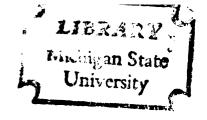
THE INFLUENCE OF MUNICIPAL AND AGRICULTURAL PRACTICES ON STREAM WATER QUALITY IN THE GRAND RIVER BASIN

Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY JAMES R. WAYBRANT 1971









ABSTRACT

THE INFLUENCE OF MUNICIPAL AND AGRICULTURAL PRACTICES ON STREAM WATER QUALITY IN THE GRAND RIVER BASIN

By

James R. Waybrant

A study of phosphorus and nitrogen concentrations in the Grand River watershed indicated that nitrate-nitrogen fluctuated significantly with changes in temperature and photoperiod. A temperature-dependent shift in nitrogenform uptake took place at approximately 10° C. Above 10° C, nitrate-nitrogen was preferentially absorbed, with an apparent shift to ammonia-nitrogen as the ambient temperature was reduced to less than 10° C.

Total phosphorus did not appear to fluctuate with changes in biological activity. However, certain sites in the river at times exceeded 100 times the 0.01 mg per liter concentration previously reported as a minimum phosphorus necessary to stimulate nuisance algal blooms in lakes.

A study of nutrient concentrations in runoff from watersheds of predominantly urban, natural, or agricultural land usages indicated significant differences: a) the natural watershed runoff contained less nitrate-nitrogen than did runoff from either the urbanized or agricultural watersheds; b) urbanized land runoff contained far greater concentrations of phosphorus than did runoff from either natural or agricultural watersheds, and c) natural and agricultural land runoff did not contain significantly different concentrations of total phosphorus.

The Grand River from August, 1969, to August, 1970, discharged an estimated 1,034,000 kg of total phosphorus into Lake Michigan. This amount was estimated to be approximately 70 percent of the calculated input by drainage from the entire watershed. Sewage treatment plant effluents along the Grand River contributed amounts of total phosphorus equivalent to the total discharge from tributary rivers.

Nitrate-nitrogen discharged by the Grand River into Lake Michigan totaled 3,996,000 kg for the period August, 1969 to August, 1970. This amount was estimated to be 33 percent of the calculated input from all types of discharge.

Approximately 35 percent of the total nitrate-nitrogen discharge was unaccounted for. It is suggested that this may be due to action of nitrogen-fixing algae in the stream system. Since about 67 percent of the nitrogen was apparently extracted within the system and 35 percent of the final discharge was unaccounted for, the Grand River indicated evidence of possible nitrogen-limitation during the period of surveillance.

THE INFLUENCE OF MUNICIPAL AND AGRICULTURAL PRACTICES ON STREAM WATER QUALITY IN THE GRAND RIVER BASIN

By James R: Waybrant

A THESIS

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TABLE OF CONTENTS

		Page
I.	INTRODUCTION	1
	A. Need for Study	1 3
II.	REVIEW OF PREVIOUS WORK	5
	A. General Eutrophication Studies B. Biological Uptake of Phosphorus and	5
	Nitrogen	6 6 6
	2. Nutrients Dissolved in Soll Solutions	7 9
	Lands b) Forested Lands	9 10 12 13
	4. Pollution	13
	E. The Importance of Nitrogen as a Func- tion of Biological Activity F. Phosphorus and Nitrogen Nutrient	15
	F. Phosphorus and Nitrogen Nutrient Budgets on Large-Scale River Systems	16
III.	FIELD STUDIES	18
	 A. Description of Study Area	18 18 19 19 20
	 B. Sampling Sites. C. Sampling Procedure. D. Weather Data. E. Sewage Treatment Plants F. Land Usage Data G. Flow Rates. 	22 22 26 27 27 27
		41

TABLE OF CONTENTS--continued

IV. 28 28 35 X-C. Nutrient Comparison of Urban, Natural and Agricultural Watersheds 38 \geq D. Flow Contribution of Sewage Treatment Plant Effluents to Rivers at Low-Discharge Periods 47 48 1. Annual Nutrient Budget by Water-48 2. "Flow-through" Nutrient Budget . . 53 v. 59 61 66 Α. Nitrate-Nitrogen Concentrations for Each Sampling Site During the Period 8-21-69 through 66 Nitrate-Nitrogen Concentration Fluctuations at Β. 71 Each Sampling Site Over the Period of Record . . с. Total Phosphorus Concentrations for Each Sampling Site During the Period 8-21-69 through 78 Total Phosphorus Fluctuations at Each Sampling D. Site Over the Period of Record 84 Ε. Wastewater Treatment Plant Monthly Average Daily Flow Rates During Calendar Year 1969 92 Analytical Procedures for the Determination of F. Total Phosphorus and Nitrate-Nitrogen. 94 G. Stream Flow Estimates at Sampling Stations During the Period 8-21-69 Through 12-20-69 . . . 97 H. Dissolved Oxygen, Alkalinity, pH and Temperature Data at the Mouth of the Grand River 99

Page

TABLE OF CONTENTS -- continued

I.	Land Use Apportionment in the Grand River Watershed	101
J.	Estimated Monthly Average Total Nitrogen Dis- charge from Wastewater Treatment Plants in the Grand River Basin During Calendar Year 1969	103
к.	Estimated Monthly Average Total Phosphorus Dis- charge from Wastewater Treatment Plants in the Grand River Basin During Calendar Year 1969	105
L.	Estimated Monthly Average Daily Total Phosphorus Discharge at All Sampling Stations During the Period August, 1969 Through December, 1969	107
М.	Estimated Monthly Average Daily Nitrate-Nitrogen Discharge at All Sampling Stations During the Period August, 1969 Through December, 1969	113

Page

LIST OF TABLES

TABL	E	Page
1.	Nutrients Discharged by Selected Land Use Practices	11
2.	Land Type and Population Comparisons Between Three Subwatersheds in the Grand River Basin (From U. S. Dept. of Agriculture)	21
3.	Sampling Sites Along the Grand River, with Their Sampling Number, Description, and Dis- tance in Miles from the River Mouth	23
4.	Comparison of Nitrate-Nitrogen Concentrations at Selected Sampling Sites, with Average Week- ly Temperatures in the Grand River Basin	32
5.	Estimated Discharge Rates from Each Land-type in Kg Mile ⁻² Year-1 and for Sewage Treatment Plants in Mg Liter ⁻¹	51
6.	Phosphorus and Nitrogen Balances in Surface Runoff (Period of Surveillance: August 1969- July 1970)	54

LIST OF FIGURES

FIGURES	Page
 A map of the Grand River and principle tribu- taries. Also shown are major cities and the thirty sampling sites 	25
2. Average nitrate-nitrogen concentrations at each sampling site (August, 1969 to August, 1970)	30
3. Average total phosphorus concentrations at each sampling site (August, 1969 to August 1970)	37
4. Comparison of nitrate-nitrogen concentrations in three watersheds of different predominant land usages	40
5. Comparison of total phosphorus concentrations in three watersheds of different predominant land usages	43
 Comparison of mean nutrient differences from different land usages (data from Sylvester, 1961) 	45
7. Proportions of flow rate in the Red Cedar River due to sewage effluents	50
B. Nitrate-nitrogen concentration fluctuations at each sampling site over the period of record	72
D. Total phosphorus fluctuations at each sampling site over the period of record	85
L. Estimated monthly average daily total phos- phorus discharge at all sampling stations during the period August, 1969 through December, 1969	108
M. Estimated monthly average daily nitrate- nitrogen discharge at all sampling stations during the period August, 1969 through December, 1969	114

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I. INTRODUCTION

A. Need for Study

Stream water quality depreciation by excessive fertilization, as evidenced by undesirable odors and floating algal scums, is very noticeable in the Grand River watershed. However, river-borne pollutants only recently were recognized as being responsible for major quality changes in the receiving Great Lakes. For example, Lake Erie has undergone important overall ecological transformations. These ecological changes have been attributed to introduction of large quantities of specific pollutants, primarily the micro-nutrients.

In view of the widely publicized Lake Erie problem and established reasons for that problem, people can no longer concern themselves with only local stream conditions. They must acknowledge that they are an element of a larger system in which the totality of small influences may result in almost irreversible change. Thus, the principle problem now becomes one of halting excessive flows of pollutional materials into the Great Lakes before the remainder suffer damage similar to that of Lake Erie.

Human populations in the Grand River watershed are increasing rapidly, producing a corresponding increase in amounts of sewage and related pollution. The six major cities totalling approximately 400,000 people utilize secondary sewage treatment, while the remaining 157 employ only primary or while the remaining 15% discharging directly to the river system employ only primary or equivalent treatment. In addition, no effective procedure for total nutrient extraction from waste water has yet been developed. Thus, the Grand River is experiencing, and will continue to experience, accelerated eutrophication. Lake Michigan is consequently undergoing continuous enrichment which may result in drastic ecological changes in the future.

About half of Michigan's phosphorus contribution to Lake Michigan appears to result from flow contributions by the Grand River. Thus, the importance of the Grand River system on the state of the lake is clear. This study constituted a first effort in the detailed examination of the sources, sinks and mechanisms of nutrient transport. In this manner, it was possible to determine amounts of nutrient pollution discharged by a specific city. It also illustrated variations in phosphorus and nitrogen concentrations in receiving waters immediately downstream from each sewage effluent. Finally, concentrations and stream flow rates together formed a phosphorus and nitrogen nutrient budget for the Grand River watershed.

Few studies of this nature have yet been attempted, although Park, Webster and Reid (1970) conducted a somewhat similar survey on the Columbia River. However, no similar study has been attempted on the Grand River watershed. The Red Cedar River has been extensively studied in the past (Brehmer, 1958, Peters, 1959, Grzenda, 1960, Kevern, 1961, Vannote, 1961 and 1963, King, 1964, Jensen, 1966 and 1969 and Hardgrove, 1969), but little data other than seasonal changes in nutrient concentrations are applicable to the present study.

B. Purpose and Scope of Study

The purpose of this study was to develop an overall description of nutrient levels, total input to the system, biological uptake and total discharge into Lake Michigan from the Grand River Basin.

There were five major objectives in this project:

1. To analyze relationships between sewage treatment **Plant** discharge and receiving water quality. Chief para **meters** studied were total phosphorus and nitrate-nitrogen. **Samples** were collected above and below discharges of major **sew**age treatment plants along the Grand River or in and **below** major tributaries.

2. Relationships outlined in the first objective, when **~om**bined with flow rates throughout the watershed, formed

comprehensive phosphorus and nitrogen nutrient budgets for the watershed.

3. The third objective of this project was to develop comparisons between overall sewage effluents and total stream flows during yearly low-flow periods.

4. An attempt was made to establish a significant correlation between land usage practices and water quality in terms of the measured parameters. For this purpose, the watershed was divided into its subwatersheds and correlations made between the nutrients, phosphorus and nitrogen, and land usages. Subwatersheds studied consisted of:

a) predominantly agricultural, b) predominantly forested, and c) predominantly urbanized land.

5. The fifth objective was to inventory several quality parameters in the Grand River watershed. Three of these parameters consisted of sewage treatment plants, their degrees of treatment and their approximate daily outputs. Tabulations were made (Appendix H) of water quality parameters at the Grand River mouth. These were dissolved oxygen, pH, alkalinity and water temperature.

II. REVIEW OF PREVIOUS WORK

A. General Eutrophication Studies

Extensive research has been conducted on phosphorus and nitrogen uptake and ecological changes resulting from excess nutrients. Hasler (1947) defined eutrophication of lakes as the intentional or unintentional nutrient enrichment of water. Hasler also indicated that increases in phosphorus and nitrogen and decreases in dissolved oxygen are acceptable indices of eutrophication. He described 37 lakes of varying size which showed eutrophication as a result of domestic sewage. Hasler concluded with the statement, "The problem is especially serious because there is no way known at present for reversing the process of eutrophy."

Beeton (1967) described the Lake Michigan pollution situation as quite dismal, since net flow-through and addition of water is only $1,492 \text{ m}^3 \text{ sec}^{-1}$ and most of the major tributaries are seriously polluted. Despite the fact that polluted streams and rivers represent a source of inflow for lakes and oceans, comparatively few workers have studied the transport of nutrients in flowing water. Mackenthun (1965) indicated a lack of research in this area.

B. Biological Uptake of Phosphorus and Nitrogen

Mackenthun, Ingram and Porges (1964) described nuisance algal blooms and nutrient budgets for several lakes. They concluded that fixed nitrogen entering a lake or reservoir is incorporated into the biomass as an element of protein. When an organism dies or excretes wastes, nitrogen is liberated, but some is lost in lake effluents, by diffusion of volatile nitrogen compounds into the atmosphere, by denitrification in the lake and by precipitation by formation of permanent sediments. Phosphorus, also assimilated into the biomass, is liberated by death or excretion. It may settle with sediment, seston or fecal pellets or it may be released at the mud-water interface.

C. Sources of Phosphorus and Nitrogen

Mackenthun, Ingram and Porges (1964) stated that, as a result of several studies, basic nutrient sources for lakes and reservoirs were: a) tributary streams carrying land runoff and waste discharges, b) the interchange of bottom sediments, and c) precipitation from the atmosphere.

1. Precipitation

Precipitation from the atmosphere contains significant amounts of phosphorus and nitrogen. Since water itself from the atmosphere should be uncontaminated, phosphorus concentrations probably originate from atmospheric particulate matter (keup, 1967). Nitrogen, being the major

component of our atmosphere, is easily absorbed by raindrops and thus provide lakes with a constant nitrogen source. The equilibrium concentration of diatomic nitrogen in water at 20[°]C is approximately 14.8 mg per liter under a normal atmosphere. This, then, represents a reasonable source for blue-green algae and other nitrogen fixing plant life. Other commonly occurring compounds of nitrogen have even higher solubilities.

Hutchinson (1957) found phosphorus concentrations in rainfall ranging from trace amounts to a "very improbable" value of 49 μ g liter⁻¹. However, that high value appears possible, since Weibel et al. (1966) found concentrations as high as 80 μ g liter⁻¹ in a Cincinnati suburb. Great variation in rainfall concentrations probably results from changes in composition and quantity of atmospheric particulate matter in the area (Keup, 1967). After several assumptions, Weibel (1967) estimated the direct rainfall contributions to Lake Erie as two percent of its total suggested load.

2. Nutrients Dissolved in Soil Solutions

Nitrate-nitrogen, because it is soluble in soil solutions, is subject to leaching (Biggar and Corey, 1967). Biggar and Corey concluded that rain dissolves nitrate quickly and carries it into the soil before the soil becomes water-saturated and forces water runoff. Thus, soil percolates contain considerably more nitrate than do surface

runoff waters. McGauhey et al. (1963) stated that percolation through soil effects only partial nutrient removal and that percolation does not significantly reduce nitrate concentrations.

Phosphorus concentrations in surface runoff and soil percolates are just the reverse of the nitrate system (Biggar and Corey, 1967). Phosphorus tends to saturate the "fixing" sites at the surface, which are in close contact with surface runoff water. Although some phosphorus percolates into the soil, it is quickly extracted from water by fixation of soil particles. Therefore, most soilrelated phosphorus reaches streams and rivers via erosional processes created by surface water runoff. Juday and Birge (1931) and other authors (Anon., 1966) described average groundwater sampled as being relatively low in phosphorus, which directly supports Biggar and Corey's assertions.

The above theories and conclusions are not applicable to frozen soils. If soils are frozen, as during spring runoffs, much of all soluble nutrients at the soil surface is washed into the waterways. This is especially true for manures and chemical fertilizers applied to frozen fields.

Groundwater contains significant concentrations of all nutrients. Even though phosphorus is very low in soil percolates, Corey et al. (1967) stated that groundwater contributed 42 percent of all Wisconsin surface water nutrient concentrations. Biggar and Corey (1967) concluded that

there is often incomplete mixing between resident groundwater and replenishment water, however, resulting in occasional nutrient "caps" over the groundwater.

3. Surface Water Runoff

Nutrient concentrations in surface water runoff are dependent upon (Keup, 1967):

Quantity of nutrients present in soils,
 Topography,
 Vegetative cover,
 Quantity and duration of runoff,
 Land use, and
 Pollution.

Surface runoff from a watershed follows a general pattern (Biggar and Corey, 1967). Most plots of surface discharge versus time indicate a peak and then recession to a base flow.

a) Irrigated and Fertilized Lands

Drainage from irrigated and fertilized land usually contains significant amounts of nutrients. Eck et al. (1957) found that phosphorus losses on a 20 percent slope were about 2 kg hectare⁻¹year⁻¹, while an eight percent slope lost only about 0.5 kg hectare⁻¹year⁻¹. He also found that significant amounts of nitrogen were lost from both fields.

Total nutrient concentrations from irrigation return drains (Sylvester, 1961) averaged 0.2 mg liter⁻¹ of phosphorus, while subsurface irrigation drains alone averaged 1.3 mg liter⁻¹ of nitrogen. Recent work by Erickson and Ellis (1970) on four different tile drain systems located on research farm areas in southern Michigan indicates a seasonal fluctuation in nitrate-nitrogen with averages ranging from 1.5 to 5.0 mg liter⁻¹.

Johnston, Ittihadieh, Daum and Pillsbury (1965) showed that filtration into drainage-tile effluent contained large percentages of applied nitrogen while phosphorus losses were not significant. Although nitrogen losses noted by Sylvester were similar to those found by Johnston et al., much less phosphorus was apparently lost from non-irrigated soils. This result is closely supported by Biggar and Corey's (1967) assertions concerning phosphorus uptake.

