to have the highest mean concentrations of ammonia-nitrogen, nitrate-nitrogen, phosphate-phosphorus, calcium, chloride, sulfate, sodium, potassium, magnesium, copper, and chromium of any of the tributaries entering Lake Michigan. With its high flow, it contributes a large fraction of the total chemical load to the lake. Sonzogni et at. (1978) estimated the Grand River load to be: total phosphous (TP) (24 percent), soluble phosphate-phosphorus (28 percent), suspended solids (16 percent), total nitrogen (23 percent), and chloride (22 percent) to Lake Michigan. (Numbers in parentheses are the 1975-76 average percentages of the total tributary load to the lake contributed by the Grand River.) These loadings, which are usually "pulsed" in during the high flow events, are bound to have a significant effect on the nearshore region.

In other studies around the Grand River, the high nutrient loads were cited as a cause of the high algal biomass in the plume and adjacent region (Stoermer, 1968) and for the characteristics of the plankton population. Shimp et al. (1971) and Fitchko and Hutchinson (1975) found that the highest concentrations of most sediment trace materials were associated with the effluent of the Grand River.

A program to examine the effect of the Grand River's input on the chem- istry of the nearshore region was designed to include both the nearshore water sampling program, primarily conducted to address questions specific to the U.S. Environmental Protection Agency, the Pollution through Land Use Activities Research Group (PLUARG) program (Eadie *et al.,* 1979), and an exper- imental program based on diver collected samples of sediments and sediment- water interface materials. The results of these investigations are presented in this report.

GRAND RIVER BASIN
MICHIGAN
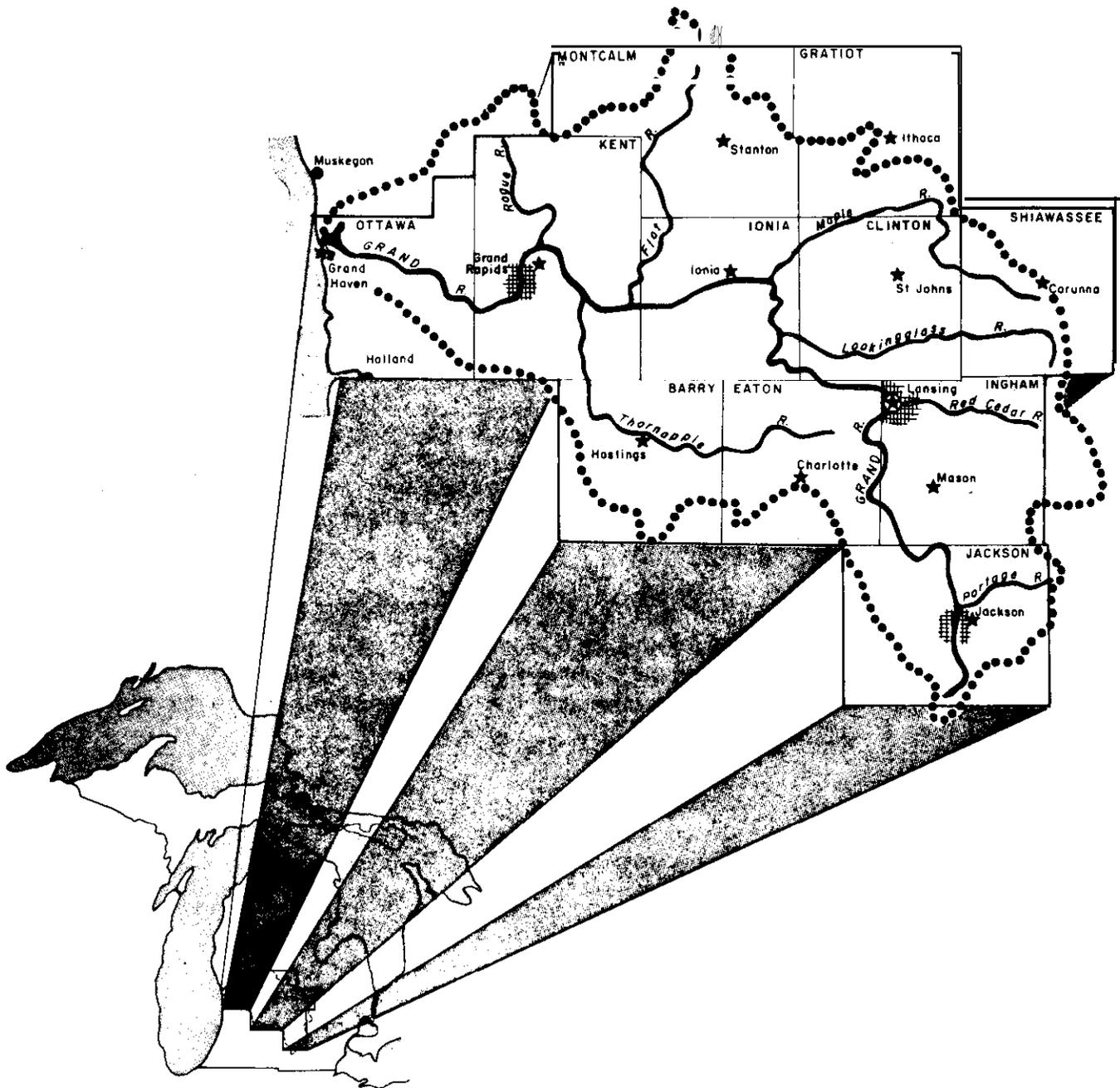
Figure 1.--Grand *River drainage basin, Mich.*

1.2 The Setting

The study area is located in southeastern Lake Michigan in the vicinity of Grand Haven (figure 2). This region of the lake has a relatively "arrow shelf, 2-5 km wide, with water depths of 25 m over the outer shelf. The slope off Grand Haven is 7 km wide, with its base at 80 m. The profundal basin is a region of water depths in excess of 80 m in the southern basin. I" general, the depth contours are concordant with the shoreline. A description of the sedimentary environments is found in appendix A.

2. DATA COLLECTION METHODS

2.1 SCUBA Sampling

The sample collection design and analytical methodologies employed in the PLUARG work are described in Eadie et *al.* (1979); briefly, standard limnological procedures were employed on samples collected primarily in spring. The supplemental program used SCUBA dives to depths of 25 m to collect water and sediment samples at nine locations (figure 3) on a monthly basis, except during July. Water was collected at the sediment-water interface in hydrochloric-acid-cleaned, distilled-water-rinsed 5-cm-diameter butyl acetate sediment core liner tubes. The diver (the first author) carefully collected the water by moving the tube horizontally through the water just above the sediment, being careful not to disturb the sediment, and sealed both ends with plastic caps. Triplicate l-liter samples were collected in this manner at each station sampled. During August, water was collected at 1 m off the bottom in Niskin bottles for comparison with the diver-collected samples. The upper 1 cm of sediment was collected in triplicate by scraping the surface with small plastic containers with snap-cap lids.

2.2 Shipboard Sampling

Bottom sediment samples were collected with a SHIPEK grab sampler. This sampler collects the upper 10 cm in an essentially undisturbed condition; however, during sampling a shock wave precedes the SHIPEK and part of the surface layer (usually very fine floc) may be lost. These samples were collected to detect differences in shipboard collection techniques versus diver-collected samples. The results of this comparison are found in appendix B.

