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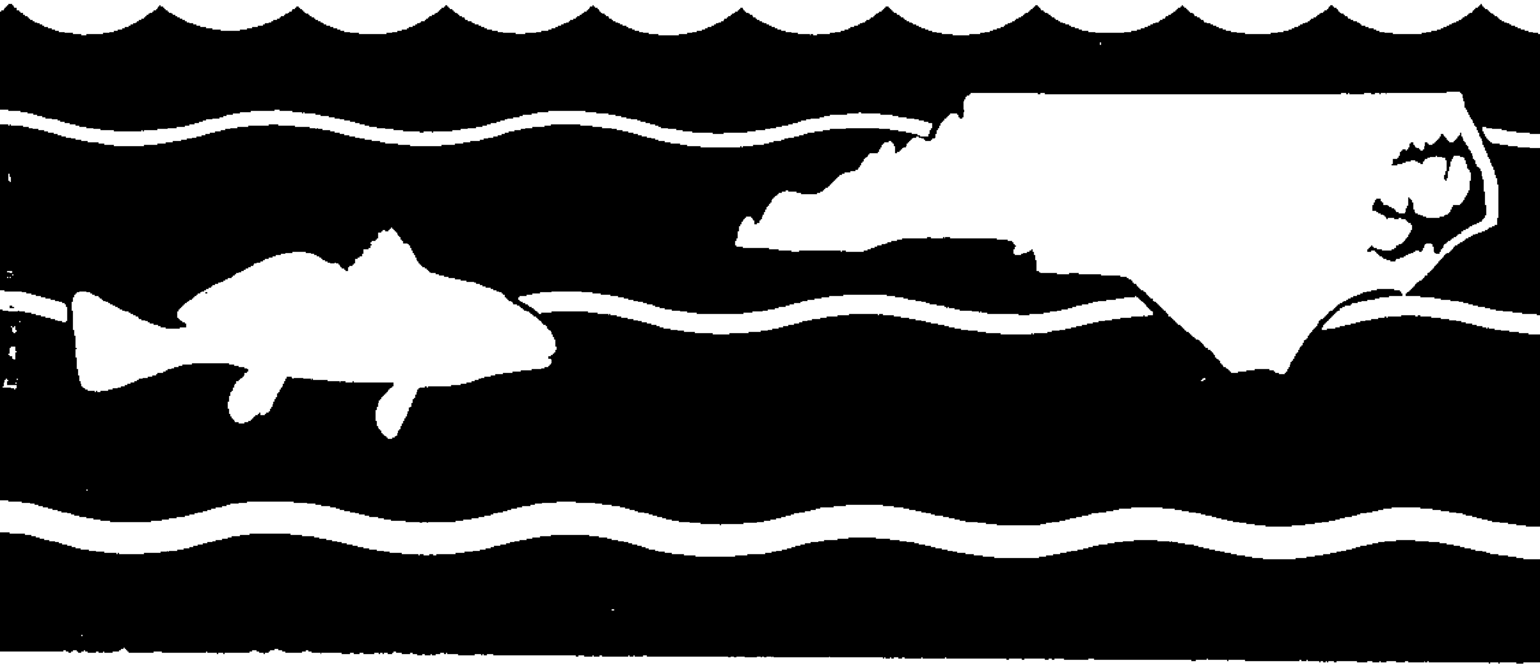

SEDIMENTARY PHOSPHORUS IN THE PAMLICO ESTUARY OF NORTH CAROLINA

by
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ABSTRACT

The amount of "available" phosphorus extracted from sediment samples along the 30 mile length of the Pamlico Estuary was observed to decrease from 1.6 mg P/gm sediment in fresh water to 0.3 mg P/gm sediment in water with a salinity of 18 ppt. The available phosphorus was measured by a modification of the HCl-H_2SO_4 (pH 1.1) acid extraction procedure. A high degree of correlation ($r = 0.99$) between oxalate-extractable iron and available phosphorus was found in the upper reach of the estuary (salinity less than 1 ppt). In the lower part of the estuary the Fe-P correlation decreased ($r = 0.86$). The decrease in the available P and in the Fe-P correlation along the length of the estuary are consistent with the suggestion that P is held to suspended sediments by some type of Fe-inorganic P complex of limited stability. Sediments entering the estuary in the freshwater inflow would lose phosphorus as they are transported through waters of increasing salinity to the mouth of the estuary.