Likens et al. (1970) kept fields bare by regular application of herbicides to simulate plowed-field conditions. They concluded that large proportions of nutrients are lost from bared earth. Midgely and Dunklee (1945) found that manured field runoffs contained on the average 3 mg liter⁻¹ of nitrogen and 1 mg liter⁻¹ of phosphorus. Sawyer (1947) found that agricultural drainage near Madison, Wisconsin contributed approximately 2040 kg of nitrogen and 10 kg of phosphorus mile⁻²year⁻¹. Runoff from plowed and/or fertilized fields therefore contribute significantly to stream enrichment.

b) Forested Lands

Forested lands lose considerably less nutrients by runoff than do agricultural lands (Table 1). Putnam and

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Table 1. Nutrients Discharged by Selected Land Use Practices.

Land Use	Specific stream or use	Nitrog e n kg/mi ² /yr.	n mg/1	Phosphorus kg/mi ² /yr. m	us mg∤l	Refer- ence
Forested	Lake Superior Tributaries(averaged) Sturgeon River, Michigan Sebasticook River, Maine Washington streams (averaged)		- - 0.13	25 17 58 175	- - 0.069	4 8 0 0
Agriculture	Corn fields (20 percent slope) Corn fields (8 percent slope) Irrigation return flow drains: Subsurface Surface Agriculture drainage near Madison, Wisconsin Manured field runoff	2 050	- - 1.25 3.00	525 145 - 102 -	- - 0.216 0.251 - 1.00	ы ы о ог о
Urban	Street drainage after rainstorms Stormwater runoff of residential drainage basin	2580	0.5	1728	0•2	QН
	 A. Putnam and Olson (1959) and (1960) B. Ball and Hooper (1963) C. Anon. (1966) D. Sylvester (1961) E. Eck et al. (1957) F. Sawyer (1947) G. Midgely and Dunklee (1945) H. Weibel, Anderson and Woodward (196 	960) (1964) .				

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Olson (1959) and (1960) found that forested land runoff averaged about 25 kg of phosphorus mile-²year⁻¹. These results were taken from rivers in Minnesota, Wisconsin and Michigan which discharged into Lake Superior. The rivers all averaged higher in phosphorus than did Lake Superior, which indicates a gradual natural enrichment of the lake. However, the rivers averaged lower in nitrate-nitrogen than did the lake.

Ball and Hooper (1963) found even less nutrient enrichment in the Sturgeon River, Michigan, since phosphorus averaged about 17 kg mile⁻²year⁻¹. Because the drainage basin was only about one-fifteenth the average basin size in Putnam and Olson's studies, however, it probably contained a more uniform soil structure and therefore fewer natural enrichment possibilities.

Sylvester (1961) found much greater nutrient losses from forested watersheds in Washington. Three rivers averaged about 175 kg of phosphorus mile⁻²year⁻¹. However, mean concentrations were quite low, so that only heavy rainfall and resulting large discharges produced the extensive nutrient losses.

c) Urban Lands

Sylvester (1961) investigated nutrient concentrations of urban drainage, but he only included drainage from major highways, arterial and residential streets in his study. Streets were sampled within 30 minutes to several hours

after a rainstorm had commenced. Results showed that runoff immediately after rainstorms had commenced carried the greatest amounts of nutrients, followed by a gradual return to base flow. Street drainages averaged about 0.2 mg liter⁻¹ of phosphorus and 0.5 mg liter⁻¹ of nitrogen. If Sylvester had included municipal wastes to get overall urban discharge, however, his phosphorus values would have been much higher.

Weibel, Anderson and Woodward (1964) found that stormwater runoff from a 10.9 hectare residential and light commercial drainage basin contained 2.8 kg of phosphate hectare⁻¹year⁻¹ and 10 kg of nitrogen hectare⁻¹year⁻¹. Phosphates in storm runoff therefore comprised about nine percent of calculated raw sanitary sewage phosphates, while total nitrogen composed about 11 percent of the total nitrogen in sewage.

4. Pollution

Stream enrichment by sewage effluent has been studied extensively for many years. Keefer (1940), Rudolfs (1947) and Buswell (1958) studied per capita nutrient contributions, while Sawyer (1960) investigated nutrient concentrations in raw sewage prior to extensive use of detergents. He found that raw sewage contained about 3 mg liter⁻¹ of phosphorus. Studies (Sawyer, 1947) also showed that biologically treated sewage contributed approximately 2.73 kg of nitrogen and 0.55 kg of phosphorus per capita year⁻¹.

During the 1960's, detergents utilizing primarily phosphate compounds as dispersing agents came into extensive use in private homes. For example, Sherman (1966) stated that phosphorus in detergents alone during 1965 amounted to 1.45 kg person⁻¹year⁻¹. With such a large increase in phosphorus discharge, our streams necessarily experience a continuously increasing enrichment.

D. Biological Nutrient Extraction in Flowing Water

Researchers have found large proportions of nutrients extracted from streams by biological activity (Davis and Foster, 1958; Ball and Hooper, 1963 and Connell, 1965). Although streams are capable of extensive nutrient extraction, however, they are not able to cope with the tremendous amounts of nutrients thrust into their environment. For example, a study conducted on the Sebasticook River in Maine showed that a four-mile stretch of the river was capable of assimilating only 29 percent of the phosphorus added as municipal waste (Anon., 1966).

Biological assimilation was shown by Cummins (1966) to occur in bottom plants rather than in phytoplankton. Ball and Hooper (1963) also fixed major nutrient-extraction sites as being in the periphyton. Phytoplankton are, therefore, of minor importance in lotic environments, probably because the constant turbulence affords little chance for development of large plankton populations.

In addition to extraction by plants, nutrients are removed by fixation to inorganic matter in water. Hepher (1958) found that phosphorus was removed from water by combination with soils. He further specified that soils especially rich in calcium fixed the greatest quantities of phosphorus. Hooper and Ball (1964) showed that phosphate in a Michigan marl lake was probably fixed to colloidal marl particles. Since Grzenda (1960) found striking differences in nutrient extraction rates between summer and winter, however, sorption to soils appears to play a minor role in nutrient extractions. Brehmer (1958), Grzenda (1960) and Kevern (1961) found large nutrient increases during March and April, which were attributed to both melted snow runoff and stream flushing of deposited sediments. Although the increases should be due mainly to melted snow runoff, no studies have yet shown just what proportion is actually due to stream flushing.

E. <u>The Importance of Nitrogen as a Function</u> of Biological Activity

Gerloff and Skoog (1957) indicated that, under normal conditions, only nitrogen, phosphorus and iron required consideration as possible limiting elements. Of the three, nitrogen appeared the most critical indicator of biological activity. Mackenthun, Ingram and Porges (1964) stated that the biological productivity of a lake is a function of the loading of inorganic nitrogen in the lake. In addition,

2: £2 2 2 ::: 15 ::: 2 2 . 120 Det 1952 1531 831 177 ia.e 1450; 223 Porges and Mackenthun (1963) found that nitrogen in waste stabilization ponds fluctuated extensively between summer and winter.

All of the above workers emphasized the importance of nitrogen as a function of biological activity. Conversely, Sawyer (1952) and (1961) maintained that productivity in most aquatic areas is probably related largely to their phosphorus budgets. Controversy exists as to which element is the most critically important. However, it is reasonable to assume that fluctuations in biological activity cause corresponding fluctuations in both elements.

Korovin and Glyan'ko (1968) studied nitrogen uptake in a hydroponic system. Their results indicated that nitrogen-form assimilation by plants was dependent upon temperature, since it shifted from primarily nitrate-nitrogen uptake above 10°C to primarily ammonium-nitrogen below 10°C Even though their results are significant only with a hydroponic system, the temperature-dependency of nitrogen-form assimilation may be true for natural systems as well.

F. <u>Phosphorus and Nitrogen Nutrient Budgets</u> <u>on Large-Scale River Systems</u>

Few authors have studied nutrient budgets of largescale river systems. However, Park, Webster and Reid (1970) studied the Columbia River watershed. Their study indicated seasonal fluctuations in nutrient concentrations, with a maxima during winter and a minima during summer. In addition,

they found that during May-August 1966, nutrients were reduced 4 to 7 times through a 440 km section of the river. During January-April 1966, both phosphate and nitrate were within 10 percent of the total above the 440 km section. However, although the workers also compared flow contributions of major tributaries with their nutrient concentrations, they did not attempt a determination of contributions by land usages and by sewage treatment plants.

MacCrimmon and Kelso (1970) attempted a "source-tomouth" investigation of nutrient changes in the Grand River, Ont., watershed. However, although they sampled biweekly, they only had five sampling sites for 3300 km² of drainage area. For this reason, the project did not adequately describe nutrient fluctuations throughout the river length.

Many workers have developed nutrient budgets for given sampling sites, such as Likens et al. (1970), but they do not analyze entire river lengths. Studies (e.g., Brehmer, 1958) have indicated ecological upsets resulting from municipal waste discharges, but they did not discuss total municipal impact on a whole river system.

III. FIELD STUDIES

A. Description of Study Area

1. <u>General</u>

The Grand River watershed is the major drainage basin of Western Michigan. It is a warm-water system about 240 miles long, draining approximately 5,570 miles² of predominantly agricultural land. The river originates in Hillsdale County south of Jackson and empties into Lake Michigan at Grand Haven, flowing through Jackson, Lansing and Grand Rapids en route. Within the 13 counties, 29 cities, 43 villages and 158 townships that comprise the Grand River watershed there resides approximately one million people. Since 15 percent or more of any township or county's total area lying within watershed boundaries warrants inclusion, the list of counties and townships somewhat exaggerates the basin size.

Seven major subwatersheds contribute to the Grand River drainage. These include: the Rogue River, Thornapple River, Flat River, Maple River, Looking Glass River, Red Cedar River and Portage River. All have varying degrees of agricultural urbanized and forested lands, but remain predominantly agricultural.

Three subwatersheds were selected and studied for comparison of nutrient contributions by basins of different land use practices. However, since all are predominantly agricultural, basins were chosen by highest relative proportions of urbanized and forested lands. Basins selected for study were the Maple River (agricultural), Looking Glass River (natural) and Red Cedar River (urbanized). The subwatersheds are grouped together, resulting from an attempt to keep the basins within as similar a geological area as possible.

2. Maple River Watershed

The Maple River basin contains about 974 miles², which includes about 82 percent cropland, 11 percent forest, 3 percent urbanized land, and about 4 percent "other" (U. S. Dept. of Agriculture, unpublished data). Several small towns are scattered throughout the basin, although most have no sewage treatment plants and therefore no discharge. The only towns with sewage treatment plants are St. Johns and Fowler, totalling about 6,700 people and utilizing trickling filter treatments. The basin houses about 12,000 people. Since the high cropland percentage is combined with few urban sewage effluents, the Maple River watershed was chosen for the "agricultural" category of the comparison study.

3. <u>Red Cedar River</u>

The Red Cedar River contains about 57 percent cropland, 18 percent forest, 14 percent urbanized land, and about

11 percent "other". However, the upper section of the 473 miles² watershed is predominantly agricultural with little forested area. The stream passes through or near Fowlerville, Webberville, Williamston, Okemos, Michigan State University and East Lansing before emptying into the Grand River in Lansing. The Red Cedar River receives treated sewage from about 74,000 people, with additions of industrial waste and untreated sewage from urban residences along its course (Kevern, 1961). Therefore, intense urbanization of the basin's lower section was the basis for selection of the Red Cedar watershed as the comparison study's "urbanized" category.

4. Looking Glass River Watershed

The Looking Glass basin, about 296 miles², includes about 62 percent cropland, 22 percent forest, 4 percent urbanized land, and about 10 percent "other". Much of the "other" category is marshland and other non-forested, nontillable land types. Much cropland in this basin resides in the soil bank and is untilled. Dewitt, a town of about 1,240 people, discharges primary-treated sewage, while the whole watershed encompasses about 2,800 people. This basin, although statistically agricultural, is therefore in actuality a very natural watershed and is categorized as such for the comparison study. Table 2 summarizes the land usage and population comparisons between these watersheds.

		Rive	rs
	Maple	Red Cedar	Looking Glass
Total Area (mi²)	974.3	473.4	296.4
Agricultural (mi ²)	795.0	268.1	182.7
For es t (mi ²)	105.8	84.9	63.8
Urbanized land (mi ²)	31.2	68.3	12.3
"Other" (mi ²)	42.3	52.1	28.6
Population (total)	12,000	~90,000	2,800
Population (discharging wastes through sewage treatment plants)	6,700	74,000	1,240

Table 2. Land Type and Population Comparisons Between Three Subwatersheds in the Grand River Basin (From U. S. Dept. of Agriculture)

B. <u>Sampling Sites</u>

Sampling sites (Table 3, Figure 1) were selected so that one sample was taken above a sewage treatment plant outfall and one below the outfall, or else so that one was taken in the major tributary and one in the Grand River after confluence. In this manner it was possible to approximately determine the extent of phosphorus and nitrogen contribution by specific tributaries or sewage treatment plants. Buck (unpublished) found variations greater than 50 percent in a cross-section profile of the Red Cedar River. Because of his results, all sampling sites in the present study were continually sampled at the same spot on a given bridge. Such consistent sampling spots should theoretically have negated all but actual phosphorus fluctuations.

C. <u>Sampling Procedure</u>

A routine water sample collection trip was conducted every second weekend, for a year's duration beginning August 21, 1969 and ending August 1, 1970. Each sampling trip lasted a total of approximately twelve hours and covered about 440 miles. Because of the long time on the road, the collection trip was sometimes extended to two days, but efforts were made to collect all samples within a twentyfour hour period. During each sample-collection trip a total of thirty water samples were collected.

Table 3. Sampling Sites Along the Grand River, with Their Sampling Number, Description, and Distance in Miles from the River Mouth.

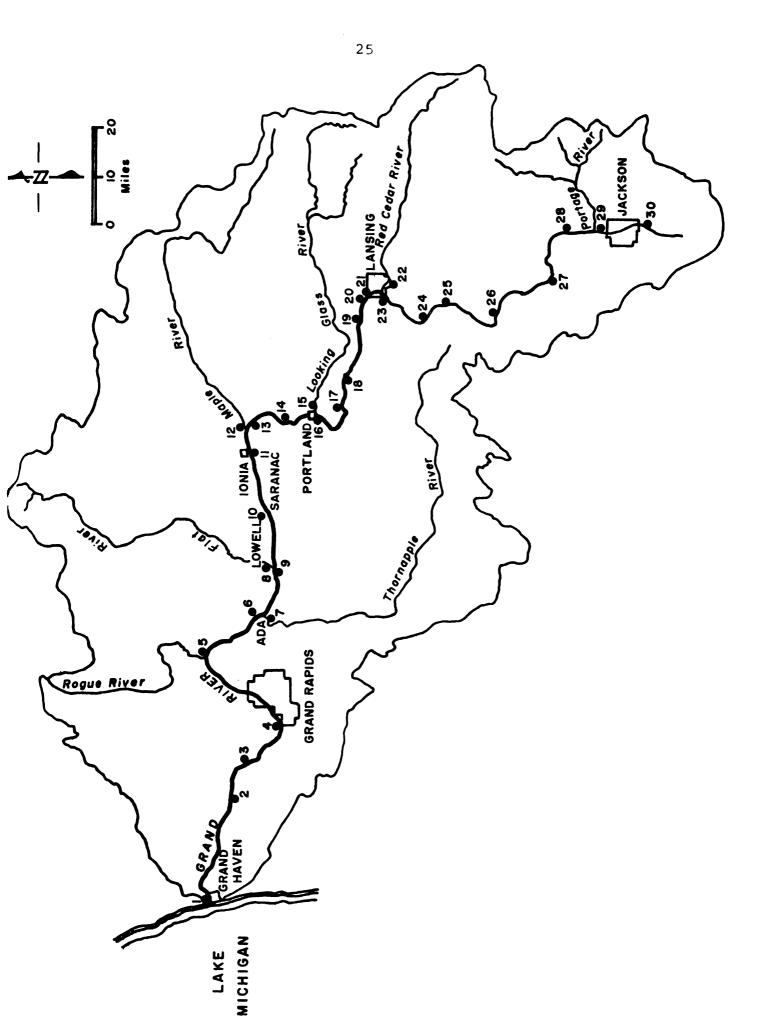
Number	Miles	Description
1	0	South Wall below Corps of Eng. Grand Haven
1 2 3	20	Eastmanville Bridge
3	25	Grand Valley, M-45 Bridge
4	34	Grandville, M-11 Bridge
5	55	U. S. 131 Bridge
6	62	U. S. 21 Bridge at Ada
7	62	Grand River Ave. in Ada (Thornapple River)
8	70	
9	70	M-91 Bridge at Lowell
10	78	Bridge at Saranac
11	89	M-66 Bridge at Ionia
12	94	Bridge at Muir (Maple River)
13	96	Bridge at Lyons
14	107	Goodwin Road Bridge
15	112	Lost Bridge, Portland (Looking Glass River)
16	112	U. S. 16 Bridge at Portland
17	126	Charlotte Highway Bridge
18	135	State Road Bridge
19	145	Webster Road Bridge at Delta Mills
	148	Waverly Road Bridge in Lansing
	152	Seymour Ave. Bridge in Lansing
22	154	Cedar St. Bridge in Lansing (Red Cedar River)
23	155	Logan St. Bridge in Lansing
2 4	165	Bailey Road Bridge near Dimondale
	174	Bunker Road Bridge
	181	Smithville Road Bridge
	192	Thompkins Road Bridge
	205	Berry Road Bridge
29	212	Parnell Road Bridge near Jackson
30	220	Brooklyn Road Bridge south of Jackson
31	218	High St. Bridge

Also shown are major cities and the thirty sampling A map of the Grand River and principle tributaries. Figure 1.

sites.

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Each sample was taken from a bridge in approximately the main current of the river and below the water surface to exclude floating debris. Two types of samplers were used, a two liter Van Dorn bottle and a 1200 ml Kemmerer Sampler. However, during the winter, ice prevented use of these samplers, and samples were taken by hand through the ice. A 500 ml polyethylene bottle was filled at each sampling site and, upon return to East Lansing, immediately refrigerated until analysis. Methods of analysis are described in Appendix F. During warm summer months, samples were stabilized with mercuric chloride at the sampling site. These were again refrigerated upon return to East Lansing.