Shipboard treatment of the samples was as follows: 1) The sediment was preserved with 5 ml of concentrated nitric acid, homogenized, and frozen immediately with dry ice. The sediment remained frozen until the time of analysis. 2) The water was treated in several ways. Unfiltered water was transferred into precleaned glass bottles to determine total organic carbon (TOC) and into prewashed polyethylene bottles treated with a few drops of 40 µg/liter mercuric chloride for TP and total Kjeldahl nitrogen (TKN). Filtered water was also stored in a glass bottle acidified with one drop of concentrated hydrochloric acid for determination of dissolved organic carbon. The preserved carbon samples were immediately frozen on dry ice. water was
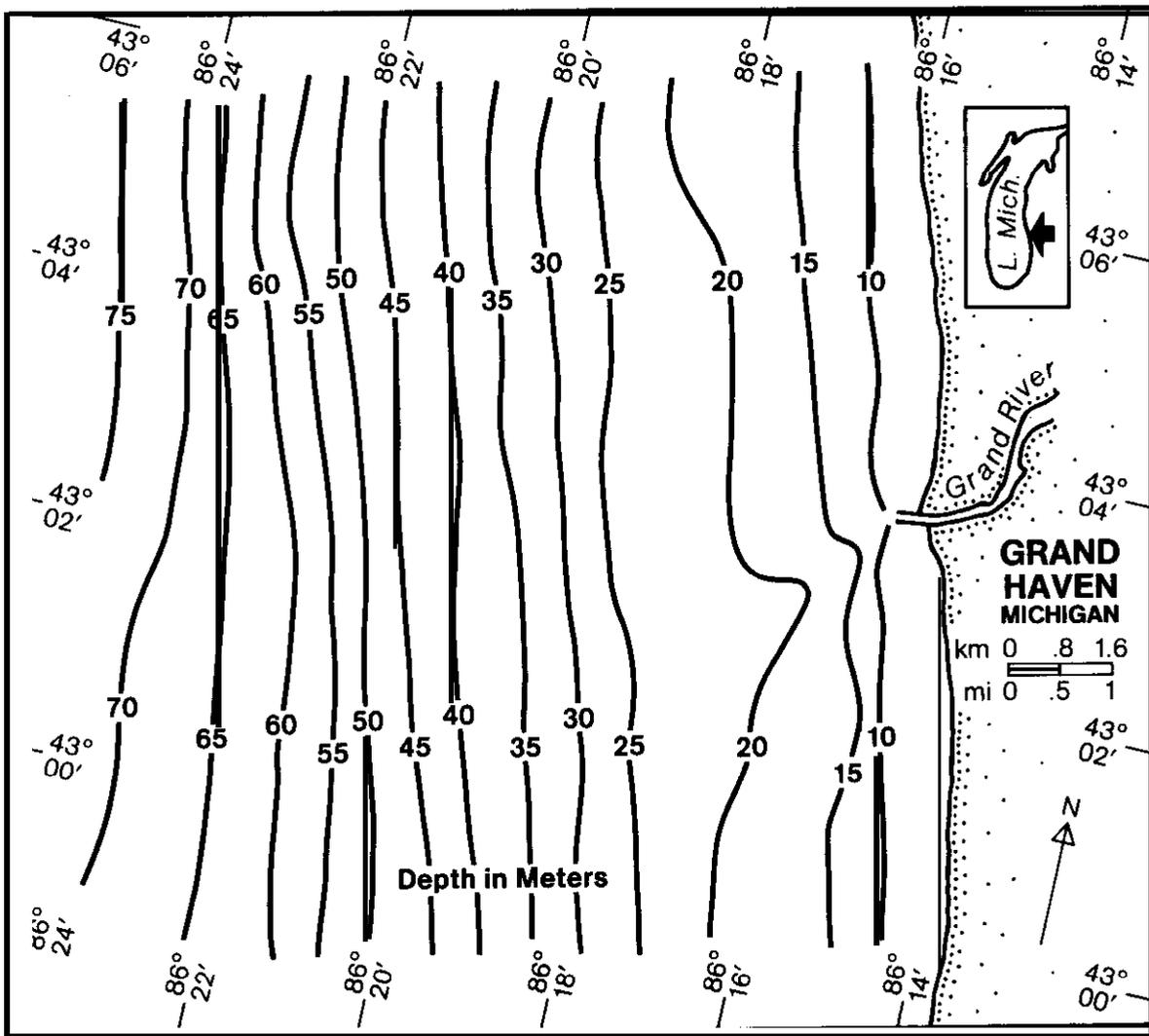
Figure 2.—Nearshore bathymetry of the study area near Grand Haven, Mich.
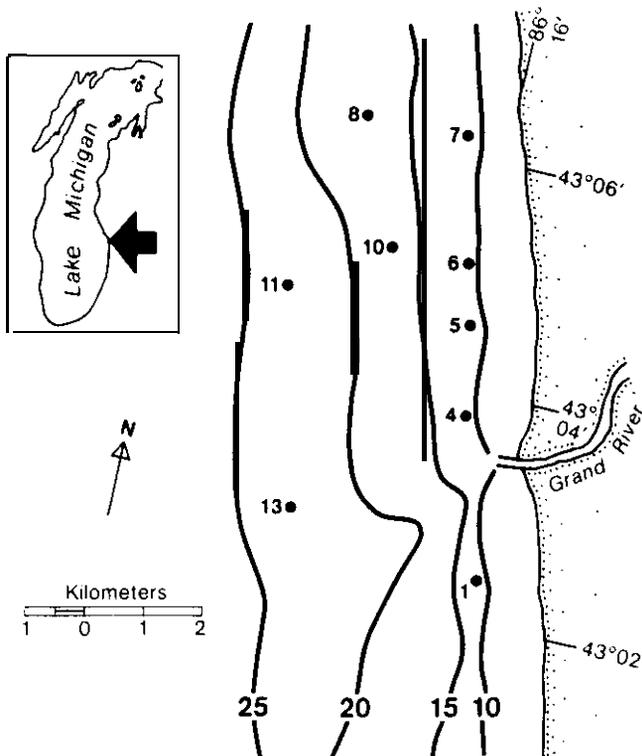
Figure 3.--*Shelf bathymetry and 1976 sampling sites near Grand Haven, Mich.*

also filtered through preweighed 47-mm polycarbonate filters (0.4 μm) for total suspended matter (TSM); the filters were stored at 4°C. Part of the filtrate was immediately analyzed for soluble reactive phosphorus (SRP) by a modified ascorbic acid combined reagent technique at 880 λ (Murphy and Riley, 1962).

3.   ANALYTICAL PROCEDURES

3.1 Sediment

For iron and manganese, three 0.5-g subsamples were accurately weighed and acid leached twice in 12 ml of aqua regia (3:1 mixture of concentrated hydrochloric acid and nitric acid) to near dryness, with occasional mixing. The aqueous solutions were filtered through glass fiber filters, which were washed several times with glass distilled deionized water and made up to volume. Two 0.1-g subsamples were acid leached by the potassium sulfate-sulfuric acid procedure (American Public Health Association, 1975) for TP. These solutions were also filtered through glass fiber filters and diluted to volume with glass distilled deionized water. A series of reagent blanks and standards were treated by the same digestion-filtration procedure.

3.2 Particulate Samples

Total suspended matter was collected on **preweighed** polycarbonate filters (47 mm diameter, 0.4 μm pore size). The volume of water filtered was recorded. The filters were weighed and digested with aqua regia for determination of iron and manganese. The solutions were made up to a **25.0-ml** volume. Reagent blanks were also prepared following the above procedure.

3.3 Water Samples

TP and TKN were measured in acid-digested whole water samples. The potassium sulfate-sulfuric acid method used for the sediment samples was used for the whole water samples. Iron and manganese were determined directly from the solutions prepared from the aqua regia extractions on a Perkin-Elmer, model 305, atomic absorption spectraphotometer. The amount of metal extracted by the aqua regia method was not determined; however, it is probably similar to the percentages reported by Trefry and Presley (1976). They found that approximately 71 percent of iron was removed and 87 percent of manganese. They also state that the type of sediment digested may determine the percentage leached. The coefficient of variation **(CV)** can be used to express the analytical **precision** for **replicate** acid extractions: For iron 5 percent (4 percent) and for manganese 4 percent (3 percent). The numbers in parentheses are the coefficients of variation reported by Trefry and Presley (1976).

TKN and TP concentrations were determined on a Technicon **AutoAnalyzer** II. TKN was measured following the methods outlined in the Technicon manual. The percent recovery of TKN is not known at this time. Phosphorus was determined by the modified Murphy and Riley (1962) ascorbic acid combined reagent technique at 880 λ. Wyeth (1973) found that approximately 90 percent of the TP was extracted when the method described in this study was used. The coefficients of variation for TKN and TP are 2.5 percent and 10 percent, respectively. Again, the type of sediment digested controls the percentage leached and reproducibility of the analysis, with sandy materials showing the poorest results.

3.4 Carbon Analysis

Organic carbon concentrations in the water were determined by a modification of the technique described in Strickland and Parsons (1972). Sediment organic carbon was also measured by the **ampoule** technique after the sediment had been acidified with 1 N hydrochloric acid to remove carbonates. Carbonate carbon was measured by weighing 1-10 **mg** of sedimentary material into a precleaned serum bottle, which was then capped and attached to the Oceanography International Carbon Analyzer by piercing the septum with an inlet and outlet needle. After the air in the bottle was replaced by nitrogen, the sample was acidified with 5 ml of lo-percent phosphoric acid and analyzed for carbon dioxide. Precision for all carbon measurements is estimated at 5 percent **(CV)** based on prior experimental work.