KEY WORDS: Phosphorus, Bottom Sediments, Estuaries, Ferric Oxides

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CHAPTER I

INTRODUCTION

A. Research Aims

During the past 20 years there has been increasing interest and research concerning the role of phosphorus in the eutrophication of natural aquatic systems. Much of this research has involved the exchange of phosphorus at the sediment-water interface in lakes and the role of this exchange in regulating the concentration of phosphorus in lake waters. Several studies have investigated the amounts of phosphorus held by the sediments and the mechanisms by which the phosphorus is held.

This study examines the amount of "available" phosphorus present in the bottom sediments of the Pamlico Estuary in North Carolina during transition from a fresh water to an estuarine environment. The term "available" phosphorus refers to a fraction of the total phosphorus that is extracted using a procedure devised by Wentz and Lee (1). This fraction provides an indication of the amount of phosphorus that is biologically usable and has been related to the ability of sediments to support algal growth (2). Some of the chemical and physical factors that might influence the amount of available phosphorus held by the sediments are discussed. Finally, correlations between the amounts of available phosphorus and the amounts of acid and oxalate extractable iron in the sediments are examined and related to the changing characteristics of the overlying waters along the length of the Pamlico Estuary.

B. Regional Description

The sediments studied in this report were obtained from the Pamlico Estuary (Figure 1). This estuary flows eastward some 35 miles from Washington, N. C., to Pamlico Point, where the estuary enters the Pamlico Sound. The principal tributary to the estuary is the Tar River which flows about 200 miles southeast across the Piedmont and Coastal Plain of North Carolina. The Tar River becomes the Pamlico River at Washington, N. C. The suspended solids load in the Tar River is generally quite high, averaging 243 tons/day over a five year period (3), and consists mainly of silt and clay. The river drains approximately 4000 square miles, much of this cultivated land, and has an average flow of about 2000 cfs at Tarboro, N. C. (3). Several cities with populations up to 50,000 discharge waste effluent into the Tar River after various degrees of treatment.

The Pamlico Estuary is a shallow, wind-mixed estuary. The average depth is about 10.5 feet and the maximum width about 8 miles. Most of the lunar tide effect is damped out by the North Carolina Outer Banks. The salinity of the estuary varies from near zero at the headwaters around Washington, N. C., to around 15 ppt at the mouth. Temperature ranges from a low of 3°C in the winter to a high of 34°C in the summer (3). Dissolved oxygen is usually present at all depths, but in the summer months can drop to less than 1 mg/l in the bottom waters. These conditions are unstable, however, and are easily destroyed by wind, flow, or both (4).