D. Weather Data

Since heavy rains would be so indicated in flow rates per sampling date, only average temperatures and cloudcover indexes were collected. This data was all available in monthly reports at the U. S. Weather Bureau in East Lansing. Information from three weather stations in or near the Grand River watershed area; Lansing, Grand Rapids, and Muskegon, was collected and averaged into weekly means for each location. A Friedman non-parametric test for two-way analysis of variance indicated no significant difference between the three sites. The sites were subsequently averaged into one set of data for the whole watershed.

E. Sewage Treatment Plants

All sewage treatment plants in the basin are listed by the U. S. Department of Health, Education and Welfare. Several treatment plants have been recently developed, but they are all aerated lagoons which to date have not yet discharged effluents (Appendix E). Treatment types listed in the appendix have been updated to present, but populations served by individual plants are only estimates.

F. Land Usage Data

Percentages for each land use practice in the three studied subwatersheds were developed from two week's research by Soil Conservation Service employees of the U. S. Department of Agriculture. Acreages per land usage were not included in the description however, they are shown in Table 2 and Appendix I.

G. Flow Rates

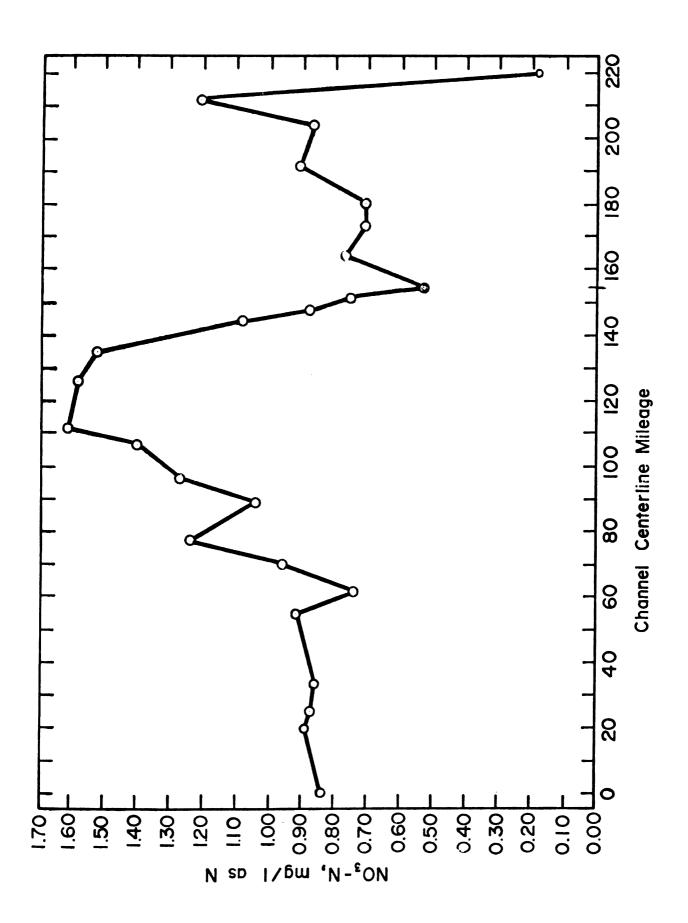
All flow rates from August, 1969 to December, 1969 were obtained from the U. S. Geological Survey. At this time, flow rates for January, 1970 through July, 1970 have not yet become available. These rates were estimated by graphing flow data from 1963 to 1969, and then extrapolating from these figures.

IV. DISCUSSION OF RESULTS

A. <u>Nitrate-Nitrogen</u>

Nitrate-nitrogen concentrations in the Grand River were characterized by several consistent zones with high values en route from Jackson to Lake Michigan. Appendix A lists all values obtained during the study by date and location. South and upstream from Jackson, the Grand River is a fairly clean warm-water stream, but addition of Jackson sewage effluent during 1969 increased nitrate concentrations to usually well over 2 mg liter⁻¹ (Figure 2). From Jackson until the river entered Greater Lansing, averaged nitrate concentrations continued to decrease, probably by biological uptake and some dilution. Lansing industries, residential areas and sewage effluents, in addition to Red Cedar River contributions, then sharply increased nitrate concentrations. These concentrations continued to increase in the river until just upstream from Portland, and then gradually decreased until it reached Ada. From Ada until Lake Michigan, the river again experienced increasing nitrate concentrations. Increases, however, were not nearly as large in concentration as those indicated further upstream.

Figure 2. Average nitrate-nitrogen concentrations at each sampling site (August, 1969 to August, 1970).



Nitrate-nitrogen appeared to fluctuate seasonally in correspondence with biological activity (Appendix B). Although nitrate concentrations were always measurable, low river velocities downstream from Ada and Wyoming and several upstream impoundments enabled macrophytes to extract large amounts of total nitrates during the growing season. Through September and October, nitrate concentrations in low-velocity river sections increased gradually with a gradual lowering of average weekly temperature (Table 4). After November 1, nitrate concentrations increased rapidly and average weekly temperatures decreased quickly. Although this correlation is one of nitrate concentration with temperature, it is indirectly one of nitrates with biological activity. However, daily photoperiod is probably as important as temperature in determining biological activity, and may have a considerable, although unknown, influence in this correlation.

Nitrate fluctuates significantly with seasonal changes in biological activity. Such close correlation is indicative that it is somewhat critical as a limiting or almostlimiting element in the Grand River drainage system. Gerloff and Skoog (1957) found that nitrogen was the most critical element for growth of <u>Microcystis aeruginosa</u> in southern Wisconsin lakes. Through algal counts and nutrient correlation, Mackenthun, Ingram and Porges (1964) found that

Week	Average Weekly Temperature ^O F	Average of Stations 1-6 (mg liter ⁻¹)	Station 23 (mg liter ⁻¹)
August			
1-7	70		
8-14 15-21	71 73	0.13	0.10
22-28	73	0.13	0.10
29-31	79	0.14	0.11
September			
1-7	74		
8-14	62	0.19	0.15
15-21	62		• • •
22–28	57	0.16	0.26
<u>October</u>			
1-7	62		• • • •
8-14	53 ≻ ~10° C-	0.21	0.37
15-21	47		
22-28	39	0.67	0.77
29-31	39		
November			
1-7	42	0.65	0.68
8-14	38	0.00	0 71
15-21 22-28	32 32	0.83	0.71
22-20	54		
December		• • -	• • •
1-7	29	0.95	0.90
8-14 15-21	32 26	0.82	0.71
22-28	26 16	0.02	0./1
29-31	26		

Table 4.	Comparison of Nitrate-Nitrogen Concentrations at
	Selected Sampling Sites, with Average Weekly
	Temperatures in the Grand River Basin

inorganic nitrogen in lakes. These conclusions agree with results from the present study. Allen (1955) concluded that, due to a relatively unlimited phosphorus supply, the most severely limiting element in raw sewage was nitrogen. Since phosphorus concentrations in the Grand River are relatively large, seasonal nitrate fluctuations in the system appear to indicate excessive enrichment.

Several authors have verified the fact that nitrate concentrations increase during winter months. For example, Porges and Mackenthun (1963) concluded that nitrate removal in waste stabilization ponds fell to as low as 6 percent in winter and rose to as high as 80-90 percent in summer. Table 4 indicates similar results from the present study. Average nitrate values are shown for several low watervelocity sampling sites (sites 1-6), while site 23 presents a description of nitrate concentrations in an impoundment in Lansing. Lackey and Sawyer (1945) also found that nitrate concentrations increased with decreasing biological activity during winter.

A further reason for fluctuating nitrate concentrations was propounded by Korovin and Glyan'ko (1968) from hydroponic studies. They found that ammonium and nitratenitrogen form uptake was temperature-dependent, and that plants appeared to absorb nitrate-nitrogen better at temperatures above 10° C, while ammonium-nitrogen was absorbed better at temperatures below 10° C. This temperature

division is marked on Table 4 and indicates a statistically significant shift in nitrate concentration. The results found by Korovin and Glyan'ko for a hydroponic system therefore appear applicable to the Grand River drainage system. Also implied in Table 4 is a gradual decrease in biological activity through decreasing temperatures and seasonal fluctuation in photoperiod.

Nitrate concentrations increased significantly during March and April. This increase is probably a combination of runoff from melting snow and spring rains with downstream flushing of silt and organic matter by the large discharges. Nutrient surveys of the Red Cedar River watershed (Brehmer, 1958; Grzenda, 1960 and Kevern, 1961) have found similar fluctuations, indicating that the increase is normal for Spring discharges. The large increase in nitrate concentration fluctuated similarly with phosphorus, except that nitrates remained higher throughout the flood period. These results are also similar to those found by Kevern (1961) and Grzenda (1960).

Sampling sites 17 and 18, upstream from Portland consistently had the highest nitrate concentrations of any site on the Grand River downstream from Lansing. They thus present something of an indeterminate, since no recognized pollution source is known to discharge into that river section. The city of Grand Ledge discharges about 0.3 MGD of primary treated sewage upstream from site 18, however,

since Grand Ledge contributes only about 0.2 percent of the total Grand River discharge, its nutrient contribution is not a sufficiently accurate explanation of the large nitrate increases.

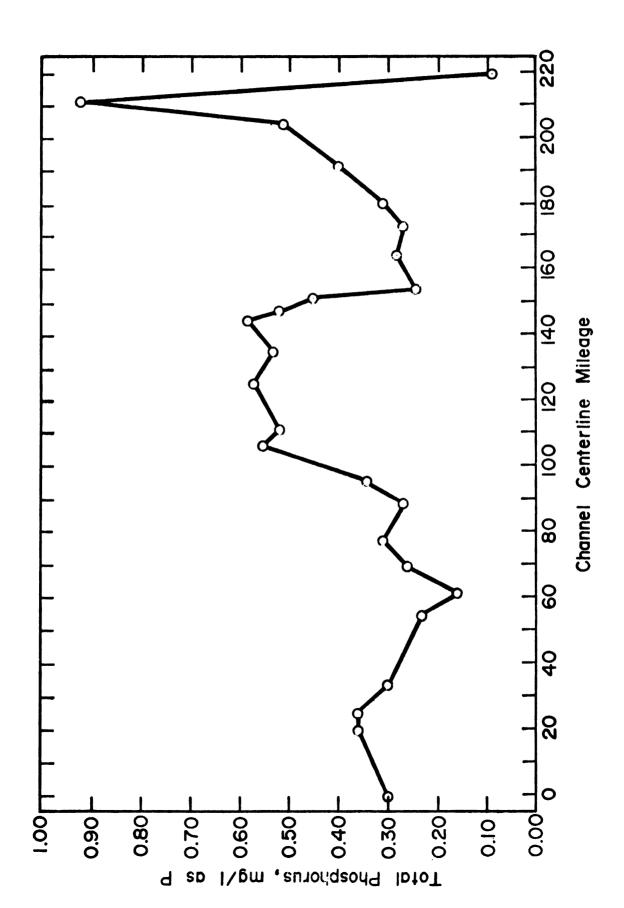
B. Total Phosphorus

Averaged total phosphorus concentrations showed several consistent peaks in the Grand River enroute to Lake Michigan (Figure 3). Generally, all peak values of total phosphorus coincided with those of nitrate concentrations. Appendix C lists the results of all phosphorus determinations by station and sampling date.

Phosphorus did not fluctuate significantly with changes in temperature and season. Sawyer (1968) emphasized that nutrient removal should relate primarily to phosphorus, since it is most often limiting. His earlier work (Sawyer, 1947) indicates that algal blooms can be stimulated by inorganic phosphorus concentrations in excess of 0.01 mg liter⁻¹. Total phosphorus concentrations at certain sites along the river at times exceed 100 times that minimal amount for nuisance algal blooms (Figure 3). The river system therefore appears to require extensive nutrient controls in order to curb cultural enrichment.

Sawyer (1947) indicated that urbanization is responsible for a very large proportion of total phosphorus in rivers. Brehmer (1958) verified this assertion with his study at Williamston along the Red Cedar River. Since wastewater

Figure 3. Average total phosphorus concentrations at each sampling site (August, 1969 to August 1970).



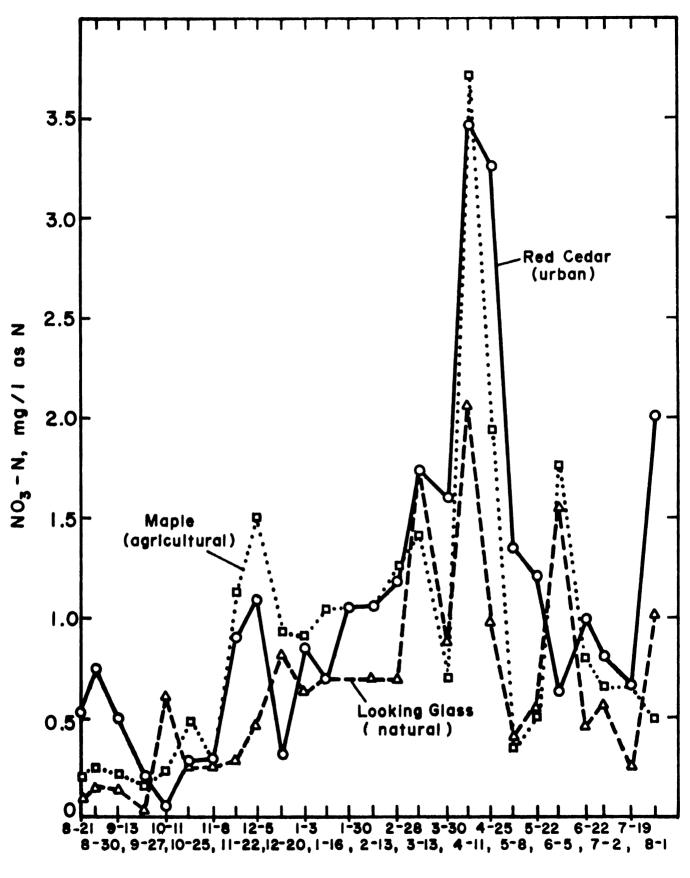
treatment plants discharge at a relatively stable flow rate throughout the year (Appendix E), little seasonal fluctuation in the amount of phosphorus discharged is expected to occur from changes in river discharge. If most of the phosphorus was contributed by sewage effluents, increased river discharge would serve only to dilute the concentration.

C. <u>Nutrient Comparison of Urban, Natural</u> and Agricultural Watersheds

Comparisons of nutrient concentrations in runoff from watersheds reflecting principally urban (Red Cedar River), natural (Looking Glass River), and agricultural (Maple River) land usages produced significantly different results.

Runoff from the urbanized and agricultural watersheds contained approximately equal concentrations of nitratenitrogen through the annual cycle, while surface runoff concentrations from the natural watershed were generally lower (Figure 4). The appearance of high nitrate-nitrogen values during the April-May period is coincident with the high spring flow and results largely from the rapid appearance of interstitial surface soil water in the stream Since the biological productivity in the stream channel. is still relatively low (ambient water temperature less than 10°C) these nitrate levels are not incorporated into the The scouring action of these high flows stream biomass. also destroys the existing periphyton crops which serve as a principal trophic level for the extraction of nitrate from the stream flow.

Figure 4. Comparison of nitrate-nitrogen concentrations in three watersheds of different predominant land usages.



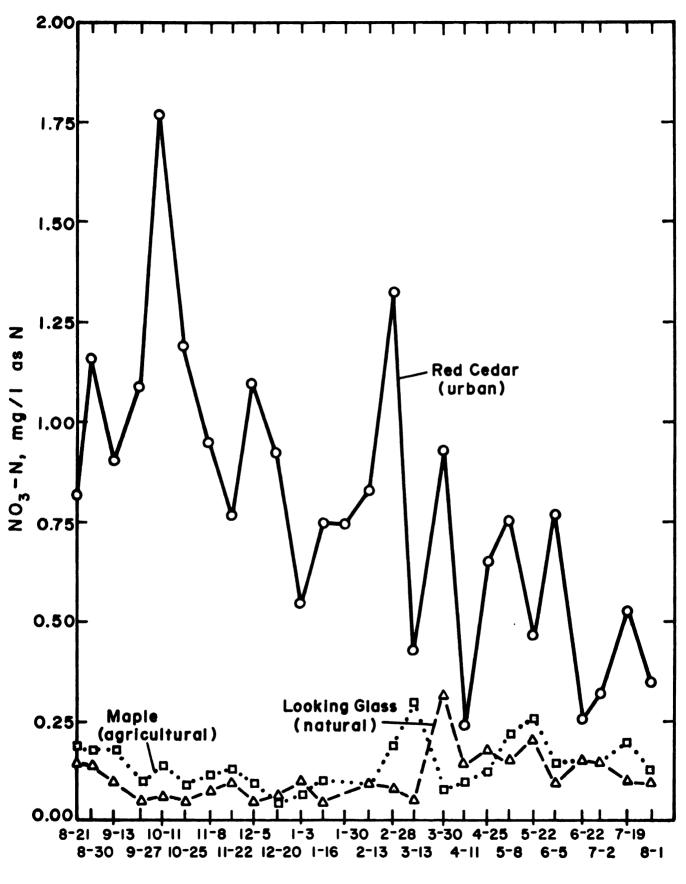
Calendar Date 1969-70

Comparisons of total phosphorus (Figure 5) indicated that urbanized watershed runoff consistently contained greater than five times the phosphorus concentration of either natural or agricultural land runoff. The linearly decreasing trend in phosphorus levels in the Red Cedar River at its confluence with the Grand River is related to the City of East Lansing's wastewater treatment plant operation. Over the period of study values of phosphorus content recorded upstream of the plant usually ranged between 0.2 0.3 ml/l. The maximum difference recorded was approximately 18 times greater than values obtained from the other watersheds. Phosphorus levels in the agricultural and natural watershed runoffs were not significantly different from each other.