3.5 PCB Analysis

Samples for polychlorinated biphenyls (PCB's) were collected in pre-cleaned (hexane washed) brown glass gallon bottles. These samples were collected in duplicate and preserved with 50 ml of glass distilled hexane. For filtered samples, precombusted glass filters were used in a cleaned Millipore filtering apparatus held at 300-400 mm mercury vacuum. The samples were extracted with three washes of hexane and concentrated in a rotary evaporator.

Under contract, the Environmental Research Group, located in Ann Arbor, used the following procedure to perform the analyses:

An Aerograph 1740 gas chromatograph equipped with tritium foil + nickel-63 electron capture detectors was used for the analyses. It was fitted with 2 m x 0.3 cm Pyrex columns packed with 4 percent S.E. 30 and 6 percent SP2401 on Supelcoport, and 5 percent O.V. 210 on Supelcoport (100/120). It was operated at a column temperature of 200°C.

The quantity of PCB present in the sample was estimated by measuring the two or three main peaks and comparing to the same peaks in standard commercial mixtures of PCB's, such as Arochlor 1242, 1254, etc.

All concentrations are reported relative to standard concentrations of the closest matching Arochlor or mixture of Arochlors.

4. RESULTS AND DISCUSSION

Our results are presented in a logical sequence of sections beginning with river chemistry and loads and sediment and sediment-water interface chemistry.

4.1 The Grand River

During the 1976 water year (October 1, 1975, through September 30, 1976), the 3 months of spring runoff (February 16-May 15, 1976) accounted for 54.3 percent of the total annual flow as reported by the U.S. Geological Survey (USGS), a daily record of which is shown in figure 4. The year 1976 was abnormal in that the peak flow (800 m^3/s) was the highest recorded by the USGS gage at Grand Rapids, Mich., in its 44 years of recorded data. The high peak flow was the result of high amounts of winter snowfall followed by an early spring melt. Mean flow for 1976 was 160 m^3/s, well above the 44-year mean of 96 m^3/s.

Table 1 is a summary of both monthly historical loadings and the 1976 loading data from this work. Results indicate that the high spring flows are responsible for a significant fraction of the total yearly loading of materials. During the 10-day period of high flow (March 5-14), 10 percent of the annual load of TP and 9 percent of the TSM are transported. The impact of this high materials flux is difficult to evaluate. Besides nutrients, the river also loads toxic substances into the lake, as shown in table 2. These are spring samples (March-April) and are thus probably diluted by melt water.

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Grand River Flow 1963-75, 1976, 1977
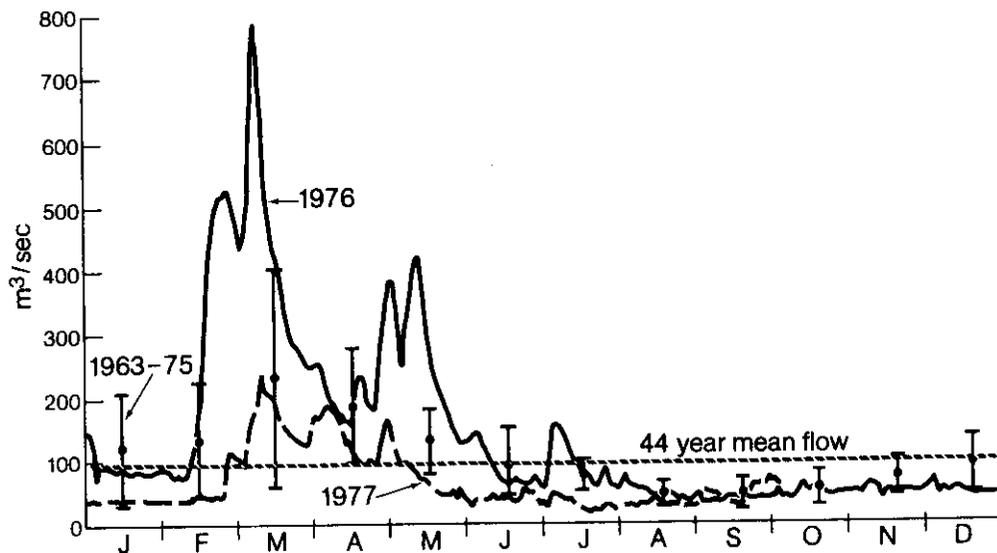
Figure 4.--*Grand River flow, 1963-75, 1 976, 1977,as reported by the U.S. Geological Survey.*

Table 1.--*Monthly loadings (percent of yearly total) 1963-75 and 1976, and estimated loads during peak flow, March 5-14, 19 76, of the Grand River*

Month	Flow (U.S. Geological Survey) 1965-70	Flow (EPA Storet) 1963-75	Flow (EPA Storet) 1976*	Mean TP	1976**	Mean TSM	1976**	Mean Cl⁻	1976**
Jan.	7.1	9.3	5.0	8.2	--	5.2	--	11.1	--
Feb.	10.9	10.7	13.5	9.0	--	5.9	--	9.9	--
MN.	11.9	18.1	22.4	18.5	16.7	20.3	19.8	15.4	16.2
Mar. 5-14	--	___	11.3	--	10.1	--	9.2		6.9
Apr.	17.5	14.7	11.3	19.1	10.0	21.6	13.4	11.2	10.4
May	10.8	10.2	13.4	8.7	10.6	11.87	11.8	9.2	10.7
June	a.3	7.2	4.3		--	8.1	--	7.5	--
July	7.3	5.9	4.9	6.2	--	7.5	--	6.2	--
Aug.	3.8	3.4	2.4	4.6	--	2.9	--	4.7	--
Sept.	3.5	3.5	2.0	3.6	--	3.1	--	4.0	--
Oct.	3.9	4.2	--	4.7	--	4.1	--	5.1	--
Nov.	5.7	5.7	--	6.6	--	4.5	--	6.8	--
Dec.	9.3	7.3	--	a.2	--	5.2	--	8.0	--
Load (MT/yr)**				840		150,000		150,000	

*1976 water year (Oct. 1975-Sept. 1976).
**1976 total loading from Sonzogni et al. (1978) based on EPA data.

The river samples were collected approximately 1.6 km up from the mouth. PCB's,

Table 2.--*IJC water* quality criteria and 1976 Grand River
and Lake Michigan *water chemistry*

Parameter	IJC Recommended	Units	River Mean	River Max	Mouth Mean	Mouth Max	400 m Mean	400 m Max	1.6 km Mean	1.6 km Max	Background Mean	Background Max
Aldrin-Dieldrin	1	p/t	<10	<10	--	--	--	--	--		<10	<10
DDT	5	p/t	<10	<IO	--	--	--	--	--	--	<10	<IO
Endrin	2	p/t	<10	<IO	--	--	--	--	--	--	<10	<10
Heptachlor	1	p/t	<5	<5	--	--	--	--	--	--	<5	<5
Lindane	IO	p/t	<5	<5	--	--	--	--	--	--	<20	<20
Methoxychlor	40	p/t	<20	<15	--	--	--	--	--	--	--	--
PCB 1254"	1	p/t	9.4	12	0.2	15	--	--	9.5	19	9.7	13
PCB 1242*	1	p/t	7.2		6.2	II	--	--	9.2	15	1.2	II
Arsenic	50	p/b	--	<0.5	--	<0.5		<0.5	--	<0.5	--	G0.5
Mercury	0.2	p/b	--	<0.2	--	<0.2		<0.2	--	<0.2	--	<0.2
Copper*	5	p/b	--		18	18	13.5	14	12	12	7	8
Chromium	50	p/b	14.8	15	12	13	8.5	IO.	9	IO	6	7
Cadmium	0.2	p/b	--	<2	--	<2	--	<2	--	<2	--	<2
Iron*	300	p/b	1003	1100	785	860	520	540	570	770	635	640
Nickel	25	p/b	20.3	22	25.5	27	17	18	13	15	--	10
Lead	25	p/b	25.5	38	19.5	21	19.5	20	19	22	15.5	16
Zinc	30	p/b	43.5	73	32.5	39	17.5	21	20	22	19.5	23
Ammonia-nitrogen	50	p/b	50.6	56	49	53	26.5	33	17	18	1.0	1.5
..		p/b	65	120	50	*110*	18.3	35	11.3	15	7.5	
TKN		p/b	696	980	652	750	393	480	415	490	280	17
TOC		p/m	15.3	27.5	16.7	36.5	16.9	30.5	10.0	13.3	a.7	7.6
TSM		p/m	20.0	37.	13.9	24.9	8.1	12.8	6.8	9.9	3.1	

*above recommended limits at all locations.

zinc, nickel, and lead were higher in concentration than the International Joint Commission (IJC) recommended levels for aquatic health. Iron was also very high during this period, presumably from soil leached during the flood stage. This high concentration of presumably hydrated iron oxides could have been acting as scavengers of trace metals and hydrophobic organics, carrying them out into the lake in particulate form.