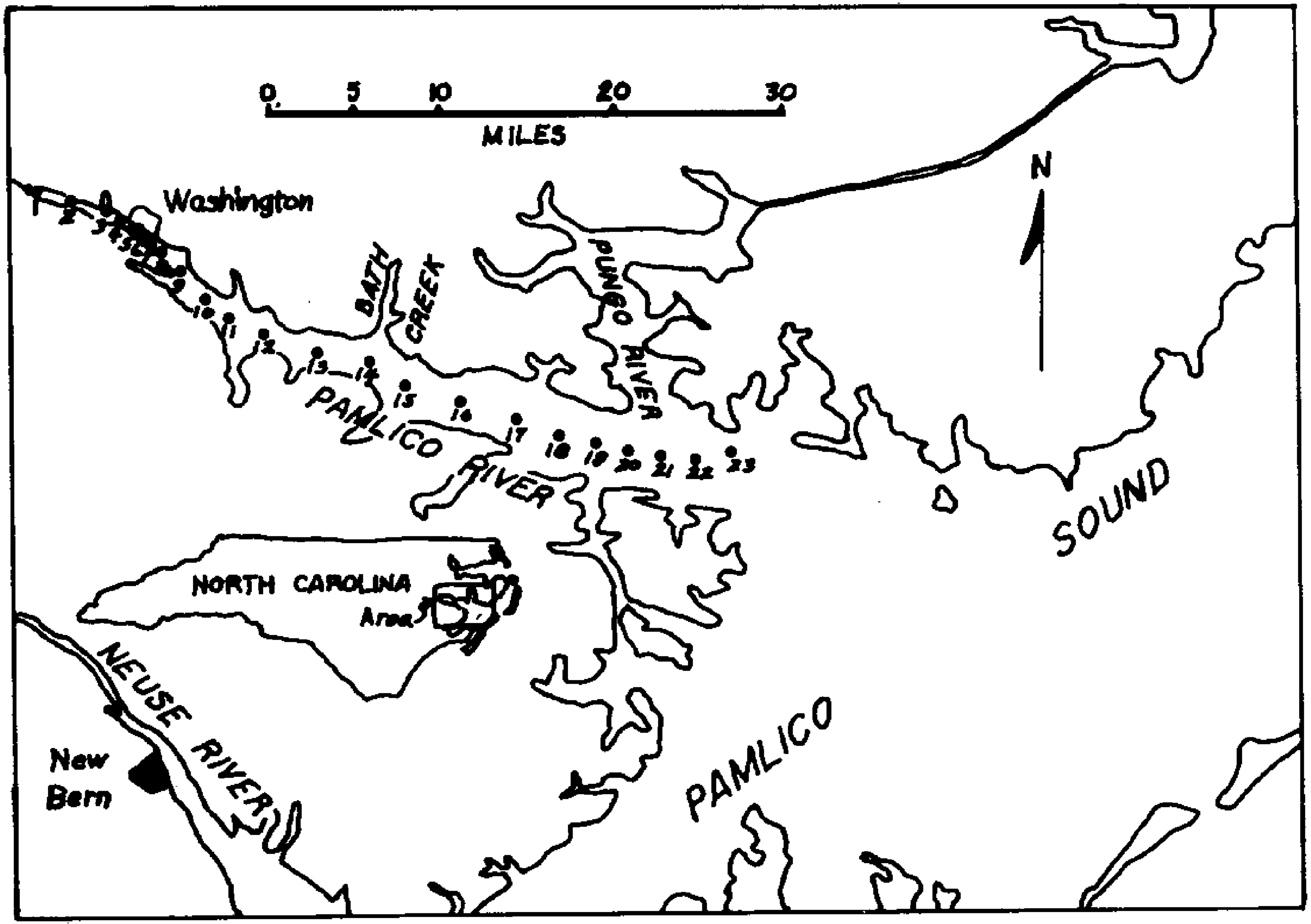

Figure 1: Map of the Pamlico Estuary. Numbered points represent sediment sample numbers and approximate locations.

The Texas Gulf Sulfur Co. began phosphate mining operations on the south side of the estuary near Aurora, N. C. in 1965. An open dry pit is used to mine the mineral fluorapatite. The waste material resulting from plant operations is pumped into a 750 acre settling basin which discharges water into the estuary. A small stream, Lee Creek, runs through the plant and into the estuary.

C. Review of Previous Work

Using field and laboratory data, Carritt and Goodgal (5) studied the sorption of phosphate by Chesapeake Bay sediments under different conditions of pH, salinity, and phosphate concentration. They found that the maximum uptake of phosphorus occurred in the pH range in which the singly charged $H_2PO_4^-$ was the predominant species (pH 2-7). Their data suggest that the uptake of phosphorus proceeds via a very rapid adsorption process and a much slower diffusion-controlled reaction. The heats of reaction measured were characteristic of van der Waals adsorption and suggested that the initial phosphorus-solid complex was of limited stability, and might be easily broken by changing environmental conditions. These authors also measured the uptake of phosphorus in sea water systems with salinities 17 and 34 ppt. They found that the uptake of phosphorus was less in sea water than in fresh water, although the reduction was not in direct proportion to the salinity. Part of the reduction was attributed to aggregation of solids at high salinity, resulting in less surface area available for adsorption. Other experiments involving the sorption of sulfate by solids indicated a competition between sulfate and phosphate during adsorption.

Pomeroy, Smith, and Grant (6) studied the exchange of phosphate between the water and sediments of Dolby Sound, Georgia. They found that the exchange was a combination of a sorption reaction and a biologically-controlled exchange. They also found that the sediments acted as a buffer on the phosphate content of the water, tending to maintain a concentration of phosphate in the water of one micromole phosphate per liter.