A land usage comparison in the Pacific Northwest (Sylvester, 1961) indicated somewhat different results, which are shown in Figure 6. Average annual total phosphorus concentrations showed those derived from urban areas equivalent to those of agricultural land and greater than forested land concentrations. Furthermore, annual nitratenitrogen averages indicated that agricultural lands discharged four to six times the urban concentrations, and 15 to 25 times the forested concentrations.

Sylvester's urban drainage study contained samples taken only from highway and residential street drains, anywhere from 30 minutes to several hours after a rain

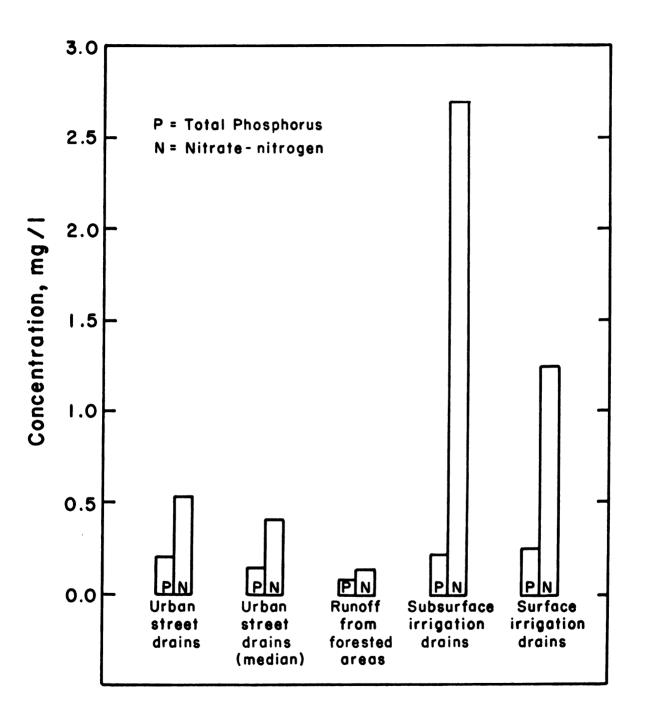
Figure 5. Comparison of total phosphorus concentrations in three watersheds of different predominant land usages.



Calendar Date 1969-70

Figure 6. Comparison of mean nutrient differences from different land usages (data from Sylvester, 1961).

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storm had commenced. His data did not include sewage effluent, a major component of urbanized land discharge. Since the Red Cedar River at times contained about 50 percent sewage effluent, one would expect it to contain greater amounts of phosphorus than did Sylvester's urban samples.

The agricultural data in Sylvester's (1961) study was derived from samples taken directly from irrigation drains. These samples, being consistently closer to sites of actual fertilization, would be expected to contain higher nitrate values than those from receiving streams.

Natural lands used by Sylvester's comparison studies were forests with some logging operations and no human habitation. However, the streams also contained large natural reservoirs which probably extracted large proportions of nutrients by biological uptake. Sylvester's forest drainage data may have been modified by the reservoirs and lower-unimpounded in nutrient runoff than that from watersheds. The Looking Glass River watershed encompassed about 2,400 people and contained approximately 50 percent fallow cropland. Because it is not entirely natural, its nutrient drainage should be greater than drainage from an uncultivated watershed.

It must be emphasized that this comparison did not produce generalized results. Although efforts were made to select these study areas near each other to ensure uniform

soil structure, close uniformity could not be assured. However, slight differences between results from the present study and results of Sylvester's study all were apparently related to differences in watershed and sampling locations. However, rational explanations for these releases can be made if sufficiently detailed analyses on nutrient inputs, storage and releases are available.

It therefore appears reasonable to justify an equivalence between this study's urban and agricultural watersheds in terms of nitrate levels and an equivalence between the agricultural and natural watersheds in terms of phosphorus levels.

Finally, it appears that each watershed is somewhat inimitable with respect to phosphorus and nitrogen releases over an annual cycle.

D. <u>Flow Contribution of Sewage Treatment</u> <u>Plant Effluents to Rivers at Low-</u> <u>Discharge Periods</u>

Average stream and river discharge rates (Appendix G) varied greatly between seasonal high and low-water periods. Sewage effluent rates varied little in comparison (Appendices J and K) so that their discharges comprised different proportions of total flow through the seasons. For example, sewage effluents during August, 1969 contributed about 16 percent of the total Grand River discharge, while September, 1969 contributions were approximately 19 percent.

Sewage effluents comprised a larger proportion of total flow in an urban watershed. For instance, the Red Cedar River discharged about 55 percent as sewage effluent in September (Figure 7). This percentage does not consider contributions by small towns such as Webberville, private industries or by residences along the river. It also does to consider volume changes by stream loss through groundwater replenishment.

E. Nutrient Budget

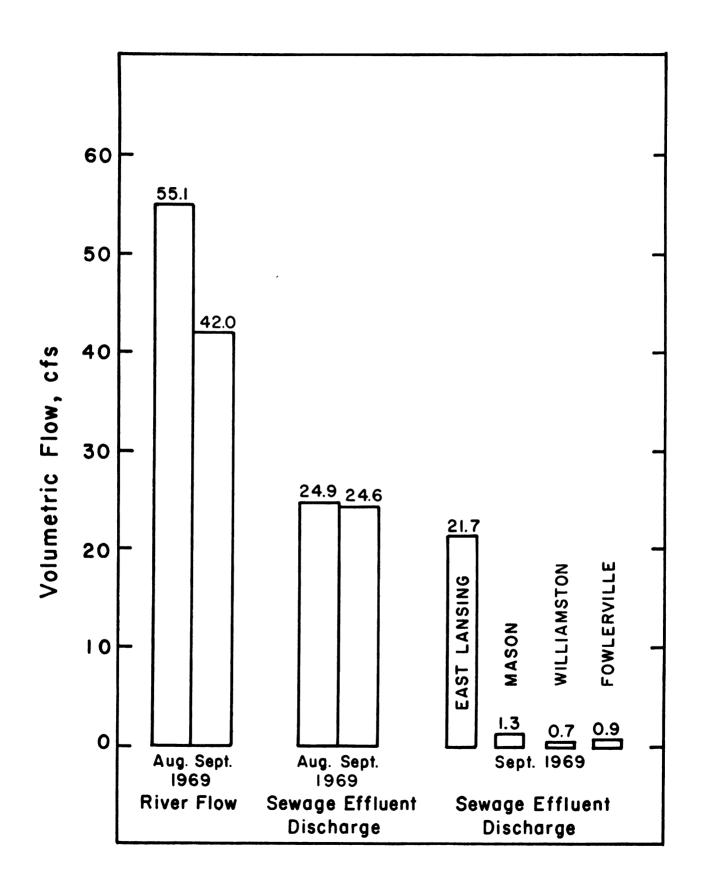
1. Annual Nutrient Budget by Watershed

To obtain reasonable approximations of total phosphorus and nitrogen inputs to the Grand River system, total areas of each land usage were multiplied by the estimated discharge from each classification. Table 5 summarizes nutrient discharges per year per square mile for each land usage.

The determination of total areas for different land use practices in both the Grand River basin and its subwatersheds appear to be reasonable approximations. Areas of various land usages per county were available from Kimball (1969), and were reapportioned to tributary watersheds.

Estimated nutrient discharge rates per year per mile² (Table 5) were multiplied by total area of miles² of each land classification for all basins. For example, the

Figure 7. Proportions of flow rate in the Red Cedar River due to sewage effluents.



Land-type	Tota Phos	l phoru s		tal trogen
Agricultural land	A)	95	в)	2045
Urbanized Land	C)	727	D)	2500
Forested Land	E)	25	F)	897
"Other" land uses	G)	45	н)	1363
Sewage Treatment Plants Primary Secondary		7 5		35 15
 A) Sawyer (1947) B) Sawyer (1947) C) Weibel, Anderson and W D) Weibel, Anderson and W E) Averaged from Table 1 F) Sylvester (1961) G) Approximation relative forest H) Approximation relative forest 	Woodward in Keuj e to ra	d (1964 p (1967 tes fro)) m agricul [.]	

Table 5. Estimated Discharge Rates from Each Land-type in Kg Mile⁻²Year⁻¹ and for Sewage Treatment Plants in Mg Liter⁻¹

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Grand River Basin, from Appendix I, contains about 3102 miles² of agriculture, 586 miles² of urbanized land, 1113 miles² of forest and 762 miles² of "other" land-types. These totals, when added together, comprised most of the total nutrient drainage into the Grand River system per year. The remaining portion of the total is contributed by sewage treatment plants, industries, private residences, and the small portion of land draining directly into the Grand River throughout its length.

Although sewage treatment plants in general do not discharge appreciable amounts of nitrate-nitrogen, their effluents contain large quantities of ammonia and organic nitrogen. They also vary in their total nitrogen concentrations, but Sawyer (1952) gave a rough estimate of 15-35 mg liter⁻¹. His limits then, for this study, became averages of 15 mg liter⁻¹ for secondary treatment, and 35 mg liter⁻¹ for primary treatment. Total phosphorus concentrations in sewage effluents are normally found at present to be about 5 mg liter⁻¹ for secondary treatment and 7 mg liter⁻¹ for primary treatment.

River flow data are measured values for the months of August through December, 1969. Because the United States Geological Survey did not have flow rates at this writing for January through July, 1970, these rates were estimated by graphing previous rates from years 1963 through 1969. Values for 1970 were then extrapolated from curves drawn for given sampling sites.

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Results from this study are shown in Table 6. The data indicate that the overall nutrient discharge is a unsteady-state system, since actual river discharges are only a fraction of calculated inputs to the system. It should be recognized that the mass discharges per land classification were derived from studies on other river basins. Calculated values can therefore only approximate actual nutrient drainage into the river system. In addition, the actual discharge factors were derived from samples taken biweekly. Thus, total nutrient discharge releases could be quite different from derived estimates.

When values given in Table 6 are examined in view of such approximations, estimated phosphorus discharges are remarkably similar to actual discharge values. Nitratenitrogen discharges are considerably less than calculated values, but they still agree reasonably well. The Grand River system therefore appears to discharge amounts of nutrients per unit area of each land classification equivalent to discharges from other areas of Michigan, Ohio, and Wisconsin.

2. <u>"Flow-through" Nutrient Budget</u>

The flow-through nutrient budget is a monthly average nutrient discharge, given in kg day⁻¹. However, at this writing, flow rates were available only for months of August through December, 1969. The yearly nutrient budget

in Surface Ru	1969 - July 1970)
alances	August
s and Nitrogen Ba	Surveillance:
Phosphorus	(Period of
Table 6.	-

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aont ce	Lbs. p	per Year	Percent of	of Total
			N	
From	the Grand River	Basin		
Inpur: Municipal Treatment Facilities	•	1,566,000	19.2	47.5
Urban Runoff	•	938, 000	12.0	
Agricultural Lands	_	652,000	51.9	
Forest Land Other	2,226,000 2.286.000	61,000 76,000	8.5 8.5	1.8
Total	•	3,293,000	100.0	
Export:	8,790,000	2,275,000	32.7	67.0
	the Thornapple River	<u></u> er Basin_		
Input: Municipal Treatment Facilities	.70.000	16,000	2.1	6.5
	331,000	96,000	6. 6	40.3
Agricultural Lands	2,267,000	106,000	67.7	44.4
t Land	345,000	10,000	10.3	4.0
Other	328,000	10,000	9.8 99.8	4.6 99.8
Total	3,341,000	238,000	100.0	100.0
Export:	1,187,000	141,000	35.0	59.0

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		I Year	Percent of	of Total
		Р	N	Ъ.
From	the Flat River	Basin		
Input: Municipal Treatment Facilities Urban Bunoff	171,000	22,000	4.9 7.7	14.3 37.2
Agricultural Lands	1,403,000	65,000	63.4	42.3
Forest Land Other	81,000 279,000	000 6,000	12.5 12.4 99.8	5.0 6.0 99.8
Total	2,044,000	154,000	100.0	100.0
Export:	487,000	152,000	22.0	98.0
From	the Maple River	<u>Basin</u>		
Input: Municipal Treatment Facilities Urban Bunoff	5,000	18,000	1.3 4 1	7.2
Agricultural Lands		167,000	86.4	68.2 68.2
Forest Land		6,000	5°0	2.3
Crief		0000 / F	99.8	99.6
Total	413,000	244,000	100.0	100.0
Export:	698, 000	72,000	168.0	29.0

Source	Lbs. pe	per Year P	Percent of N	of Total P
From the	From the Looking Glass	River Basin		
Input: Municipal Treatment Facilities	6,000	1,000	0.6	1.8
Urban Runoff	67,000	20,000	6.7	29.9
Agricultural Lands	820,000	39,000	82.6	58.5
Forest Land	12,000	3,000	1.2	5.3
Other	85,000	3,000	8.6 99.7	4. 3 99.8
Total	000,006	66,000	100.0	100.0
Export:	384,000	53,000	39.0	80.0
Trant.	Kea Ceaar KIVER	er basın		
Aupue: Municipal Treatment Facilities	427,000	139,000	18.3	44.3
Urban Runoff	375,000	109,000	16.1	34.6
Agricultural Lands	1,206,000	56,000	51.7	17.9
Forest Land	167,000	5,000	7.1	1.4
Other	154,000	5,000	6.6 99.8	1.6 99.8
Total	2,027,000	314,000	100.0	100.0
Export:	1,027,000	402,000	44.0	128.0

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Table 6--continued

into Lake Michigan was calculated by extrapolating flow rates for months of unavailable flow data. Similar averages for upstream sites were not estimated due to larger flow variations in smaller catchment areas.

Although the phosphorus budget should theoretically increase throughout the Iength of the river, it decreased consistently from Portland until just upstream from Grand Rapids. Not only did this decrease occur in the summer, it also occurred during November and December.

During August and September, sewage treatment plants (Appendix K) discharged about three times the total amount discharged into Lake Michigan. This is evidence of considerable removal by soil fixation and plant activity. In December only did final discharge exceed total sewage treatment discharge, indicating that plants had exerted a noticeable effect during the growth period.

Total nitrogen discharges fluctuated in correspondence with seasonal changes in biological activity (Appendix M). August and September average discharges were minimal for the five-month period. The October average final discharge at Lake Michigan was about five times those of August and September, showing a gradual increase in discharge with the decrease in temperature. November and December final discharges averaged about twelve times those of August and September.

Although the nitrogen budget does not increase in the summer beyond about 60 miles from the river headwaters, colder months produced expected increases. Much fluctuation occurs even during November and December, but the budget shows a gradual increase from source to mouth.

Nitrogen was continually utilized by plants, since the final discharge in December was only one-half of the total contributed by sewage treatment plants alone (Appendix J). Even so, a considerable decrease in utilization was shown, because the final discharge during August was only onetwentieth the total contributed by sewage treatment plants.

Assuming that the river system is in a long term "steady state" position with respect to nutrient discharge, a very large nutrient load must be flushed downstream during spring floods to compensate for such retention in the system.

V. CONCLUSIONS

- Nitrate-nitrogen concentrations appeared to fluctuate significantly with changes in temperature and photoperiod.
- 2. A temperature-dependent shift in nitrogen-form uptake by plants apparently takes place at approximately 10°C. Above 10°C, nitrate-nitrogen is preferentially absorbed, with a shift to ammonium-nitrogen as the ambient temperature is reduced to less than 10°C.
- 3. Total phosphorus did not appear to fluctuate significantly with changes in biological activity. However, certain sites in the river at times exceeded 100 times the 0.01 mg liter⁻¹ previously reported as the minimum phosphorus concentration necessary to stimulate nuisance algal blooms in lakes.
- 4. A study of nutrient concentrations in runoff from watersheds of predominantly urban, natural, or agricultural land usages indicated significant differences:
 - a) The natural watershed discharged less nitrate-nitrogen than did either the urbanized or the agricultural watersheds.

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- b) Urbanized land discharge contained far greater quantities of total phosphorus than either natural or agricultural land discharges.
- c) Natural and agricultural lands did not discharge
 significantly different quantities of total phosphorus.
- 5. The Grand River from August, 1969 to July, 1970 discharged an estimated 1,034,000 kg of total phosphorus into Lake Michigan. However, this amount was only 69 percent of the calculated input from the overall watershed.
- 6. Sewage treatment effluents along the Grand River contributed amounts of total phosphorus equivalent to the total discharge from tributary rivers.
- 7. Nitrate-nitrogen discharged into Lake Michigan totaled 3,995,821 kg for the year of August, 1969 to July, 1970. This amount, however, was only 33 percent of the calculated input.
- 8. Tributary rivers contributed about 43 percent of the total nitrate-nitrogen discharge. However, they contained only 35 percent of the total calculated nitrate input.
- 9. Approximately 35 percent of the total nitrate-nitrogen discharge was unaccounted for. It was suggested that that proportion might be due to action of nitrogen-fixing algae.