During the 1976 field season, the U.S. EPA had samples of near-mouth river *water* collected daily and analyzed for phosphorus fractions. The results, extracted from STORET, are plotted in figure 5. Spring showed several loading peaks, which decreased in early summer. The fraction of the TP input in the form of particulate matter was also shown to vary seasonally. In spring, approximately 50 percent of the TP is particulate, but in summer and fall this fraction increases to 70-90+ percent. It is generally recognized that dissolved phosphorus is more available to the biota than particulate phosphorus and that it will have a longer residence time in the water column. In 1976 the late winter-spring input of dissolved phosphorus accounted for most of this fraction's annual load.

4.2 Nearshore Lake Michigan

For this study our operational definition of nearshore is the region comprising the shelf (water depth of less than 25-30 m, generally within 3 km

Grand River Phosphorus Loading (1976)
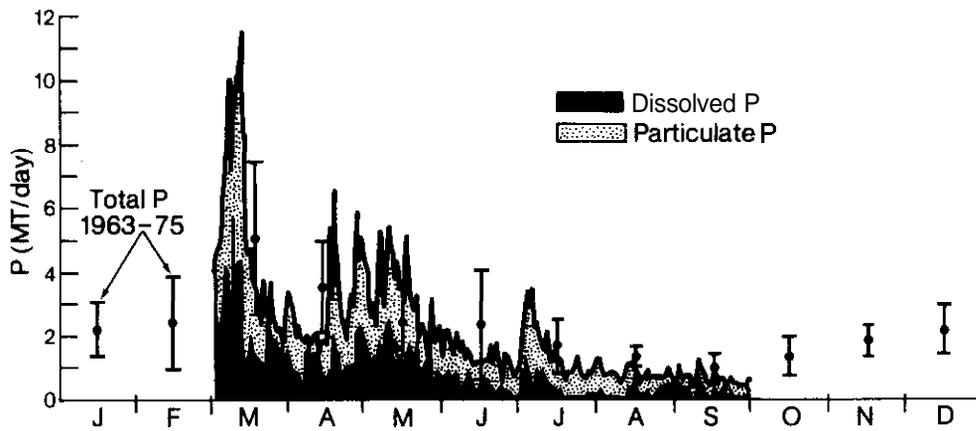
Figure 5.--Grand *River phosphorus loading, 1976.*

of shore). In this region, water quality characteristics are strongly influenced by sporadic runoff events and wind-induced wave resuspension of sedimentary materials, the effects of which literally mask normal conditions. Figure 6, a plot of chlorophyll a and temperature from three cruises between March 19 and April 2, suggests that the biomass may be limited by temperature, which changed rapidly during this period. During the March 19 and 23 cruises, chlorophyll a, SRP, silica, and TSM mixed conservatively (i.e., linearly with respect to specific conductance and chlorine ions), while on April 2 there appeared to be a biostimulation due to the increased nutrient load. Figure 7 shows the effect through the in *situ* loss of SRP, ammonia, and TSM accompanied by an in *situ* gain in chlorophyll a. It appears that during this period of high spring loading the nutrient environment is conducive to high algal growth, but the thermal environment is changing so rapidly that stable populations cannot optimally exploit it.

Unfiltered samples for copper, chromium, zinc, nickel, cadmium, iron, lead, mercury, and arsenic were collected at the surface and 1 m above bottom on the April 2 cruise. Variability was quite high, probably because of the difficulty of obtaining representative samples in the river plume area. Table 2 shows the reduced results, with significant differences between predominately river water samples and those collected offshore. Similarities between samples from the surface and those from 1 m above bottom are characteristic of the well-mixed unstratified period. Comparison of our unfiltered metal data with those of Robbins *et* al. (1972), which were for dissolved metals, shows that our iron results are much higher, with copper and zinc higher, but nickel and chromium lower. The higher concentrations can be attributed to particulate matter, while the lower values are questionable; a possible explanation for the latter is dilution of our samples by melt water.

The data in table 2 illustrate the influence of the Grand River and the rapid assimilation of the river's load. In our work we found that the river plume retained its identity for only a few kilometers even under the peak flow
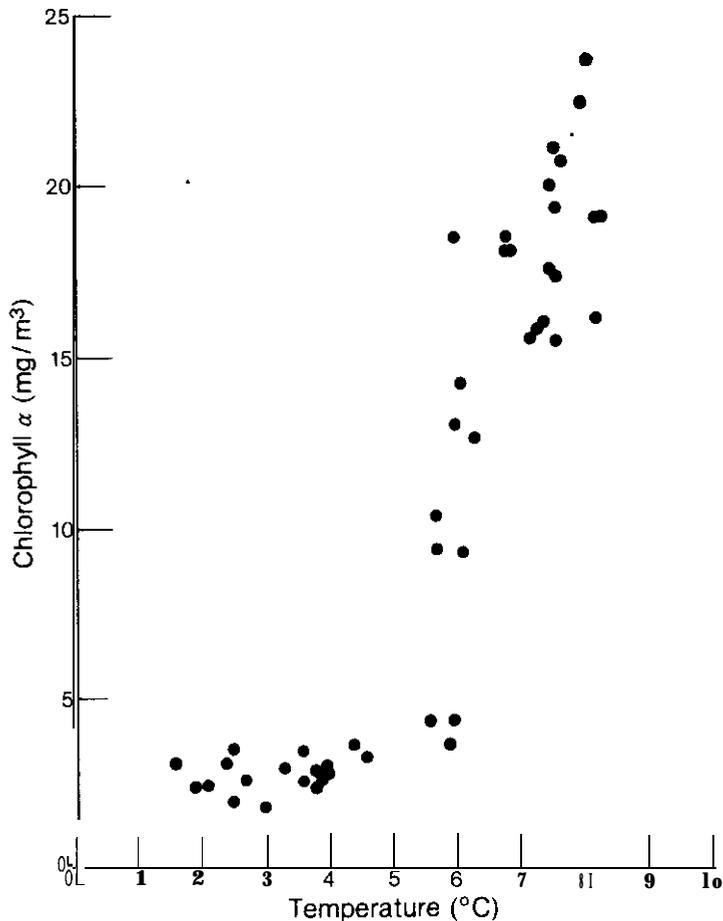
Figure *6.--Plot of chlorophyll a and temperature from three cruises between March 19 and April 2, 1976. These data suggest that biomass may be temperature limited.*