Olsen (7,8) studied lake sediments in the oxidized and reduced state. He demonstrated that the exchange of phosphorus is a very rapid process and that the uptake of phosphorus from the water by algae will be followed by a release of phosphorus from the sediments. He also found that the sediments in an oxidized state exchange and adsorb more phosphorus than those in a reduced state. Olsen (9) described three types of reactions by which phosphorus may become fixed in the sediments: (1) biologically, by metabolic processes in bacteria, phytoplankton and higher plants; (2) chemically, by reaction with calcium, iron, and aluminum, and (3) by sorption whereby the phosphorus is fixed to the surface of solids.

Mackereth (10,11) studied the distribution of phosphorus in three English lakes. He concluded that in the noncalcareous sediments of these lakes, phosphorus was deposited by either coprecipitation with iron and manganese, or incorporation into biological matter. Schleicher and Kuhn (12) analyzed 177 bottom sediments from southern Lake Michigan and found a fair correlation between the phosphorus and iron content of the sediments.

More recently, Shukla et al. (13) and Williams et al. (14) have studied the sorption of inorganic phosphate and the relationship between phosphate and iron in the sediments from 14 Wisconsin lakes. They found that treatment of noncalcareous sediments with oxalate virtually eliminated the ability of the sediment to sorb inorganic phosphorus. The amount of phosphate sorbed was directly related to the amount of oxalate-extractable iron in the sediment. They concluded that a Fe-inorganic P complex exists in variable amounts in lake sediments and largely accounted for variations in levels of total Fe, inorganic P, and total P. This complex is potentially capable of responding in a sensitive manner to changes in the concentration of P in lake waters and to other limnological characteristics of both the water and the sediment phases.

CHAPTER II

EXPERIMENTAL

A. Sediment Collection

Bottom sediments were collected from the middle of the Pamlico River at the 23 stations indicated in Figure 1. An Ekman dredge was used to collect all sediment samples. Samples 7 through 25 were collected on July 20-22, 1971. Samples 1 through 6 were collected on October 2, 1971. The samples were placed in polyethylene bags and about 2 ml of formaldehyde solution added to retard biological activity. The sediments were frozen using dry ice during the return to the laboratory.

B. Phosphorus Analysis

In the laboratory the sediments were thawed, mixed, and dried in an oven at 110°C for 24 hours. A modification of the procedure proposed by Wentz and Lee (1) was used to extract the available phosphorus from the sediments. Exactly 0.50 gram of the crushed sediment was weighed out and placed in 50 ml of acid extractant. The extractant had a pH of 1.10 and was prepared by adding 12 ml of concentrated hydrochloric acid and 9 ml of concentrated sulfuric acid to distilled water and diluting to 3 liters.

About 0.5 gram of activated charcoal (P free) was then added to the sediment-extractant mixture in order to remove the brownishyellowish color which interfered with the colorimetric method used to measure phosphorus. In separate tests it was found that the use of activated charcoal did not alter the amount of phosphorus or iron extracted from the sediments. The sediment-extractant mixture was stirred for 2 hours on a Lab-Line magnetic stirrer. All extractions were performed at room temperature which varied from 24° to 26°C. After extraction, the mixture was filtered immediately through a 0.45 micron membrane filter.

Experiments were conducted to determine the effect of the length of extraction and the number of extractions on the amount of available phosphorus removed from the sediments. The results of these experiments indicated that an extraction of 2 hours removed 94 percent of the amount extracted in 17 hours. In successive two-hour extractions of the same sample, 90 percent of the available phosphorus was removed by the first extraction.

The Vanadomolybdophosphoric Acid Colorimetric Method (15) was used to measure the amount of orthophosphate in the filtered extractant. Ten ml of filtered extractant were placed in a 50 ml volumetric flask, 10 ml of vanadate-molybdate reagent added, and distilled water added to make 50 ml. After allowing 20 minutes for color development, the transmittance at 420 mμ was measured with a Beckman DB Spectrophotometer. The extraction and analysis procedure was performed twice for each sediment sample.

C. Iron Analysis

Iron in the sediment samples was extracted by two methods. First, 5 ml of the filtered acid extractant described above was diluted to

50 ml with distilled water. The iron in this solution was measured with a Perkin-Elmer Atomic Absorption Spectrophotometer (16). The iron in the sediments was also extracted with an oxalate solution using a procedure similiar to that described by Saunders (17). Exactly 0.50 gram of dried sediment was placed in a 250 ml beaker and 50 ml of oxalate reagent (0.2 M ammonium oxalate/0.1 M oxalic acid) added. The mixture was stirred for an hour on a magnetic stirrer and filtered through a 0.45 micron membrane filter. Five ml of the filtered extractant were diluted to 50 ml with distilled water and the iron measured by atomic absorption.