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LITERATURE CITED

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APPENDICES

APPENDIX A

NITRATE-NITROGEN CONCENTRATIONS FOR EACH SAMPLING SITE DURING THE PERIOD 8-21-69 THROUGH 8-1-70

Sampling			Date of	Collecti		
Site	8/21	8-30	9-13	9-27	10-11	10/25
	<u>-</u>					
1	0.13	0.13	0.17	0.17	0.24	0.56
2	0.18	0.22	0.19	0.15	0.68	0.76
2 3 4	0.15	0.18	0.18	0.14	0.23	0.70
4	0.12	0.15	0.08	0.27	0.74	0.49
5	0.10	0.07	0.13	0.09	0.21	0.59
5 6 7	0.07	0.11	0.35	0.32	0.11	0.72
7	0.07	0.10	0.12	0.25	0.24	0.43
8	0.16	0.11	0.11	0.18	0.21	0.41
9	0.09	0.11	0.12	0.17	0.38	0.86
10	0.35	0.13	0.41	0.52	0.42	1.29
11	0.43	0.18	0.52	0.20	0.33	0.85
12	0.20	0.25	0.22	0.17	0.24	0.48
13	0.30	0.11	0.50	0.39	0.50	1.33
14	0.25	0.36	0.75	1.05	0.76	1.87
15	0.09	0.15	0.13	1.02	0.62	0.25
16	0.33	0.70	0.80	0.90	0.99	1.53
17	0.80	0.88	0.83	1.30	1.01	1.28
18	1.43	1.78	0.80	1.4 0	1.42	0.94
19	1.44	0.88	0.68	1.30	0.52	0.89
20	0.48	0.50	1.05	0.66	0.48	0.68
21	0.20	0.24	0.23	0.46	0.27	0.71
22	0.53	0.74	0.50	0.20	0.04	0.28
(23)	0.10	0.11	0.15	0.26	0.37	0.77
24	0.71	0.40	0.70	1.03	0.58	0.55
25	0.63	0.68	1.14	0.80	0.62	0.74
26	0.61	1.00	1.00	1.30	0.95	0.54
27	0.95	1.60	1.90	1.78	1.40	0.82
28	1.63	1.35	1.44	1.43	0.86	1.33
29	2.30	2.80	3.60	3.40	2.86	2.32
30	0.12	0.12	0.13	0.12	0.06	0.12

Table A.--- Nitrate-nitrogen concentrations (mg/l) for each sampling site.

Table .	Acon	tinued
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Sampling		1	Date of	Collectio		
Site	11-8	11-22	12-6	12-20	1-3	1-16
1	0.68	1.00	0.91	1.01	0.73	1.01
2	0.76	1.02	I.06	0.82	0.93	0.82
3	0.66	0.80	1.03	0.95	0.94	0.84
1 2 3 4	0.49	0.84	0.96	0.55	0.83	
5	0.72	0.79	0.92	0.98	0.80	0.99
5 6	0.59	0.52	0.81	0.62	0.79	1.01
7	0.54	0.51	0.55	0.71	0.73	0.72
8	0.49	0.48	0.39	0.70	0.66	0.81
9	0.83	0.95	1.06	1.12	1.12	1.20
10	1.30	1.47	1.47	1.69	1,23	1.64
11	0.96	1.02	1.56	1.43	1.46	1.25
12	0.33	1.13	I. 50	0.93	0.92	1.05
13	1.75	1.15	1.67	1.71	1.41	1.53
14	1.15	1.24	2.07	1.27	2.27	1.92
15	0.25	0.28	0.47	0.82	0.63	0.72
16	1.67	1.73	2.28	1.25	1.91	1.60
17	2.19	1.51	2.54	1.51	1.44	2.19
18	2.81	1.52	1.70	1.95	1.57	1.29
19	1.54	0.86	1.32	0.70	0.95	1.84
20	2.15	0.84	1.13	0.70	0.77	0.75
21	0.80	0.98	1.12	0.72	0.56	0.75
22	0.29	0.91	1.08	0.32	0.84	0.69
23	0.68	0.71	0.90	0.71		0.50
24	0.89	0.86	1.13	1.05	0.50	0.5 9
25	0.29	0.74	1.15	1.14	0.48	0.48
26	0.63	0.71	1.38	0.93	0.44	0.43
27	0.79	0.89	1.06	1.38		0.39
28	1.36	0.84	1.84	1.03	0.27	0.29
29	2.20	0.72	1.52	2.49	0.59	0.32
30	0.19	0.10	0.18	0.16	0.19	0.29

Table	Acont	tinu	\mathbf{ed}
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Sampling		Date of Collection							
Site	1-31	2-13	2-28	3-13	3-30	4-11			
1	0.87	1.03	0.94	0.96	0.94	2.31			
2	1.09	0.89	0.92	1.44	0.91	1.69			
3	0.85	1.13	0.93	2.18	1.02	1.77			
4	0.90	1.16	0.92	1.80	1.01	2.18			
5	1.07	1.16	0.92	1.98	0.83	2.57			
6	0.87	1.13	0.97	1.41	0.82	2.31			
7	0.72	0.78	0.78	2.05	0.87	2.20			
8		0.70	0.66	0.73	0.45	0.53			
9		1.31	0.91	2.22	0.95	2.82			
10		1.71	1.24	1.47	0.85	2.91			
11		1.39	1.45	1.48	0.71	3.17			
12		1.06	1.27	1.42	0.70	3.72			
13		1.83	1.79	1.83	0.94	3.20			
14		1.41	1.76	1.83	1.28	3.82			
15		0.70	0.69	1.75	0.88	2.07			
16		2.05	2.01	2.24	2.24	3.94			
17		1.56	2.25	2.28	1.93	2.01			
18		1.38	1.40	2.22	1.45	2.14			
19		0.89	1.21	1.49	1.12	2.01			
20		0.79	1.00	1.37	0.87	1.85			
21		0.80	0.91	1.42	0.83	2.25			
22	1.05	1.06	1.18	1.73	1.59	3.47			
23	0.52	0.56	0.56	0.87	0.64	1.71			
24	0.93	0.56	0.97	0.95	0.52	2.14			
25	0.60	0.57	0.76	0.82	0.71	1.34			
26	0.38	0.46	0.53	0.67	0.57	1.39			
27	0.82	0.48	0.65	0.94	0.57	1.64			
28	0.67	0.43	0.66	1.18	0.70	1.38			
29	0.44	0.74	0.58	0.35	0.15	0.38			
30	0.31	0.33	0.28	0.37	0.32	0.19			

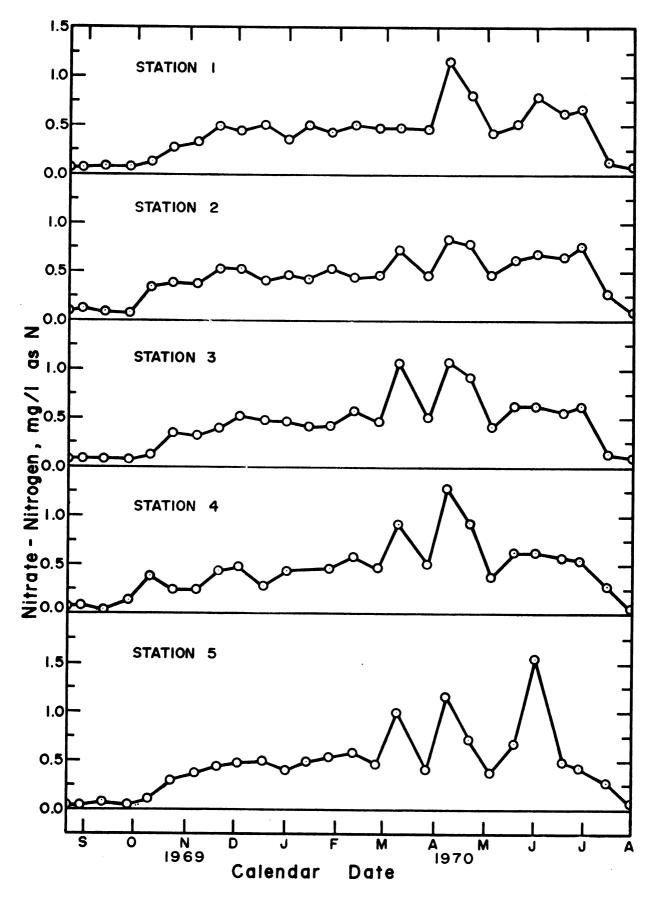
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31 0.20 0.25 0.05 0.12 0.12 0.26 0.12								
	TC	0.20	0.25	0.05	0.12	0.12	0.20	0.12

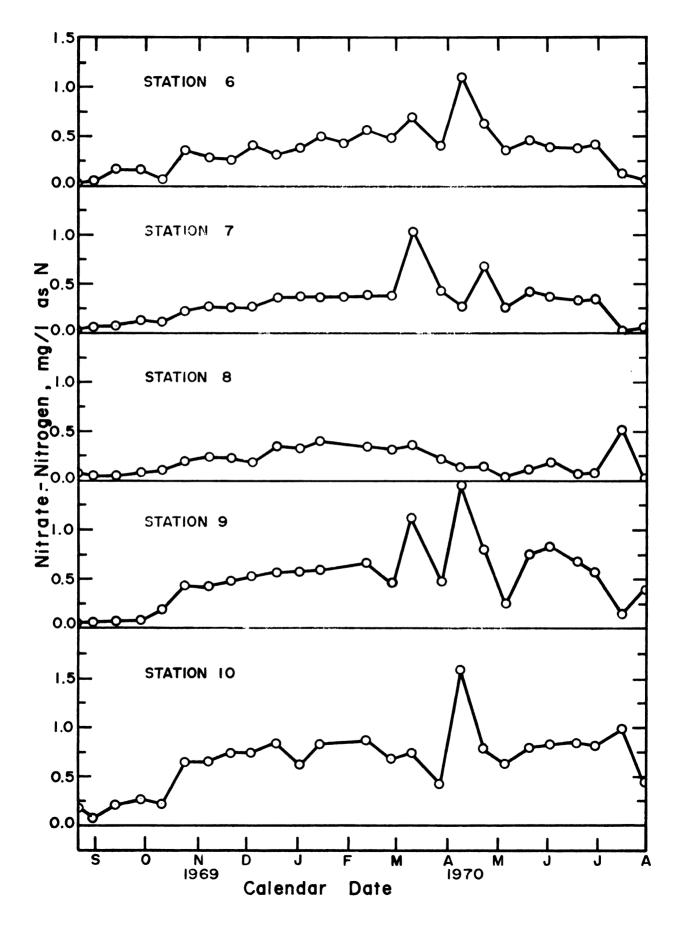
APPENDIX B

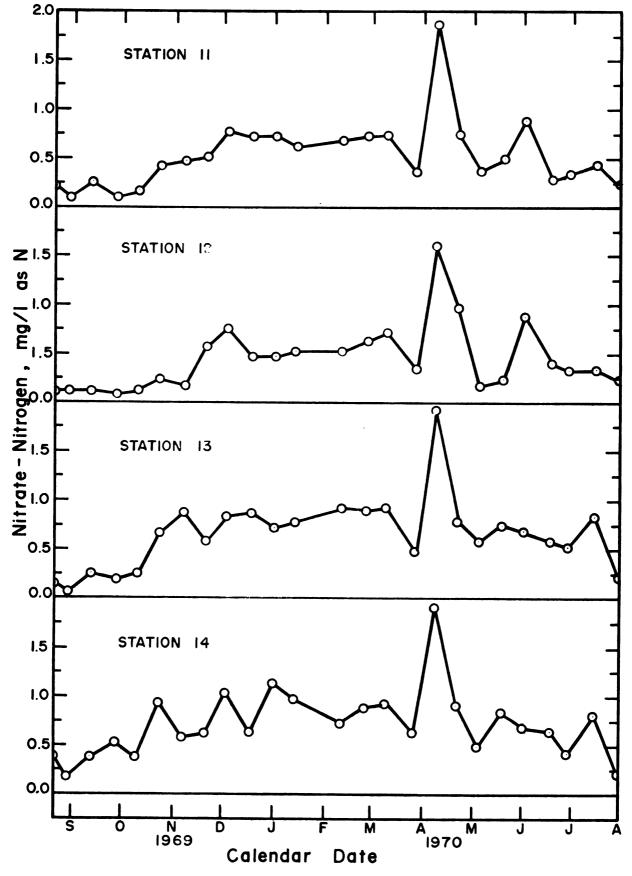
NITRATE-NITROGEN CONCENTRATION FLUCTUATIONS AT EACH SAMPLING SITE OVER THE PERIOD

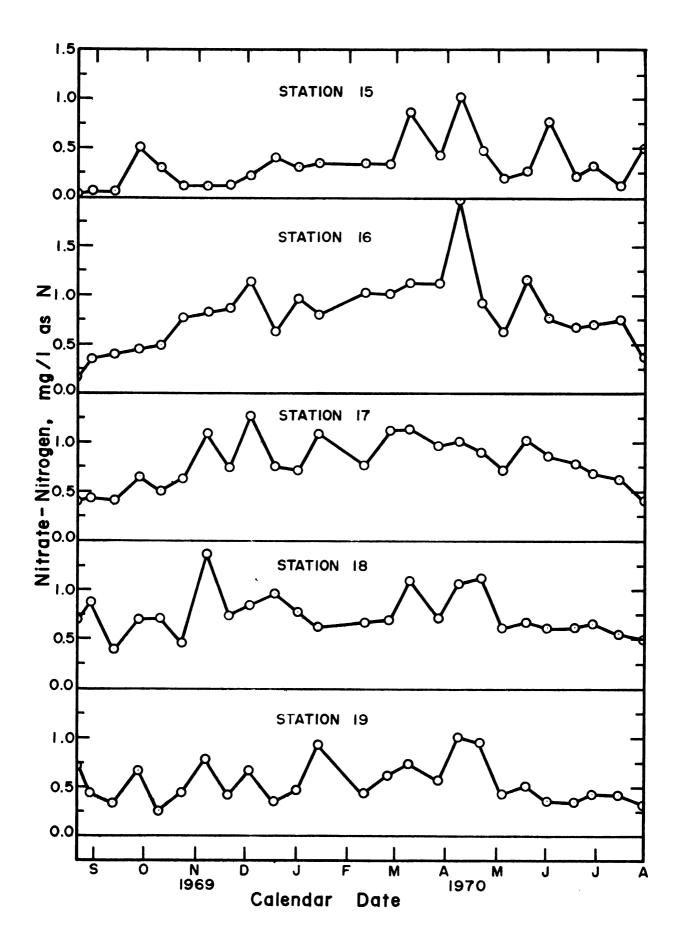
OF RECORD

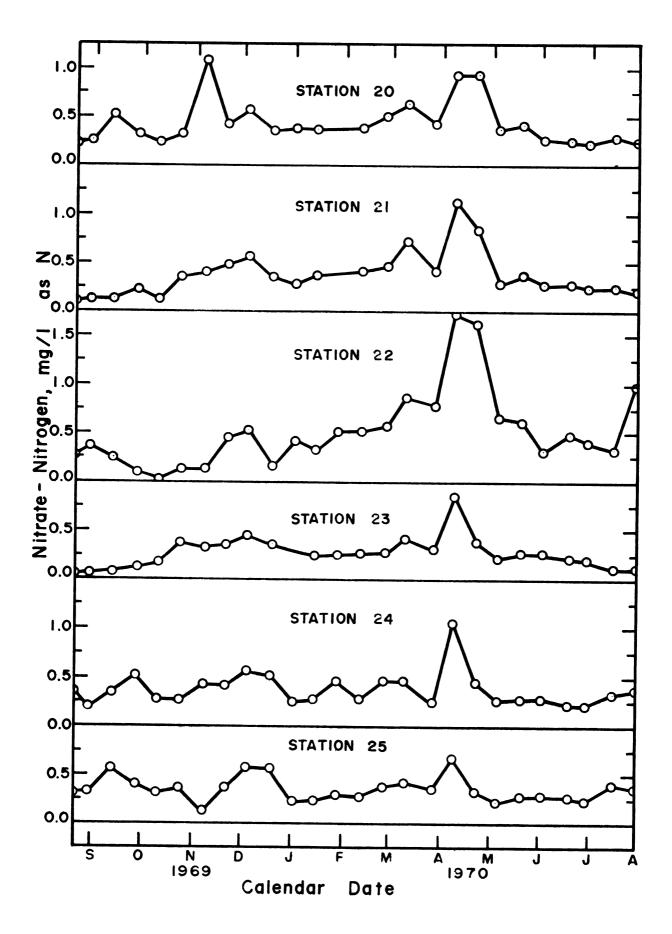
> : 2 ; •••••

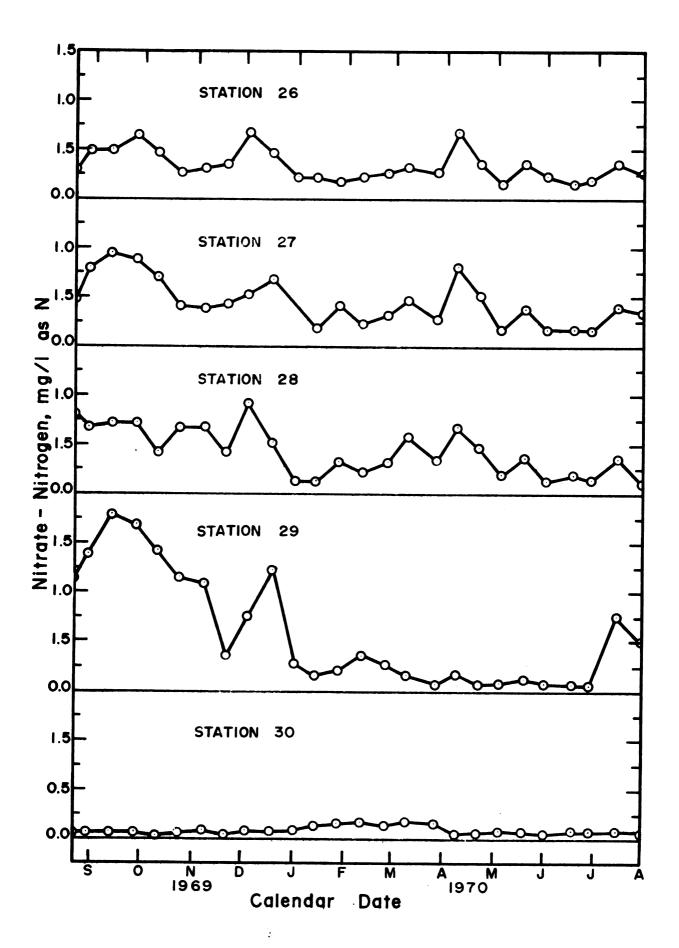












APPENDIX C

TOTAL PHOSPHORUS CONCENTRATIONS FOR EACH SAMPLING SITE DURING THE PERIOD 8-21-69 THROUGH 8-1-70

Sampling		Dat	e of Colle	ection	
Site	8-21	8/30	9/13	9–27	10-11
1	0.27	0.28	0.33	0.24	0.35
1 2	0.46	0.47	0.40	0.44	0.37
3	0.45	0.45	0.56	0.47	0.45
4	0.40	0.45	0.38	0.32	0.33
5	0.21	0.15	0.21	0.16	0.20
5 6	0.14	0.21	0.27	0.08	0.08
7	0.07	0.12	0.11	0.08	0.07
8	0.15	0.15	0.14	0.11	0.11
9	0.25	0.12	0.15	0.14	0.33
10	0.26	0.25	0.33	0.28	0.38
11	0.22	0.18	0.32	0.25	0.26
12	0.19	0.18	0.18	0.11	0.14
13	0.28	0.22	0.40	0.42	0.48
14	0.50	0.59	0.64	0.65	0.75
15	0.15	0.14	0.10	06	0.07
16	0.66	0.57	0.89	0.73	0.69
17	1.19	0.78	0.91	0.80	0.76
18	0.46	0.63	0.64	0.70	1.03
19	0.63	0.65	0.86	0.74	0.80
20	0.53	0.44	1.36	0.62	0.72
21	0.46	0.49	0.55	0.52	0.75
22	0.82	1.16	0.91	1.09	1.77
23	0.25	0.24	0.30	0.30	0.33
24	0.29	0.44	0.32	0.34	0.32
25	0.32	0.33	0.41	0.41	0.39
26	0.41	0.33	0.41	0.44	0.36
27	0.75	0.52	0.64	0.67	0.48
28	0.92	0.60	0.95	1.04	0.92
29	1.35	1.87	1.82	1.55	1.30
30	0.11	0.11	0.12	0.13	0.12

Table	C	Total	pho	sp horus	concentrations	(mg/l)	for	each
		sampli	.ng	site.				