conditions of the river in spring (determined during the first six cruises between February 23 and April 2). The table lists mean and maximum values recorded at five locations for each cruise, 1.6 km upriver, the mouth, 400 m and 1.6 km down the plume spine, and a background sample taken approximately 8 km offshore. Metal and pesticide samples were collected only once during spring, while the remaining variables were collected for most cruises. The table shows PCB's, total iron, and copper above IJC recommended levels at all five locations for the dates collected and ammonia, zinc, and nickel above recommended levels at the mouth. Concentrations decrease rapidly along the plume out to background. Levels of TP, TKN, TOC, and suspended matter are included for reference as no water quality criteria exist for these substances. Examining spatial distributions of these data has led to the conclusion that there are two phases and three regions in which the materials from the river and nearshore are transported into the offshore. The phases and regions with their associated observed characteristics are:
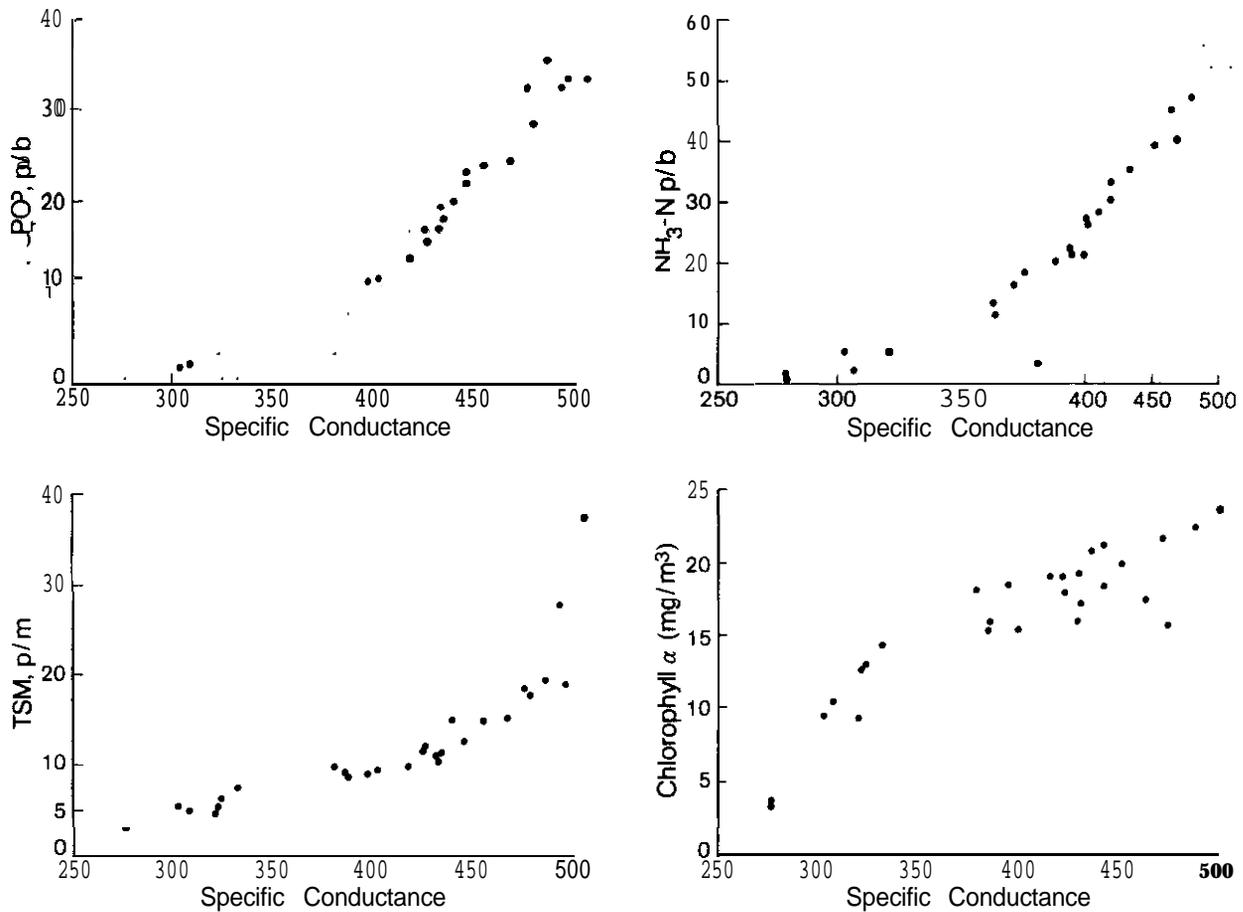
Figure *J.--These figures show the effects of an* in situ loss of *soluble reactive phosphorus (SRP), ammonia, and total suspended matter (TSM)* accompanied *by an* in situ gain in *chlorophyl a.*

Phase	Characteristics
(1) Dissolved	Apparent conservative behavior over shore time scales investigated (day) unless plankton bloom conditions perturb "available" nutrients.
(2) Particulate	Nonconservative behavior influenced by plankton productivity, settling, and resuspension.

Region

(1) Surface microlayer	High concentrations of very fine particulate and organics, region of atmospheric input, and photolysis.

(2) Thermocline   High density gradient and high biomass and particulate matter, region of internal wave impingement on the bottom, which apparently influences resuspension.

(3) Nepheloid   Near bottom region of high particulate matter concentration apparently being transported downslope.

The dissolved and particulate materials are dispersed throughout the water column primarily under the control of physical mixing. Both contain a nonconservative biological component for some of their constituents, which we have seen only once in our nearshore work during the 11 cruises (figure 7). The particles have components of settling, aggregation, and in *situ* generation that increase their tendency to nonconservative behavior. We have seen evidence from light transmissometer data, as well as discrete sampling, of an increase of material in the region of the thermocline. There are three sources for this increased material, 1) sinking epilimnetic matter reaching surfaces of neutral density, 2) material resuspended by the action of the thermocline rubbing along the bottom, both through internal waves and upwelling/downwelling transients, and 3) in *situ* production in the region. The microlayer zone (upper 100 μm) has been shown to concentrate trace metals and trace organics (Liss, 1975). Through photo-oxidative processes, this layer is presumably highly reactive, leading to major in *situ* alterations.

Resuspension through surface wave action, the thermocline's movement along the bottom, and bottom currents combine to generate a zone of high suspended-matter concentration extending 5 or more meters above the bottom. This nepheloid layer moves downslope to a final sink out in the deep lake, carrying with it a significant portion of the clay-silt material originally deposited nearer the top of the slope (Chambers and Eadie, in review). Weak bottom currents (S-10 cm/s) would be sufficient to maintain this material in suspension (Saunders, 1976) and sedimentary evidence indicates these currents must exist. The southwest and *western* sides of the southern basin of Lake Michigan have been shown to be areas of almost zero deposition (Edgington and Robbins, 1975, 1976; Robbins and Edgington, 1975). As yet, we have no quantitative estimates of the magnitudes of these transport mechanisms. Resuspension of materials contributes a very fine floc of almost neutral density to the water column. An analysis of a small number of these floc samples shows then to contain very high concentrations of TOC (3 percent), TP (1 percent), TKN (2-3 percent), iron (2-3 percent), and manganese (1 percent). These are average percentages by weight of sediment. Only small amounts of energy are required to mobilize this floc, as was empirically observed in the diving program.

The results of PCB analysis for unfiltered nearshore water samples are presented in table 3. In the unfiltered water samples there did not appear to be any discernible pattern in either time or space. Statistically, the river samples collected approximately 2 km from the mouth were the same as those samples collected 8-15 km offshore in well-mixed lake background water.

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Table 3.--*PCB (p/t) (as PCB 1242 and PCB 12541 in unfiltered water samples collected in spring (February-June) 1976*

Location	PCB 1242				PCB 1254		
	Mean	SD	N		Mean	SD	N
Grand River	7.2	2.9	10		9.4	2.8	10
Mouth	6.2	3.8	6		8.2	4.3	5
0.8 km offshore	10.2	5.8	5		11.1	5.0	7
1.6 km offshore	9.2	4.1	6		9.5	5.1	6
>8 km offshore (background)	7.2	3.1	6		9.1	2.9	6

In six nearshore sediment samples, the PCB's ranged from l-10 p/b (PCB 1242) to l-60 p/b (PCB 1254) and averaged 5 and 20 p/b, respectively. Variability was great owing to the high sand content of the surface samples.

Microlayer samples collected via a stainless steel screen were collected at four locations. The sampler was estimated to collect materials from the upper 200-300 pm. Samples were also collected at 1 m below the surface for bulk water comparison (table 4).

Bulk water samples were somewhat lower in PCB 1254, but there is insufficient information for any definitive statements on the concentration factors in the microlayer. It can be said, however, that the screen samples were significantly higher than the average nearshore PCB concentrations as reported in table 3.

While PCB's are certainly an acknowledged problem in Lake Michigan, the problem does not appear to be intensified in the nearshore region studied for this report.

Table 4.--*PCB (p/t) measured in the* surface *microlayer (upper 100 μm) versus the upper 1 m*

Samples	microlayer (upper 100 μm)		Surface (1 m)	
	PCB 1242	PCB 1254	PCB 1242	PCB 1254
7610 5A	19	<10	--	--
B	16	10	--	--
7606 5	<15	<10	<15	<10
7606 Plume edge	14	a4	25	64
7605 Tower	37	77	<15	26
7605 Tower (filtered)	41	<20		

4.3 Sediment and Sediment-Water Interface Chemistry

Spatially, the sediment data (TP, TOC, iron, manganese) had a southwest-northwest gradient, indicating that the river loading had a predominant northward component. Wind data from a NOAA National Weather Service station in Muskegon (16 km north of Grand Haven) show the average prevailing winds to be out of the southwest, which would tend to drive the plume northward. Temporal variability of the prevailing winds should be a factor in the nearshore sediment record because of the rapid response of the longshore drift to the wind and wave patterns.

For the sediment data, very high correlations were found for iron-manganese, manganese-TP, and TP-iron. Significant, but much lower correlations were found for carbon-TP, carbon-manganese, and carbon-iron (table 5).