D. Manganese Analysis

The manganese in the filtered acid extractant was measured by atomic absorption.

E. Silt and Clay Fraction Analysis

The silt and clay fraction in selected sediment samples was measured using a wet sieving analysis described by Ingram (18). Approximately 10 grams of air-dried sediment were weighed out and placed in a beaker containing 200 ml of distilled water and 10 ml of 10 percent Calgon Solution. After soaking overnight, the solution was stirred with a magnetic stirrer for 5 minutes at high speed. The solution was then wet sieved through a 63 micron sieve (U.S. No 230) until all fines had washed through. The material remaining on the sieve was collected, dried, and weighed. The percent silt and clay was calculated by dividing the total sample weight into the weight of material that passed through the sieve.

CHAPTER III

RESULTS & DISCUSSION

The general characteristics of the sediment samples are listed in Appendix A. The majority of the samples were classified as mud and were composed predominately of clay and silt. The exceptions, samples 1A, 4, 5, 6, 7, 19, and 23, contained a mixture of medium sand and mud.

A. Available Phosphorus in the Sediments

The amount of available phosphorus (in milligrams P per gram of dried sediment) in each sample is presented in Appendix B. The phosphorus content of the sediments varied from a high of 1.61 mg P/gm sed. at station 9 to a low of 0.02 mg P/gm sed. at station 23. A part of the observed variation in phosphorus content was due to the composition of the sediments. Samples containing a substantial amount of quartz contained less phosphorus than the sediments composed of clay and silt. This is consistent with the available surface and with measurements of the sorption capacities of sand and clay made by Stumm and Leckie (19) in which silica adsorbed very little phosphorus and kaolinite adsorbed phosphorus very strongly.

In Figure 2 the phosphorus content of the sediments is plotted as a function of distance downstream from station 1. Station 1 corresponds to the location at which sample 1 was taken. This figure