Table C	conti	nued
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Sampling	Date of Collection						
Site	10-25	11-8	11-22	12-5	12-20		
1 2	0.28	0.37	0.32	0.83	0.28		
2	0.90	0.34	0.33	0.48	0.25		
3 4	0.41	0.37	0 .3 5	0.45	0.28		
4	0.37	0.33	0.29	0.27	0.21		
5 6	0.22	0.21	0.33	0.14	0.31		
6	0.20	0.25	0.25	0.11	0.08		
7	0.08	0.10	0.08	0.06	0.10		
8 9	0.08	0.13	0.10	0.10	0.10		
9	0.42	0.35	0.39	0.17	0.28		
10	0.43	0.42	0.49	0.34	0.35		
11	0.31	0.31	0.28	0.26	0.27		
12	0.09	0.12	0.13	0.10	0.05		
13	0.41	0.41	0.40	0.45	0.42		
14	0.63	0.59	0.68	1.39	0.91		
15	0.06	0.08	0.10	0.11	0.07		
16	0.61	0.66	0.53	0.50	0.62		
17	0.56	0.63	0.60	0.95	0.61		
18	0.52	0.79	0.80	0.67	0.67		
19	0.84	0.66	0.49	0.70	0.76		
20	0.76	0.59	0.40	0.47	0.39		
21	0.57	0.48	0.42	0.52	0.75		
22	1.09	0.95	0.77	1.09	0.93		
23	0.29	0.33	0.36	0.26	0.28		
24	0.34	0.35	0.35	0.36	0.32		
25	0.30	0.29	0.25	0.36	0.25		
26	0.38	0.35	0.25	0.40	0.27		
27	0.53	0.36	0.51	0.56	0.50		
28	0.60	0.62	0.61	0.86	0.49		
29	1.16	0.94	0.88	0.86	0.85		
30	0.06	0.07	0.05	0.05	0.08		
50	0.00	0.07	0.03	0.05	0.00		

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Sampling		Da	te of Coli	lection	
Site	1-3	1-16	1-30	2-13	2-28
					<u> </u>
1	0.30	0.33	0.41	0.20	0.24
2	0.30	0.44	0.29	0.22	0.42
3	0.34	0.35	0.36	0.31	0.31
3 4	0.30	0.43	0.39	0.25	0.24
5 6	0.33	0.45	0.30	0.18	0.30
6	0.13	0.47	0.14	0.14	0.11
7	0.11	0.08	0.11	0.20	0.07
8	0.07	0.27		0.15	0.13
9	0.30	0.50		0.29	0.36
10	0.47	0.51		0.30	0.33
11	0.30	0.68		0.26	0.24
12	0.07	0.11		0.10	0.19
13	0.37	0.70		0.30	0.33
14	1.00	0.59		0.30	0.5 9
15	0.10	0.05		0.09	0.08
16	0.72	0.67		0.56	0.47
17	0.54	0.81		0.47	0.34
18	0.71	0.88		0.39	0.49
19	0.80	0.67		0.56	0.75
20	0.53	0.55		0.34	0.37
21	1.45	0.60		0.26	0.26
22	0.55	0 75	0.74	0.83	1.33
23	0.21	0.35	0.41	0.19	0.20
24	0.45	0.27	0.31	0.16	0.23
25	0.20	0.23	0.34	0.23	0.22
26	0.30	0.38	0.43	0.18	0.45
27	0.55	0.36	0.49	0.29	0.23
28	0.55	0.58	0.35	0.37	0.47
29	0.90	0.93	0.57	0.65	0.86
30	0.05	0.09	0.05	0.03	0.04

Table C--continued

Sampling	Date of Collection							
Site	3-13	3-30	4-11	4-25	5-8			
1	0.17	0.35	0.31	0.20	0.24			
1 2	0.23	0.43	0.19	0.27	0.30			
3	0.25	0.47	0.26	0.27	0.26			
4	0.27	0.39	0.29	0.22	0.26			
5	0.30	0.32	0.21	0.17	0.21			
5 6	0.24	0.16	0.19	0.11	0 17			
7	0.09	0.09	0.13	0.18	0.19			
8	0.17	0.20	0.17	0.10	0.12			
9	0.28	0.14	0.20	0.19	0.22			
10	0.19	0.38	0.16	0.30	0.24			
11	0.35	0.26	0.21	0.28	0.26			
12	0.30	0.08	0.10	0.13	0.22			
13	0.22	0.39	0.28	0.25	0.32			
14	0.35	0.44	0.33	0.36	0.34			
15	0.06	0.32	0.14	0.18	0.15			
16	0.25	0.56	0.35	0.56	0.30			
17	0.26	0.41	0.41	0.28	0.43			
18	0.34	0.38	0.37	0.18	0.37			
19	0.30	0.63	0.27	0.26	0.38			
20	0.26	0.71	0.21	0,37	0.34			
21	0.15	0.28	0.22	0.35	0.34			
22	0.43	0.93	0.24	0.66	0.76			
23	0.19	0-25	0.15	0.18	0.23			
24	0.09	0.09	0.13	0.22	0.29			
25	0.13	0.17	0.24	0.15	0.26			
26	0.20	0.49	0.11	0.18	0.25			
27	0.25	0.41	0.17	0.11	0.21			
28	0.24	0.28	0.17	0.15	0.41			
29	0.56	0.98	0.25	0.45	0.78			
30	0.18	0.22	0.12	0.14	0.13			

continued

Sampling	Date of Collection								
Site	5-22	6-5	6-22	7-2	7-19	8-1			
1	0.30	0.16	0.25	0.22	0.33	0.30			
2	0.32	0.15	0.30	0.31	0.43	0.33			
3	0.29	0.24	0.32	0.29	0.35	0.36			
4	0.23	0.14	0.21	0.27	0.31	0.19			
5 6	0.31	0.12	0.22	0.18	0.21	0.14			
6	0.13	0.11	0.13	0.12	0.16	0.09			
7	0.10	0.09	0.11	0.06	0.11	0.07			
8	0.13	0.19	0.14	0.10	0.27	0.12			
9	0.28	0.14	0.26	0.28	0.18	0.24			
10	0.34	0.14	0.24	0.18	0.29	0.24			
11	0.32	0.16	0.20	0.16	0.20	0.18			
12	0.27	0.14	0.15	0.13	0.20	0.13			
13	0.32	0.15	0.26	0.20	0.25	0.23			
14	0.45	0.23	0.31	0.44	0.33	0.31			
15	0.21	0.09	0.16	0.14	0.10	0.09			
16	0.37	0.30	0.42	0.42	0.39	0.32			
17	0.47	0.49	0.26	0.37	0.51	0.29			
18	0.44	0.46	0.22	0.35	0.37	0.27			
19	0.70	0.38	0.37	0.5 3	0.47	0.26			
20	0.53	0.69	0.49	0.79	0.39	0.26			
21	0.35	0.35	0.21	0.27	0.36	0.30			
22	0.47	0.77	0.26	0.32	0.53	0.35			
23	0.20	0.13	0.14	0.23	0.08	0.21			
24	0.23	0.21	0.27	0.27	0.50	0.25			
25	0.25	0.14	0.16	0.23	0.32	0.22			
26	0.21	0.25	0.24	0.22	0.39	0.23			
27	0.31	0.24	0.20	0.32	0.44	0.37			
28	0.51	0.28	0.36	0.32	0.46	0.25			
29	0.64	0.49	0.95	0.96	0.89	0.51			
30	0.16	0.05	0.04	0.06	0.05	0.06			

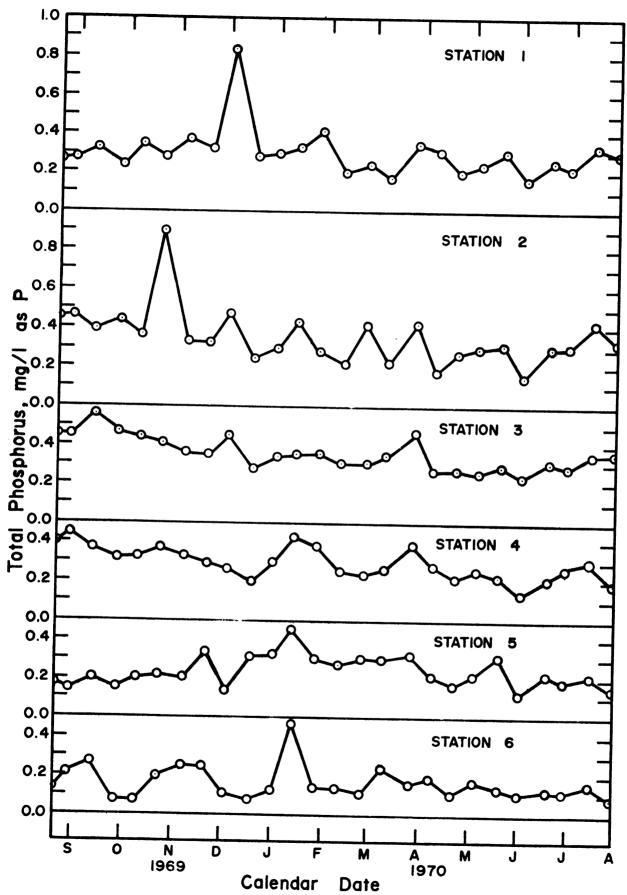
Table C--continued

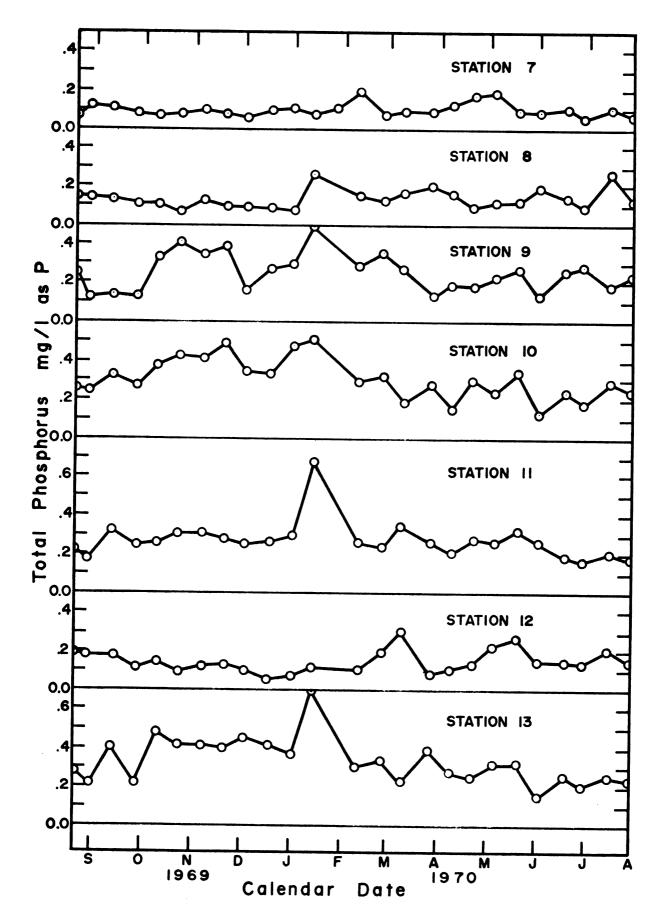
APPENDIX D

TOTAL PHOSPHORUS FLUCTUATIONS AT EACH SAMPLING SITE OVER THE PERIOD OF RECORD

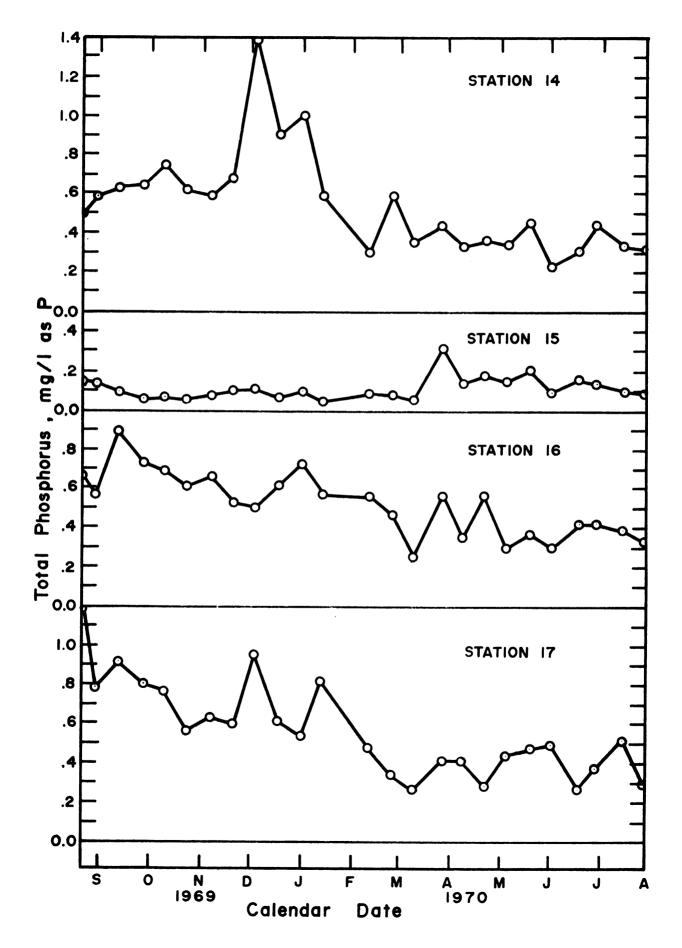
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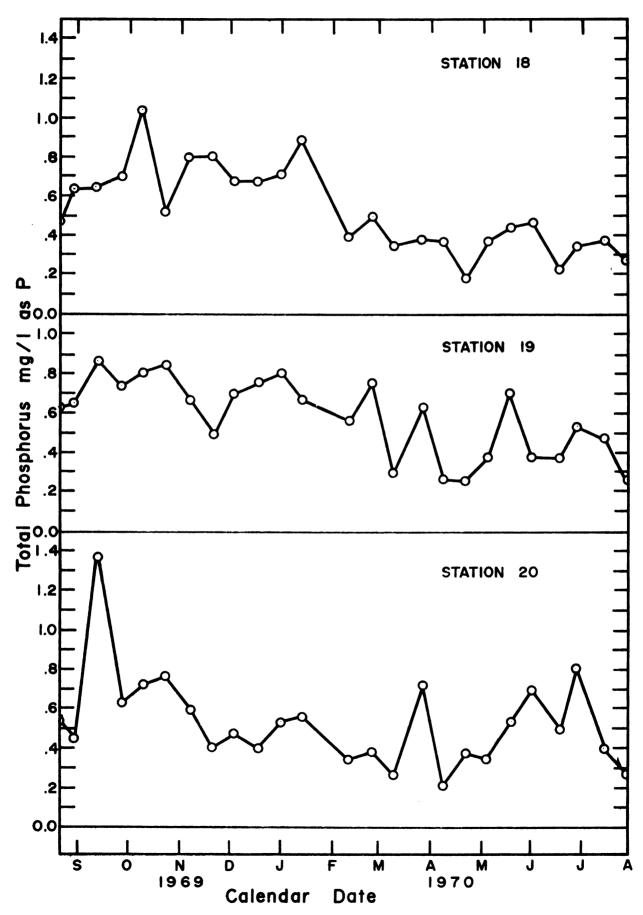
: 3 :2