Table 5.--*Correlation coefficients* for *sediment TP, carbon, manganese, and iron*

	TP	carbon	mangenese	iron
TP	1.00			
Carbon	0.72	1.00		
Manganese	0.97	0.65	1.00	
Iron	0.97	0.64	0.97	1.00

n = 20
r = 0.561, a = 0.01

Principal component analysis of these data (see Morrison, *1967;* Davis, *1973;* Chambers, *1975;* Chambers and Upchurch, *1979)* shows that the first component accounts for *72* percent of the variability and is composed mainly of iron, manganese, and TP. The second component is loaded most highly by organic carbon and accounts for 21 percent of the variability. A plot of the principal components' scores (figure 8) reveals something of a south to north grouping of stations, both temporally and spatially, similar to trends detected by plotting the raw concentration values. The high correlations between iron-manganese, iron-phosphorus, and manganese-phosphorus seem to suggest that these elements are related to the same "fraction" of the sediment. However, it has been found that in sediments dominated by iron and manganese oxides the TP associates with the iron phases and not with the manganese (Williams *et al.,* 1971a,b,c). Since the river is the major phosphorus source in this area, it is possible that a significant fraction of the phosphorus in the sediment is in an inorganic form, coprecipitating with the iron and manganese. It is also possible that the organic phosphorus in the sediment is remobilized differently than the organic carbon. In the former case one would expect to see high sediment phosphorus:carbon ratios, while in the latter case the results are unclear.

The sediment phosphorus:carbon ratio in this nearshore region is high with respect to the Redfield-Ketchum phytoplankton ratio of 1:106. These

1976 Grand Haven Sediment Chemistry

Transformed Variable II (21%)

```
  3
                 04-4
                  02-4
  2           05-D4
             04-10 06-4       04-1
 04-11        04-13          02-13 04-5   04-7
  1            02-10
                    05-D10              04-6    04-8
                06-13
  0                     05-S10
                  05-D13
               05-S4
 -1
                 06-10
 -2
  -3    -2    -1    0     1     2     3     4
```

Transformed Variable I (72%)
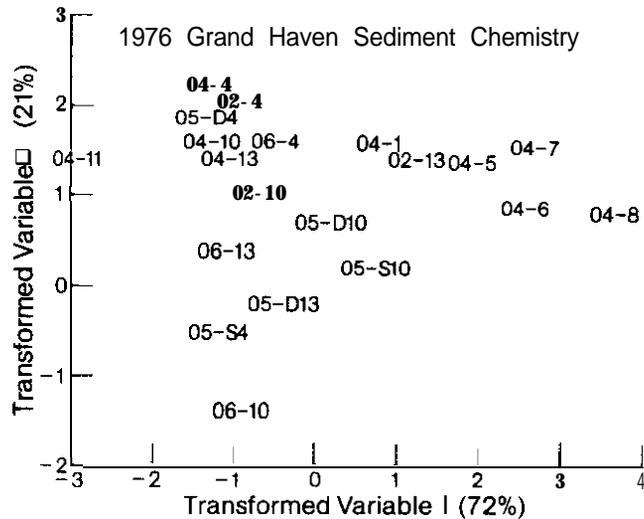
Figure 8.--*Principal latent* vector scatter *diagram* of *the first two transformed variables of the* sediment *chemistry data. Sampling codes are: June (02), August (04), September (05), October (06). Undesignated samples or those labeled with a D were diver collected. S-labeled samples were collected with a SHIPEK grab sampler.*

ratios show significant temporal variability, with the highest ratios occurring during fall. The ratios change primarily because of a decrease in the organic carbon content of the sediment, while the phosphorus remains relatively constant over the study period. Figure 9 illustrates the trend in phosphorus:carbon ratios for three stations during the period of June through October 1976. Phosphorus:carbon ratios for whole water samples collected at the sediment-water interface show a trend just opposite to the one seen in the sediment (figure 10). The very low phosphorus:carbon ratios are a result not only of decreasing TP values with time but also of a concurrent increase in the TOC concentrations. The higher levels of particulate iron and TP found in spring and progressively decreasing into fall agree with the observed Grand River loading pattern. (See table 1.)

Figure 11 shows nitrogen:phosphorus ratios for the unfiltered interface water. Like the phosphorus:carbon ratios, the nitrogen:phosphorus ratios are highest in June, decreasing through November, with TP decreasing at the fastest rate. Combining the facts of decreasing nitrogen:phosphorus and phosphorus:carbon ratios in the unfiltered interface samples and increasing sediment phosphorus:carbon ratios from spring through fall, we conclude that the sediment phosphorus content increases relative to TKN and organic carbon. The TKN is probably lost through denitrification, while lower carbon values result from oxidation and ingestion by benthic organisms and from nondeposition in the nearshore of the fine grained material with which organic carbon associates.

17

Sediment
C/P Seasonal Ratios
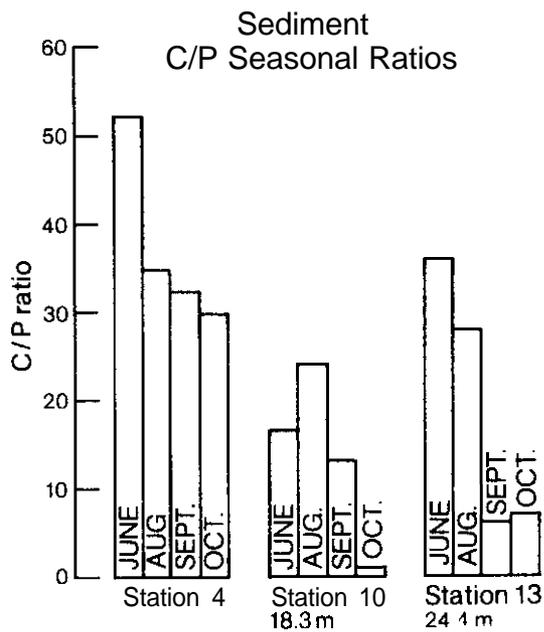
Figure *9.--Sediment carbon:phosphorus ratios at three stations during June-October 1976.*

Sediment/ Water interface
C/P Seasonal Ratios
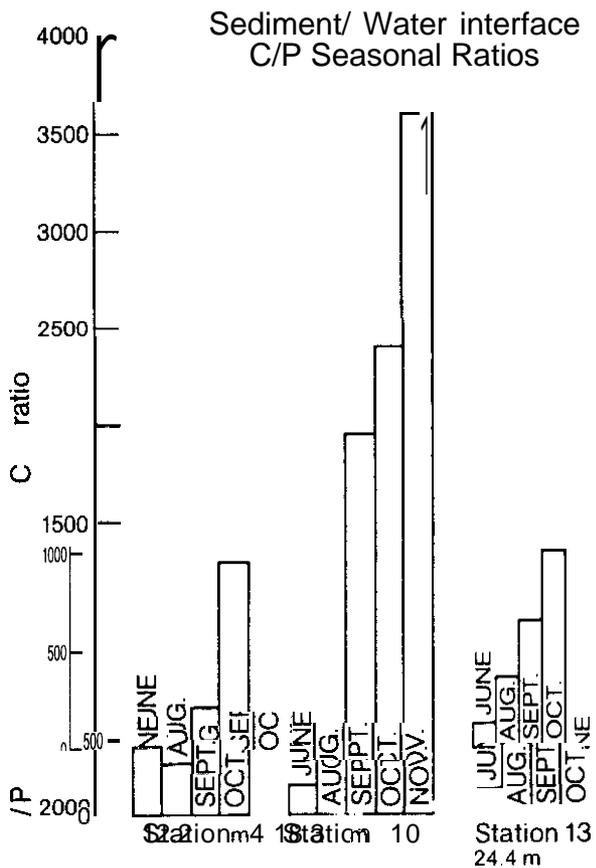
Figure 10.*--Carbon:phosphorus ratios for whole Later samples collected at the sediment-water interface during June-October 1976.*
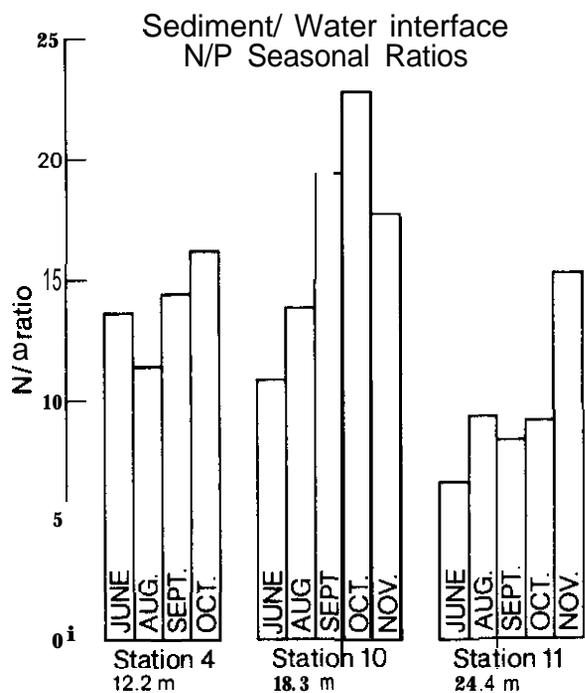
Figure 11.—*Nitrogen:phosphorus ratios for the samples in figure 10.*

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Appendix A--SEDIMENTARY ENVIRONMENTS

The sediment descriptions are based on more than 175 samples, including SHIPEK grab samples, gravity cores, and diver-collected samples, in a 260-km^2 grid in the vicinity of Grand Haven (figure 12). Many of the descriptions and the related discussion about the environments are based on in situ observations by the senior author, who made approximately 130 SCUBA dives in the research area. Descriptions of the sediment deeper than 30 m are based on SHIPEK grab samples.