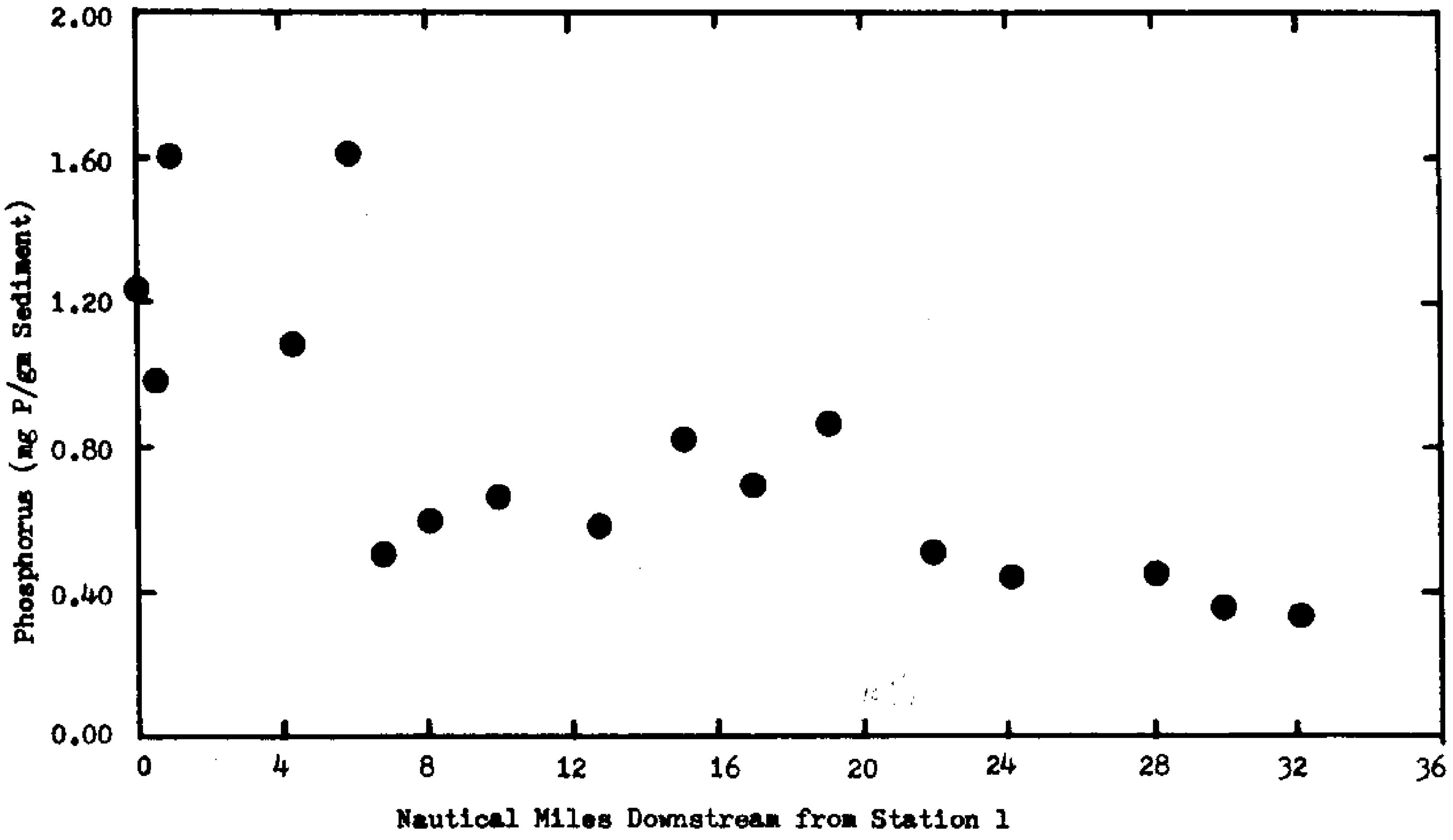

Figure 2: The amount of available phosphorus in the sediments as a function of the distance downstream.

includes only those samples composed predominantly of silt and clay (clay and silt fraction greater than 0.90). Beginning at mile 7, there is a sharp drop in the phosphorus content of the sediments. An increase in the sand content of the sediments could produce such an effect. In order to evaluate this possibility the amount of silt and clay in samples 3, 9, 11, 17, and 21, was measured using a wet sieving analysis. The results of this analysis were as follows:

Sample	% Silt and Clay
3	86.0
9	94.8
11	94.1
14	94.0
17	98.2
21	98.0

From these values, it is apparent that the reduction in phosphorus was not due to an increase in the sand content of the sediments.

Another possible cause for the drop in phosphorus content along the length of the estuary is the increase in salinity of the overlying water. In Figure 3, the average salinity of the surface water is plotted as a function of distance downstream. The salinity values are based on bimonthly measurements made from Jan. 1969 to Dec. 1970 by Hobbie (20) and from Water Resources Data for North Carolina (21). The exact shape of the curve between mile 2 and mile 7 is not known. However, based on hydrodynamic and geomorphic considerations, it is felt that the curve as plotted is a good approximation of actual conditions. The sharp decline in phosphorus content around mile 7 coincides very closely to the increase in salinity in this area. It is