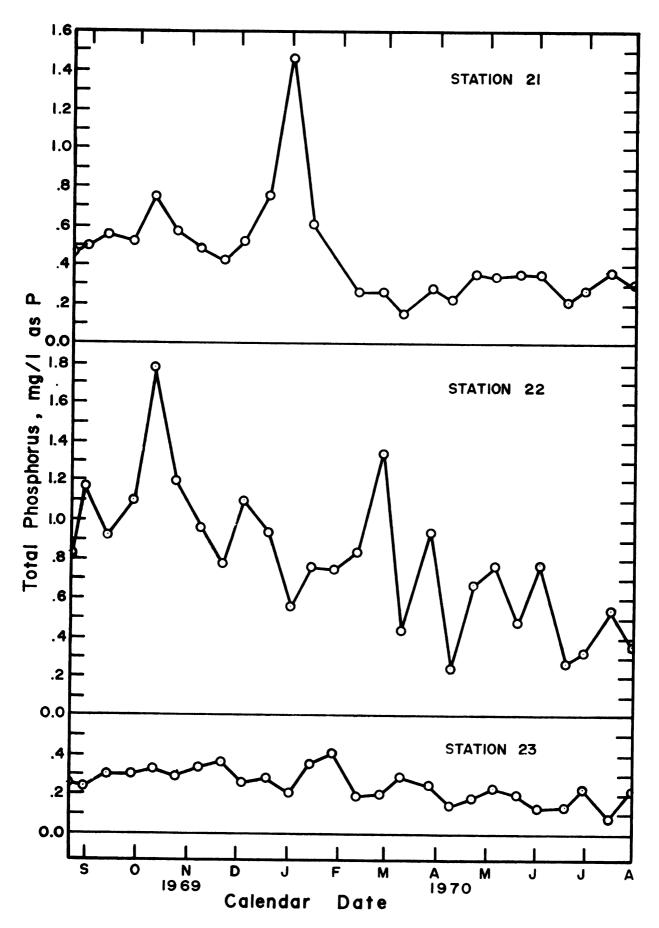


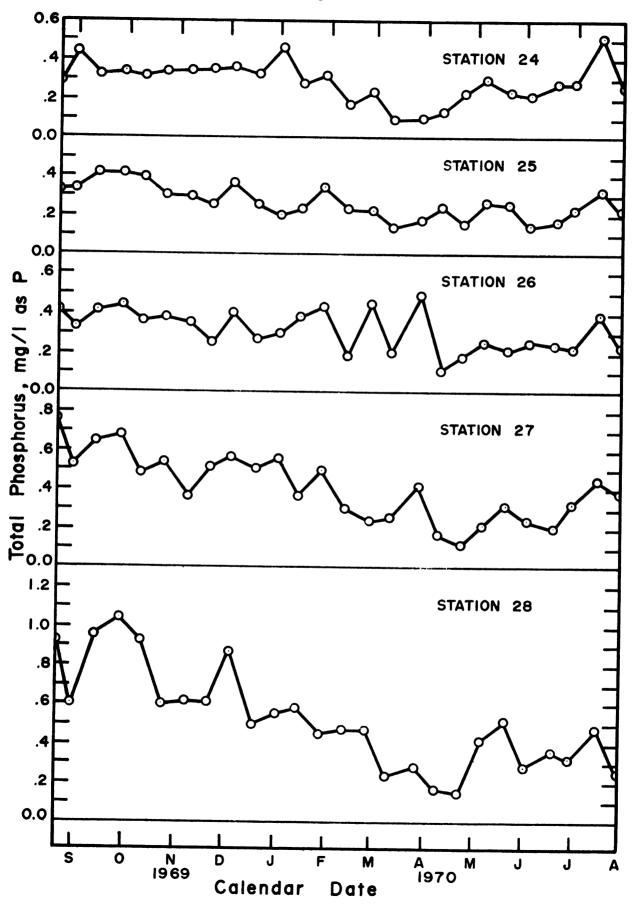
Total Phosphorus may 2 - B





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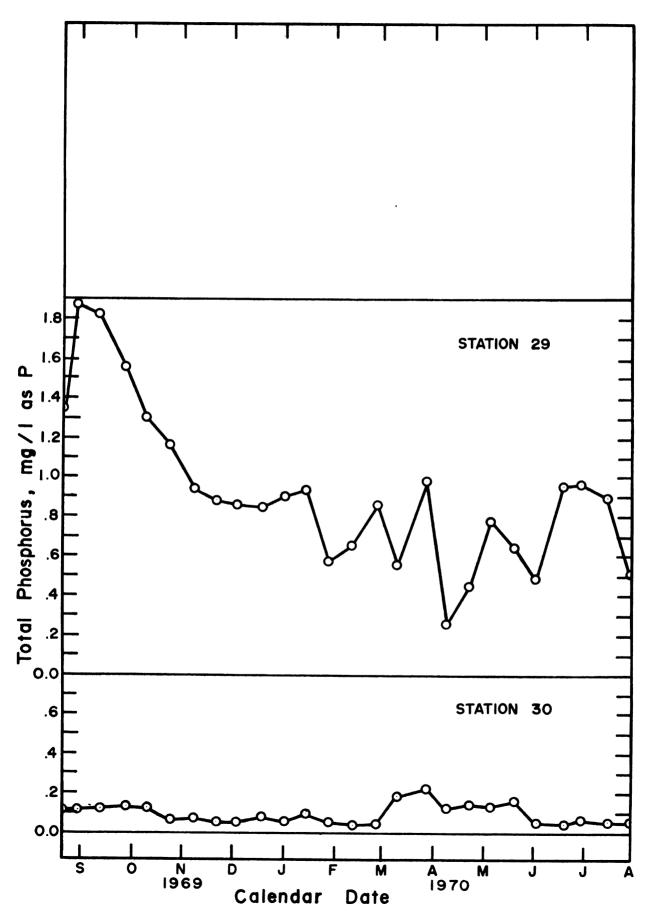




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APPENDIX E

WASTEWATER TREATMENT PLANT MONTHLY AVERAGE DAILY FLOW RATES DURING CALENDAR YEAR 1969

Sewage Treatment Plants in the Grand River Watershed. Types of treatment and the populations which they serve, and monthly average MGD for months January through December 1969. Table E.

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Agency	Type of Treatment	Popula- tion (approx.)	Jan.	۲. ف	Nar.	Apr .	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Ada	aerated lagoon	1,000	1	scharge	to date									
Belding Rvron Center	lagoon			s tamati	to date									
Carson City	aerated lagoon	1,201	No dia	charge	to date									
Cedar Springs	lagoon	1,768	0.55			0.83	0.81					0.33	0.35	90 0
Coopersville	trickling filter	1, 584	0.35	0.43			0.38	0.35	0.39	0.28		0.29		n .
Delhi Township	primary	5,000	0.45	0.42		0.68	0.57	0.53	0.58	0.38	67.0	17.0	00	97.0
elta Township	primary		1.50	1.27		1.92	1.98	8.4	1.63	1.18	1.13	1.20		1.18
Dewitt	primary	1,238	6.0	6.0		80.0	0.10	0.0	90°0	60.0	9.0	6		
East Lansing	activated sludge	37,800	8.6	96 . 8		11.50	11. 1 0	2.4	20.0	07.0		0 48	0.90	0.46
aton kapins	pr umary	4, 500												
Ecumore Fowler	trickling filter	1.2.4 R54	0.43	0.41	0.37	0.55	0.41	0.38	0.43	0.63	0.65	0.61	0.36	0.39
Fowlerville		1.674	Unobta	inable										
Grand Haven	primary	11,700	2.32	2.09		2.42	2.43	2.41	2.70	2.54	2.42	2.59	2.69	
Grand Ledge	primary	5, 500	0.56	0.51		0.72	0.78	0.65	0.62	0.49	.45	0.42	0.34	0.29
Grand Rapids	activated sludge	220, 300	55.95	51.50	44.00	51.80	48.70	45.40	46.50	37.30	.60	41.50	38.90	32.00
Grand Valley														
State College	Lagoon			-			101	00 0		1 07	1 07	00.1	101	1.02
Grandville	activated stude	a, 500	1.43						10.1			80.0	0.07	0.07
Grant	Trickling Tites	1000					2	00.0	00.0	1.25	0.0	1.21	1.13	1.05
Greenville Usetisse	pr imar y	000 2	0.46		96.0	0.46	0.47	64.0	0.53	0.50	0.47	0.46	4.0	0.44
Tonia		6.500	1.10		0.93		1.54	.9	0.93	0.91	0.85	0.96	0.91	0.82
Ionia Reformatory	primarv	2,500	0.5	- 3	(p									
Jackson	activated sludge	48, 500	12.58		10.53	13.66	13.86	15.60	14.64	11.71		11.29	10.57	8.92
Jackson Prison	trickling filter	6, 500	66.0		0.97	1.14	1.19	1.18	1.18	1.12		1.05	1.01	0.99
Kent City	lagoon	617	1			ł		0.11	60.0	0.06		0.06	0.05	0.05
Lake Odessa	trickling filter	1, 806	0.22			0.29	0.27	0.18	0.37	0.24		60.0	0.08	10.02
Lansing	activated sludge	122,000	25.19	24.37	23.03	27.47	27.15	26.40	23.12	23.12	22.47	23.55	22.14	47 . OZ
Leslie	~	1,807	0.39			0.46	64.0	4 .0	0.45	65.0		030	0.34	17.0
Lovell	septic tank	2, 600			en date									
	activated sludge	5 000	0.37		0.40	0.68				1				
Middleville	Imhoff tank	1, 196	Unobta			•								
Montcalm Community														
College	aerated lagoon		No die	ischarge.	to date									
	primary	1, 525			0.15	0.24	0.24	0.19	0.16	0.12	0.22	0.13	0.15	
	aerated lagoon	1, 505	No di							•			:	
	primary	3, 500	0.16							0.13	c1.0	0.1 4	0.13	61.0
lle	aerated lagoon	1,028		charge	to date		24.0	20			0000		74.0	
	primary	4 / O / 7											1	0 67
st. Johns	CELCKLING ILLUST	006			to date			5.5						
	serated lagoon	1.081	No di		to date									
	trickling filter	3,000	0.27		0.24	0	0.32	1	0.37	0.32	0.19	0.32	0.30	0.36
Lake	Imhoff tank	2,063	0.30	0.25	0.26	0.26	0.27	0.28	0.29	0.28	0.28	0.30	0.32	0.28
	aerated lagoon	1, 139	No die		to date				,		•			•
Williamston	primary	2,214	0.34		0.25	0.46	0.45	0.37	0.38	0.26	0.24			61.0
Woodland		374	0.0		0.02	0.05	0.03	0.03	0.02	0.02	0.02	0.03	0.03	.03
			,										0 0 1	

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APPENDIX F

ANALYTICAL PROCEDURES FOR THE DETERMINATION OF TOTAL PHOSPHORUS AND NITRATE-NITROGEN

LABORATORY ANALYSES OF TOTAL PHOSPHORUS AND NITRATE-NITROGEN

a) Nitrate-Nitrogen

Either a ten-ml water sample or an aliquot diluted to ten ml was placed in a large test tube and emersed in a cool water bath. To each sample was then added 2 ml saturated salt solution, 10 ml strong acid solution and 0.05 ml brucine-sulfonilic acid.

The test tube rack was then placed in a hot water bath of not less than 95C for exactly twenty minutes. After return to room temperature, the samples were analyzed for absorbance at 410 m μ in a Beckman DK-2A spectrophotometer. Values obtained were read in μ g sample⁻¹ of nitrate-nitrogen on an absorbance curve drawn from processed nitrate standards. Processed standards were analyzed with every set of thirty water samples.

b) Total Phosphorus

A 50-ml water sample was placed in a boiling flask and 4 ml of 3.6 N sulfuric acid and 0.5 ml concentrated nitric acid added to it. The sample was then digested on a hot plate until sulfuric acid fumes evolved.

Samples were analyzed for total phosphorus according to modifications by Kolter (unpublished) and D'Itri (unpublished) of the method employed by Sugawara and Kanamori

(1961). After addition of distilled water and neutralization, samples were placed in 500-ml separatory funnels and the flasks rinsed with 4 mI concentrated hydrochloric acid and distilled water. The rinses were placed in the same separatory funnel. Fifteen ml N-butyl alcohol and 15 ml of 3:7 chloroform-butanol were added, the funnel then shaken for five minutes and the organic layer drawn off and discarded. Butanol-chloroform was again added and the extraction process repeated. After these steps to remove interference, 10 ml butanol-chloroform and 3 ml of 10 percent ammonium molybdate were added and the funnel again shaken for five minutes. The extracted bottom layer was drawn off and read for absorbance at 310 m μ in a Beckman DK-2A spectrophotometer. Values obtained were read in μg sample⁻¹ of total phosphorus on an absorbance curve drawn from processed phosphorus standards.

APPENDIX G

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STREAM FLOW ESTIMATES AT SAMPLING STATIONS DURING THE PERIOD 8-21-69 THROUGH 12-20-69

date.
sampling
each
for
site
per
(CFS)
Rates
Flow
G
Table

lame				E	ated D	ailv F	Cf.	7		
Station	8-21	8-30	9-13		10-11	10-25	11-8	11- 22	12-5	12-20
T	8	45	40	35	16	51	02	46	85	46
2	1780	1295	1248	1202	1700	2230	2680	3070	2530	2180
m	71	24	20	15	63	14	58	56	43	20
4	61	17	12	08	53	01	43	78	29	97
S	36	97	94	89	28	66	96	36	16	64
9	18	2	-	ŝ	P	39	62	07	63	40
7	30	4	S	T	48	51	55	67	58	49
8	Ś	0	2	ω	9	σ	ē	0	2	7
6	4	2		4	Ō	Õ	7	86	ñ	22
	90	Ο	Ē	ŝ	2	σ	Ц	4	22	4
	\sim	9	7	σ	4	4	σ	35	9	T
	σ	ഹ	S	4	9	ω	ω	12	Ч	σ
	\sim	H	Г	9	2	S	Ч	e	ŝ	Ч
14	7	Э	2	Ч	ω	N	0	06	σ	7
	đ	S	c	e	S	S	9	0	6	7
	0	0	ω	δ	4	Ó	S	ω	Ч	Ō
	Ó	ω	ω	9	0	2	N	0	ω	e
	S	ω	ω	4	σ	Ч	Ē	Ó	Ô	0
	m	7	σ	2	7	σ	σ	N	7	7
	m	7	σ	2	9	Ó,	σ	0	4	S
	\mathbf{N}	2	σ	Ч	9	σ	σ	Ō,	7	S
	S	7	9	c	Ē	Ч	m	9	4	σ
	Ч	9	7	0	e	Ó	9	Ы	4	m
	S	S	-	9	9	7	Ū.	m	'n	Õ
	N	0	9	ŝ	δ	σ	4	Ñ	4	9
	0	ω	S	Ч	9	Ó	0	ŝ	δ	ē
	4	m	0	88	ŝ	Ñ	S	4	Ó	9
		82	65	61	6		6	ñ	2	
		53	46	44				9	7	
		21	19	19				ŝ		

APPENDIX H

DISSOLVED OXYGEN, ALKALINITY, pH AND TEMPERATURE DATA AT THE MOUTH OF THE GRAND RIVER

Date (1968)	Time	Di ssolved Oxygen mg/l	Tot al Alkalinity as CaCO ₃ mg/l	Tempera ture F	– PH
C 25	1200		102 0		
6-25	1200	11.8	183.0	64	7.4
7-2	1900	6.2	150.0	66	7.2
7-11	1 500	7.0	216.0	74	7.7
7-16	1730	9.8	275.0	81	8.4
7-24	1330	7.7	306.0	77	8.0
7-30	1000	12.5	261.0	72	8.2
8-7	1630	13.7	318.0	80	8.5
8-14	1230	11.8	230.0	75	8.5
8-19	1715	9.6	235.0	79	8.5
8-26	1730	6.6	226.0	72	7.9
9-5	1230	8.7	252.0	72	8.2
9-10	1000	6.7	225.0	67	8.0
9-17	1330	9.0	187.0	71	8.0
10-5	122 0	9.7	188.0	5 9	8.0
10-19	1120	8.9	221.0	62	8.2

APPENDIX I

LAND USE APPORTIONMENT IN THE GRAND RIVER WATERSHED

Attended to a subscript A

Basin	Designation		Area, mi
Grand River	Agriculture		3102
	Urban		586
	Forested		1113
	"Other"		762
		Total	5563
R ed Ce dar River	Agriculture		268.1
	Urban		68.3
	Forested		84.9
	"Other"		52.1
		Total	473.4
Looking Glass River	Agriculture		182.7
	Urban		12.3
	Forested		63.8
	"Other"		28.6
		Total	287.4
Maple River	Agriculture		795.0
	Urban		31.2
	Forested		105.8
	"Other"		42.3
		Total	974.3
Flat River	Agriculture		312.0
	Urban		31.2
	Forested		143.0
	"Other"		93.0
		Total	579.2
Thermorpho Divor	Nari au Itura		504.1
Thorn apple River	Agriculture Urb a n		60.3
	Forested		174.7
	"Other"		110.4
	U MICI		
		Total	849.5

APPENDIX J

ESTIMATED MONTHLY AVERAGE TOTAL NITROGEN DISCHARGE FROM WASTEWATER TREATMENT PLANTS IN THE GRAND RIVER BASIN DURING CALENDAR YEAR 1969