The Shelf Environment

The beaches consist of fine to medium sized, clean, well-sorted quartz sand and are backed by aeolian dunes. The sediments between the strand line and about 18 m are composed of very fine to medium sized, moderately well- to well-sorted quartz sand with trace amounts of rock fragments and heavy minerals. The heavy mineral suite consists of the iron species, hornblende, pyroxenes, garnet, and epidote (Hulsey, 1963). From the mid- to outer shelf (18-25 m), the sediments tend to become slightly coarser with poorer sorting. Hough (1958) and Cote (1962) also noted an increase in grain size offshore in the region between 17 and 32 m before decreasing in size toward deeper water. This trend has also been noted on the continental slopes (Hough, 1958). Generally, the shelf sediments contain less than 2 percent of the $64\text{-}\mu\text{m}$ material (figure 13A). The "delta" like structure shown in figure 13B shows little topographic expression, except for an indication of the old Grand River channel formed during the Pleistocene low water strands. The "delta" structure is probably the result of hydraulic sorting by the Grand River.

The sediment distribution in shallow water is controlled largely by wave-induced currents and by lake currents resulting from normal lake circulation. For most of the year, there is a well-established counterclockwise circulation pattern in the southern basin. However, nearshore, the littoral drift is highly dependent on wind direction, which can cause reversals in the dominant northward drift in the Grand Haven area (Lineback et al., 1972).

Before thermal stratification, the sediment surface between the outer limits of the offshore bars and about 10-m water depth is dominated by fairly large-scale symmetrical oscillation ripple marks. These ripple marks become progressively smaller in scale in water from 18 to 20 m deep. At 25 m the sediment surface is only slightly undulatory to almost flat. Several dives were made before stratification, when surface waves were between 1 and 2 m in height. It was possible to observe sediment entrainment to water depths of at least 18 m. As the waves passed over, very fine sand was lifted several centimeters from the ripple crests and dropped back almost vertically with the passing waves. Horizontal oscillatory motion at 18 m was estimated to be between 15 and 30 cm.

After stratification, the ripple marks disappeared, apparently owing to bottom currents, producing a planar bed. However, storm events can cause the bottom to become rippled again for a few days until bottom currents produce a
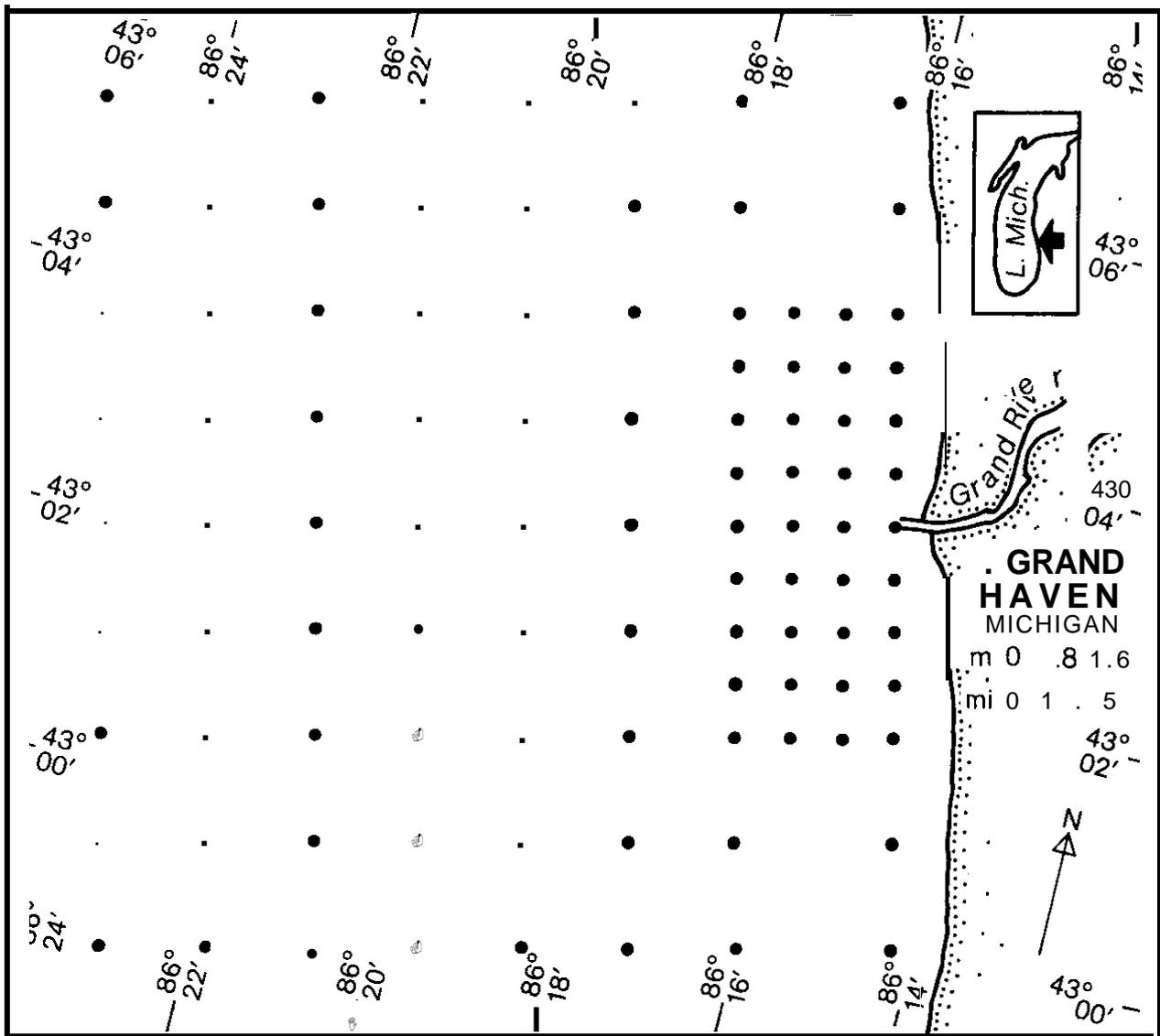
Figure 12.—*Samples sites for the 1977 sediment collection program.*
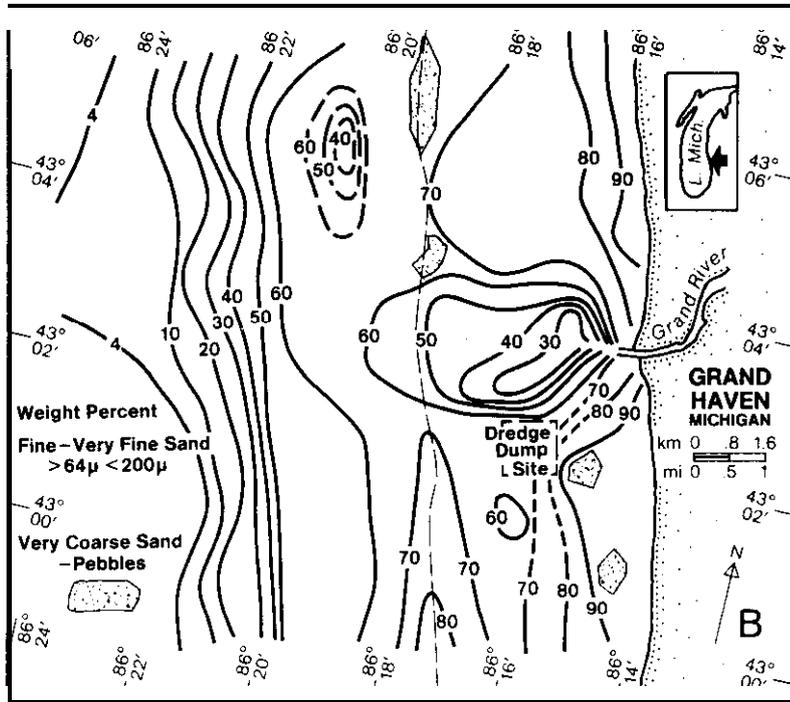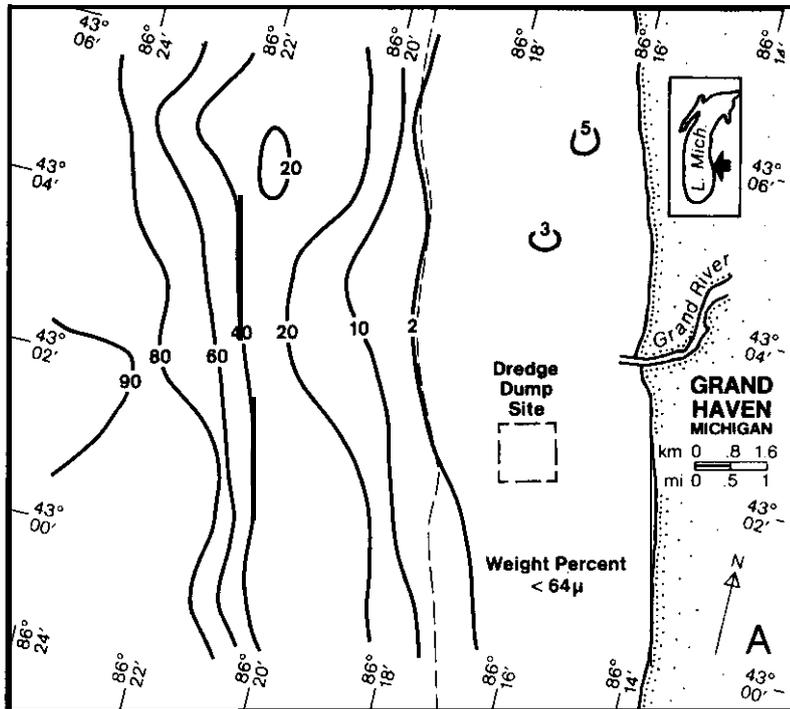
Figure 13.—Illustration of the amount of material finer than 64 pm (A) and the material >64 µm and <200 µm (B). Notice the influence of the Grand River on the distribution of the fine to medium sized sand in figure 13B.

flat bed. Several times during the summer, bottom currents greater than 10 cm/s were experienced at the 25-m depth. These speeds were crudely estimated by timing pieces of algae moving across the bottom. Transport of very fine sand to silt due to the bottom currents was also observed at this time. Very often currents produced lineations on the sediment surface, as the fine sediment was "shadowed" by small pebbles on the surface.

An interesting phenomenon observed during May and June of both 1976 and 1977 was local accumulations of brown flocculent material in depths less than 15 m. These materials appear to be very soft, highly water-saturated, flocculated, brown-colored clays and silts. The brown coloration is in part due to the high organic carbon content, up to 3 percent dry weight. The greatest accumulations were found approximately 2 km north of the Grand River at station 6 during late June 1976 in 11 m of water. Large, patchy accumulations were also noted approximately 1 km south of the Grand River from early May through early June 1977 in 11 m of water. The dominant sediment type at this depth is fine to very fine, well-sorted quartz sand. During late June 1976 the lake bottom was flat, with rather large localized patches (up to 3 m by 15 m) of the brown flocculated material. In some cases the highly water-saturated patches were as much as 10 cm thick. Several samples of this material were collected along with the dominant sediment type for chemical analysis. During May several sets of sediment traps were installed 1 m off the bottom. After 1 month, station 6 had the only retrievable traps. Several grams of material were collected during the previous month.

Smaller accumulations of this material were observed at other stations both north and south of the Grand River. These accumulations normally occurred in the more protected ripple troughs. As would be expected, these accumulations are very ephemeral deposits, which even the slightest currents are able to remove (presumably into deeper water) or spread into a very thin veneer over the bottom. Traces of this floc were found in all SCUBA collected samples from depths greater than 11 m. Except for occasional coastal mass wastage and large storm effects on the beaches, the shelf probably has little, if any, net accumulation of sediment.

The Slope Environment

The sediment at the top of the slope is very silty sand grading into very clayey, medium-gray-colored silts at its base. Several gravity cores were collected to obtain undisturbed sediment-water interface samples. Integrity of the cores was indicated by the presence of very delicate tubificid worm mounds at the interface. The upper several centimeters consist of very soft, reddish-colored, highly water-saturated, aggregated clayey sediment. Below this horizon the sediment was stiff, gray-colored clays with irregular black mottling.

It has been shown by seismic profiling and coring (Lineback et al., 1972) and by radiometric dating with lead-210 and cesium-137 (Robbins and Edgington, 1975, and Edgington and Robbins, 1976) that the eastern slope is an area of active sediment accumulation and that maximum accumulations occur on the middle and lower parts of the slope, with much less accumulation in the deeper basin.

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The **Profundal** Environment

These are the sediments in water deeper than about 80-100 m, and they are very fine silty-clay deposits. The sediment-water interface consists of very soft, highly water saturated, reddish-colored, aggregated clayey sediment.

Appendix B--SHIPEK BUCKET SAMPLES VERSUS DIVER-COLLECTED SAMPLES

During September 1976 triplicate SHIPEK grab samples were collected at each station in addition to the triplicate hand collected sediment samples. We retained only the upper 0.5 cm of the grab sample for analysis, being careful not to collect sediment in contact with the metal bucket.

Six replicates of each triplicate sample were analyzed for iron and manganese for stations 4, 10, and 13. An ANOVA (analysis of variance) was performed on each of the six subgroups--three diver-collected sets at three depths and three SHIPEK sets at three depths. Similar results were found for each subset; therefore, the samples collected at station 13 will serve as an example of the ANOVA.

The ANOVA results are listed in table 6. In both cases (SHIPEK and diver) the between-group variance for iron is highly significant (<0.01) as is the diver-collected manganese results. Only the SHIPEK-collected manganese results gave non-significant between-group results, which is atypical when compared to the other ANOVA results. On the basis of the above results a comparison between the SHIPEK and diver-collected samples cannot be made. The very small coefficient of variation for each replicate indicates minimal subsampling errors resulting in the small within-group variance. However, the significant F for the variability between samples suggests very heterogeneous sediment in a relatively small area. The diver-collected samples were collected within a 10-m radius, while the SHIPEK samples were collected from a less defined area, less defined in the sense that although the ship was at anchor it could pivot on the anchor line in response to current and wind action.

Although the triplicate samples were collected over a very small area, the grain-size differences between the individual samples contributed signif- icantly to the ANOVA results. One of the determinants of nutrient or trace metal concentration is dilution of the concentration by quartz, carbonates, and other coarse-grained material (Trefrey and Presley, 1976). If a coarse- grained "dilution factor" had been used to compensate for grain-size differences, the variability between samples would probably have produced non-significant ANOVA results. This procedure has been used in recent years (Chambers and Eadie, in preparation). The dilution factor consists of

$$[C_{200}][P_{200}]/100,$$

where C_{200} is the concentration in the <ZOO μm fraction and P_{200} is the per-
cent of material <200 pm.   Similar "dilution factors" have been used by
others (e.g., Cline and Chambers, 1977; Thomas and Jaquet, 1976).

*Table 6.--ANOVA table for   the   chemical   analysis   of   SHIPEK   collected   sediment
samples versus diver-collected samples*

			Iron	
Source	df	ss	MS	F
Diver				
Total	17	2426667		
Between Groups	2	1613333	1613333	19.8**
Within Groups	15	813333	81333	
SHIPEK			Fe	
Total	17	1600000		
Between Groups	2	910000	455000	9.89**
Within Groups	15	690000	46000	
Diver			Mn	
Total	17	12053		
Between Groups	2	10614	5307	55.3**
Within Groups	15	1439	96	
SHIPEK			Mn	
Total	17	2774		
Between Groups	2	600	300	2.07
Within Groups	15	2174	145	

$^*F_{0.05(2,15)} = 3.68$
$^{**}F_{0.01(2,15)} = 6.36$