				۷.	Monthlv Av	Average Daily	ilv Discha	Discharge, lbs/day	'day			
Ayency	Jan.	Feb.	Mar.	Apr.		June	July	Aug.	Sept.	Oct.	Nov.	Dec.
	L 61	0 Q V	0 0 4	0	1 67	5 95	6 77		0 66	0 22	0 66	0 1 6
	10.4	10.4		7.12	4 • 0 7	7 0 0 1			6.0T	10.4 1	10.1 10.1	13.3
Delni Twp.	119.0	111.0	89.9	180.1	151.0	140.0	154.U		16.8	(1. 5	4.6/	68.8
Delta Twp.	397.0	336.0	293.0	508.0	524.0	476.0	432.0		352.0	318.0	357.0	313.0
East Lansing	1112.0	1010.0	0.806	1305.0	1294.0	1055.0	1112.0		919.0	950.0	1010.0	829.0
Eaton Rapids	214.0	177.0	116.0	278.0	220.0	167.0	246.0		138.0	127.0	143.0	122.0
Fowler	48.8	46.5	42.0	62.4	46.5	1.65	48.8		73.8	69.2	40.8	44.2
Grand Haven	614.0	553.0	598.0	641.0	661.0	630.0	715.0	673.0	641.0	686.0	712.0	661.0
Grand Ledge	148.0	135.0		191.0	207.0	172.0	164.0		119.0	111.0	0.06	76.8
Grand Rapids	2350.0	5845.0		5879.0	5527.0	5153.0	5277.0		4040.0	4710.0	4415.0	3632.0
>	40.0	132.0		120.0	115.0	0.111	115.0		121.0	113.0	115.0	116.0
Grant	5.7	5.7	5.7	6.8	6.8	6.8	6.8		9.1	9.1	7.9	7.9
Greenville	270.0	278.0	ŝ	307.0	310.0	318.0	368.0		289.0	320.0	299.0	278.0
Hastings	122.0	114.0	103.0	122.0	124.0	130.0	140.0	•	124.0	122.0	110.0	116.0
Ionia	291.0	286.0	۵	352.0	350.0	249.0	246.0	241.0	225.0	254.0	241.0	217.0
Ionia												
Reformatory	132.0	132.0	2	132.0	132.0	132.0	132.0	132.0	132.0	132.0	132.0	132.0
	1428.0	1284.0	1195.0	1550.0	5173.0	1771.0	1661.0		1266.0	1280.0	1200.0	1012.0
cison	112.0	112.0	0	129.0	135.0	134.0	134.0		120.0	119.0	115.0	112.0
Y	6.0	6.0	5.7	12.0	13.2	12.4	10.2		5.7	6.8	5.7	5.7
essa	24.9	23.8	19.3	32.9	30.6	20.4	42.0	27 2	20.4	10.2	9.1	7.9
Lansing	2859.0	2766.0	2614.0	3118.0	3081.0	2996.0	2624.0		2550.0	2673.0	2581.0	2297.0
้อ	103.0	95.3	-	122.0	130.0	119.0	119.0		71.5	79.4	84.7	71.5
	45.0	42.0	• •	77.2	80.0	75.0	50.0		45.0	45.0	40.0	41.0
e	40.0	47.6	•	63.5	63.5	50.3	45.0		31.7	29.0	39.7	40.0
Portland	42.4	32.0		40.0	40.0	35.0	35.0		39.7	36.9	29.0	29.0
	103.0	108.0	~ 1	143.0	122.0	93.0	135.0		101.0	113.0	124.0	115.0
suc	112.0	95.3		137.0	133.0	93.0	108.0		80.6	84.0	80.6	76.0
	30.6	28.4	-	31.8	34.0	38.0	42.0		21.6	36.3	34.0	40.8
Lake	79.4	. 65.0	\sim	ċ8 •8	71.5	74.0	76.5		74.0	84.7	79.4	74.0
is ton	89.9	79.4		122.0	0.011	98.0	101.0		63.5	60.0	55.0	50.3
Wood1 and	4.5	2.2	2.2	5.7	3.4	3.4	2.2		2.2	3.4	3.4	3.4
Wyoming	724.0	792.0	758.0	739.0	644.0	716.0	640.0		672.0	631.0	600.0	666.0

And a second second second second

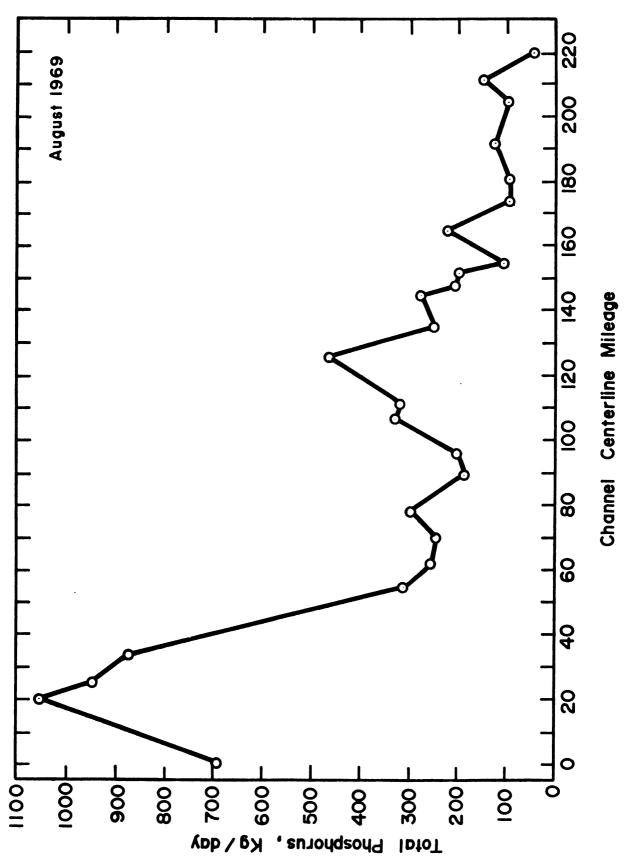
APPENDIX K

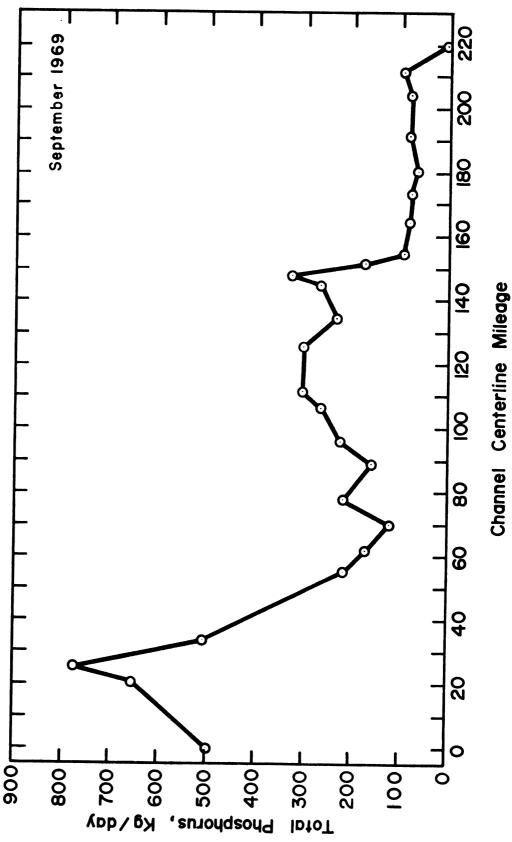
ESTIMATED MONTHLY AVERAGE TOTAL PHOSPHORUS DISCHARGE FROM WASTEWATER TREATMENT PLANTS IN THE GRAND RIVER BASIN DURING CALENDAR YEAR 1969

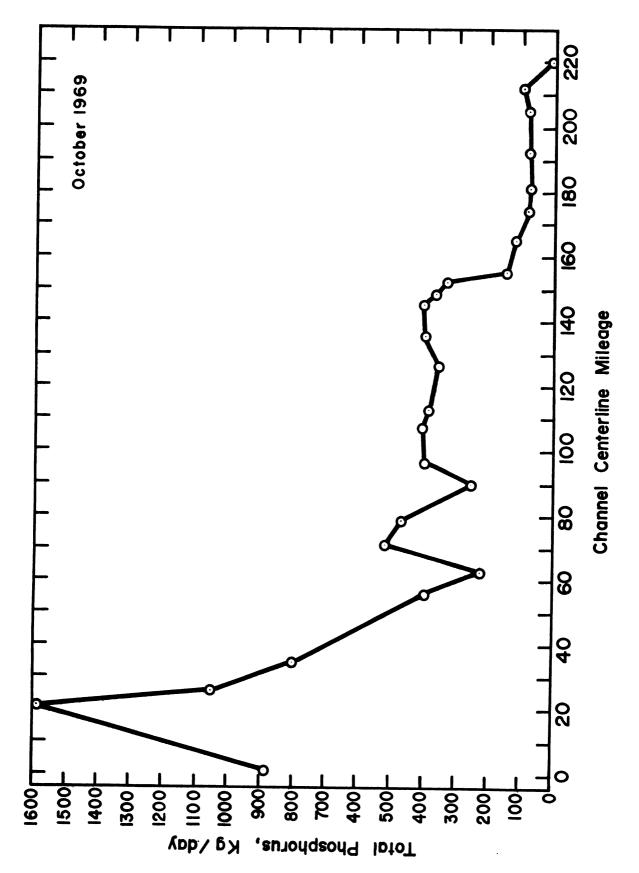
					Monthly Average		Daily Discharge		1bs/day			
Agency	Jan.	Feb.	Mar.	Apr.	Мау	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Coopersville	13.2	16.2	16.2	14.5	14.4	13.2	14.8	10.6	11.3	11.0	11.3	10.6
Pewitt	3.7	3.7	2.1	4.2	5.3	8.7	3.2	3.6	3.2	3.2	2.6	2.6
uelhi Township	23.0	22.2		36.0	30.2	28.1	30.9	20.2	15.8	4	16.3	13.9
Delta Township	79.4	67.3	58.8	101.7	104.9	95.3	86.3	73.3	\sim	\sim	71.5	62.6
East Lansing	370.6	336.8	302.7	435.0	431.0	351.0	370.0	310.0	()	-	337.0	276.0
Eaton Rapids	42.9	35.5	23.3	55.6	43.9	33.4	49.2	26.5	\sim	S	28.5	24.4
Fowler	16.2	15.5	14.2	20.8	15.5	14.4	16.2	23.7	< *	23	Ц	14.7
	123.0	0.111	120.0	128.0	129.0	128.0	143.0	135.0	(II)	7	142.0	138.0
	29.7	27.0	22.8	38.1	41.3	34.4	32.8	26.0	\sim	22	18	15.4
Grand Rapids	2115.0	1947.0		1960.0	1415.0	1718.0	1759.0	1411.0	~	0	1472.0	1211.0
Grandville	40.0	43.9	7.65	40.1	38.2	37.1	37.1	40.5	\sim	37	38.2	38.6
Grant	۲. ч	1	1.9	2.3	2.3	2.3	2.3	2.3	3.0	m	2.7	2.7
Greenville	54.0	5.		61.4	61.9	63.6	73.6	6 .2	~	4	59.8	55.5
Hastings	23.0	22.6		23.0	24.0	25.0	28.1	26.4	24.8	24.4	23.2	23.2
Ionia	58.3	57.2		70.4	81.5	49.7	49.2	48.1	S	0	48.1	43.4
Ionia												
Reformatory	26.4	26.4	•	26.4	26.	6.	9	26.4	Q	9	26.4	6.
Jackson	476.0	428.0	398.0	517.0	524.0	590.0	554.0	443.0	419.0	427.0	400.0	337.0
Jackson State												
Prison	37.4	37.4	36.0	43.1	45.0	44.5	44.5	42.3	40.0	•	•	37.4
Kent City	1.) 	 •	ي. د	3.5	m	4.Ì	3.4	2.3	1.8	•	•	1.8
Lake Odessa	8.3	7.9		11.0	2	9	14.0	đ١	Q	т.	щ.	\sim
pans ing	953.O	922.0	871 . 0	1039.0	1027.0	0.999	875 .0	874.0	850.0	•	•	766.0
Leslie	20.6	19.1	18.0	24.4	Q	m	23.8	4	4	6.	ė	4
Mason	14.5	14.0	15.1	25.7	α	œ	18.8	œ	ω	ω.	ω.	æ
ないていたいのでの	רי. כ	്. ന	7.9	12.7	2	С	8.3	6.3	5.7	٠	•	7.9
Portlari	ຕ ວ	6.3	7.0	7.0	~	~	7.0	Q	~	-	و	Ð
Rockford	20.6	21.5	23.0	28.6	\sim	ω	27.0	Ч	20.0	5.	4.	4
St. Johns	37.4	31.8	30.5	46.0	4	7	19.3	9	S.	5.	ΰ.	ഹ
Sparta	10.2	9.5	9.2	10.6	2	m	14.0	\sim	7.1	5.	÷	13.6
Spring Lake	15.9	13.3	13.8	13.8	14.3	14.8	15.3	14.7	14.7.	•	•	4
Williamston	18.0	15.9	13.3	24.4	m	σ	20.0	ŝ	12.7	5	2	9.9
wood1and	1.5	0	0.7	2.0	1.2		0.7	0.7	0	1.0	1.0	
Wyoming	241.0	264.0	253.0	246.0	215.0	239.0	213.0	214.0	224.0	•		222.0

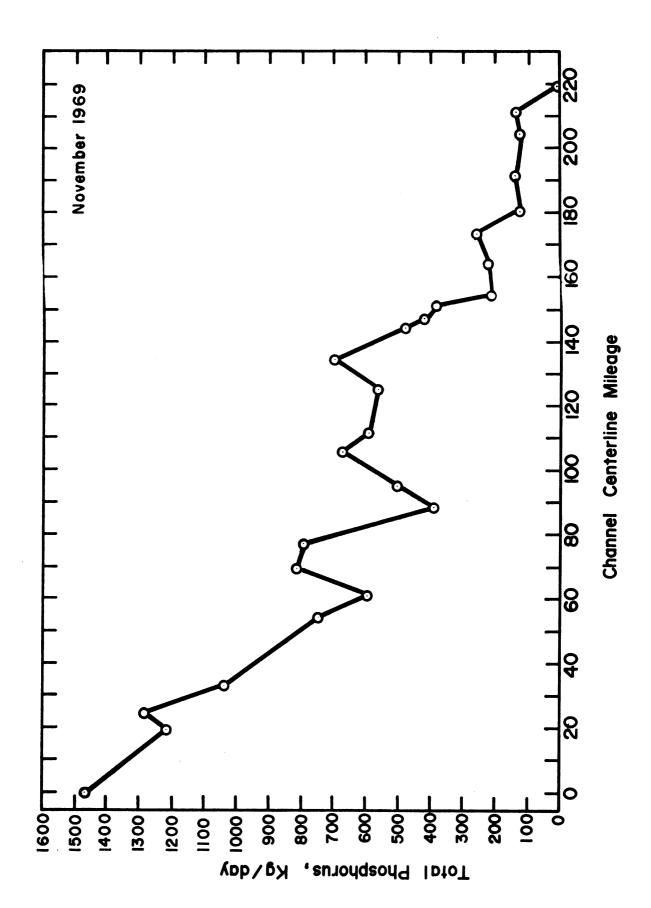
APPENDIX L

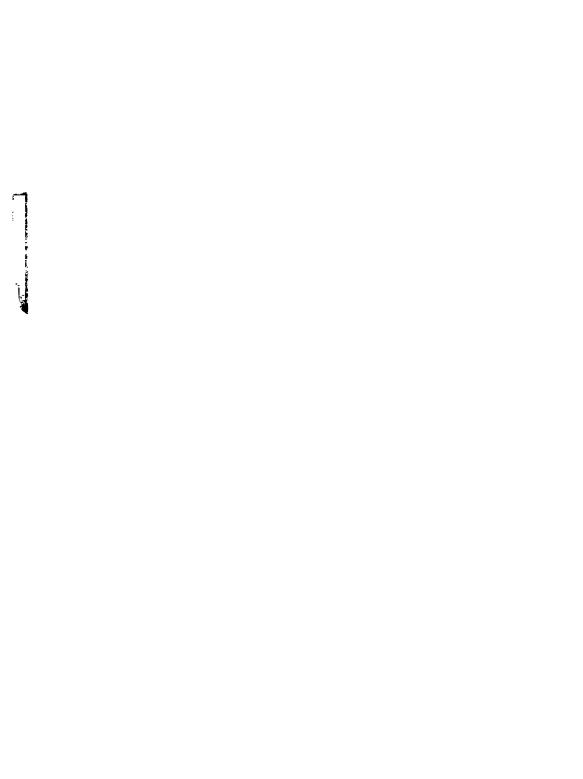
ESTIMATED MONTHLY AVERAGE DAILY TOTAL PHOSPHORUS DISCHARGE AT ALL SAMPLING STATIONS DURING THE PERIOD AUGUST, 1969 THROUGH DECEMBER, 1969

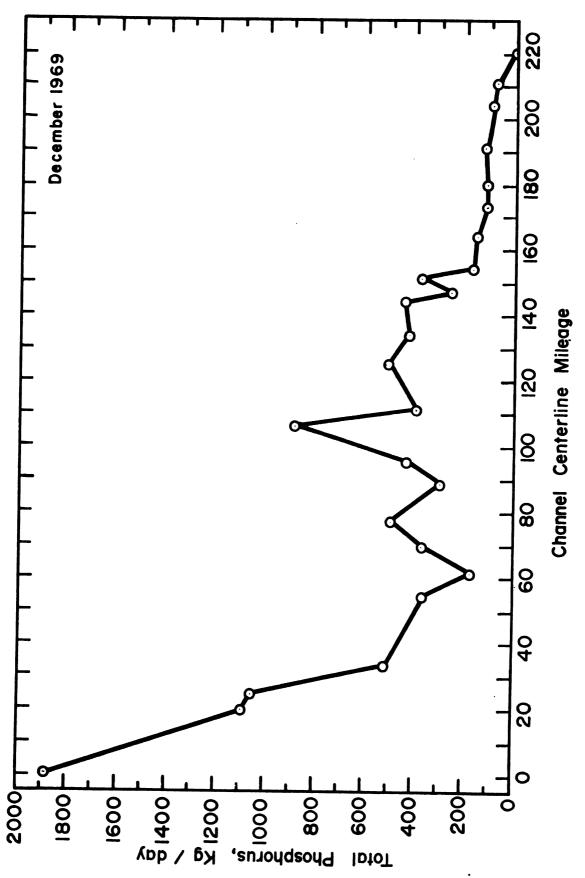












APPENDIX M

ESTIMATED MONTHLY AVERAGE DAILY NITRATE-NITROGEN DISCHARGE AT ALL SAMPLING STATIONS DURING THE PERIOD AUGUST, 1969 THROUGH DECEMBER, 1969