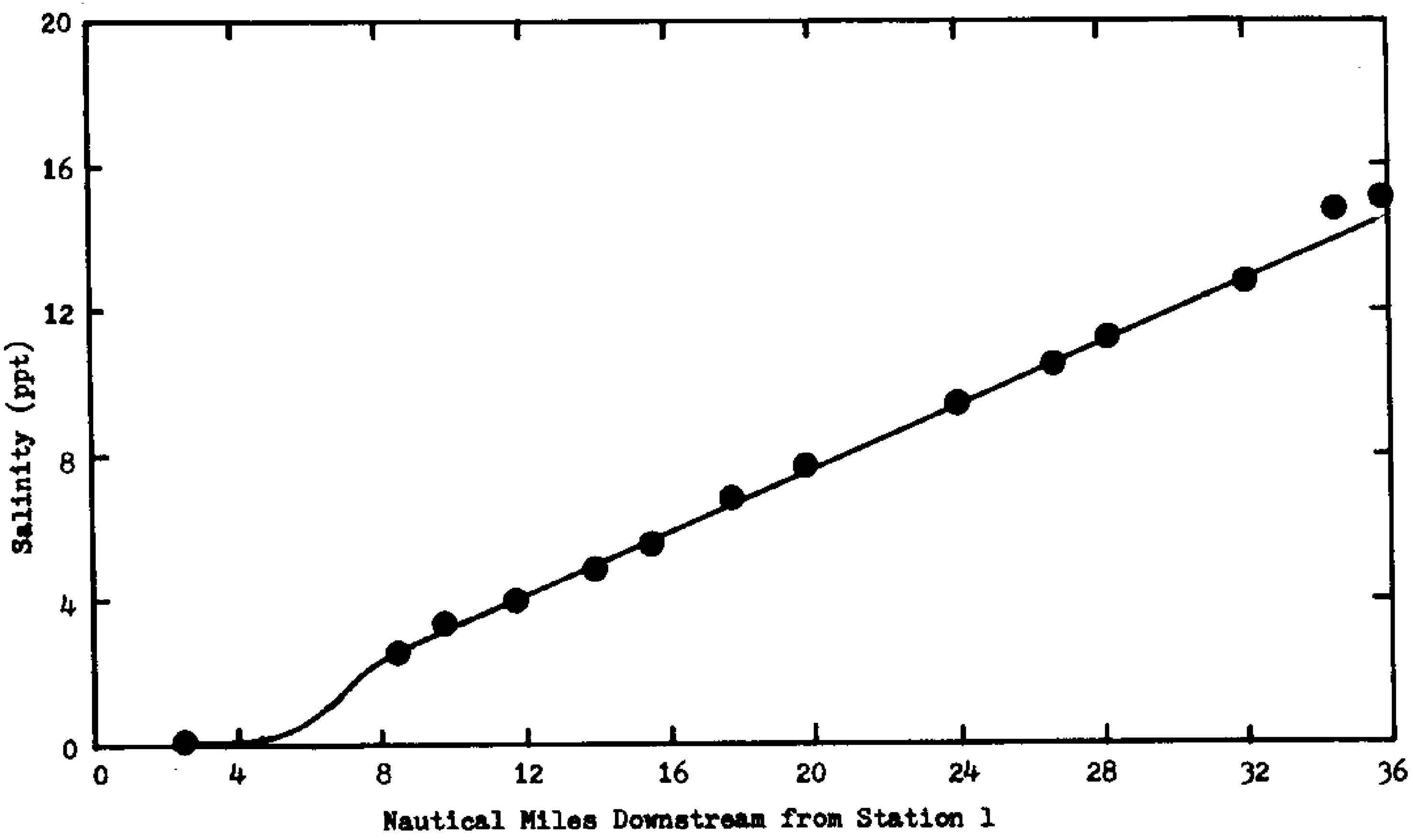

Figure 3: Salinity of the surface waters in the Pamlico Estuary as a function of distance downstream.

possible that with increasing salinity, phosphorus that is adsorbed or held in a complex may be released or displaced by competing ions such as sulfate or chloride.

From mile 8 to mile 32, there was a general decrease in the phosphorus content of the sediments from around 0.70 to 0.30 mg P/gm sed. This decrease in phosphorus may be related to the increasing salinity in the same manner as described above. It was felt that the decrease might also be related to the phosphorus content of the overlying waters. Hobbie (21), in a two year study of phosphorus concentration in the Pamlico Estuary, measured the reactive phosphorus in the surface water at various stations along the length of the estuary. Reactive phosphorus consists essentially of particulate and dissolved orthophosphate and is similiar to the fraction defined as available phosphorus. Using Hobbie's data, an average value of reactive phosphorus was calculated at each station and is plotted as a function of distance downstream in Figure 4. The shape of this curve resembles a point input of phosphorus at mile 18, the location of the Texas Gulf Sulfur mining plant. The mineral mined by Texas Gulf Sulfur is fluorapatite $\left[Ca_5\ (PO_4)_3\ F\right]$, which is dredged from a large open pit alongside the estuary. It is improbable that the dissolution of the mineral intself would result in the observed input of phosphate. However, the seepage or overflow of wash or process wastes into Lee Creek or directly into the estuary are possibilities and could account for the high input of phosphate.

A comparison of Figures 2 and 4 reveals that there is very little relation between the phosphorus content of the sediments and the concentration of phosphorus in the surface water. Dissolved inorganic

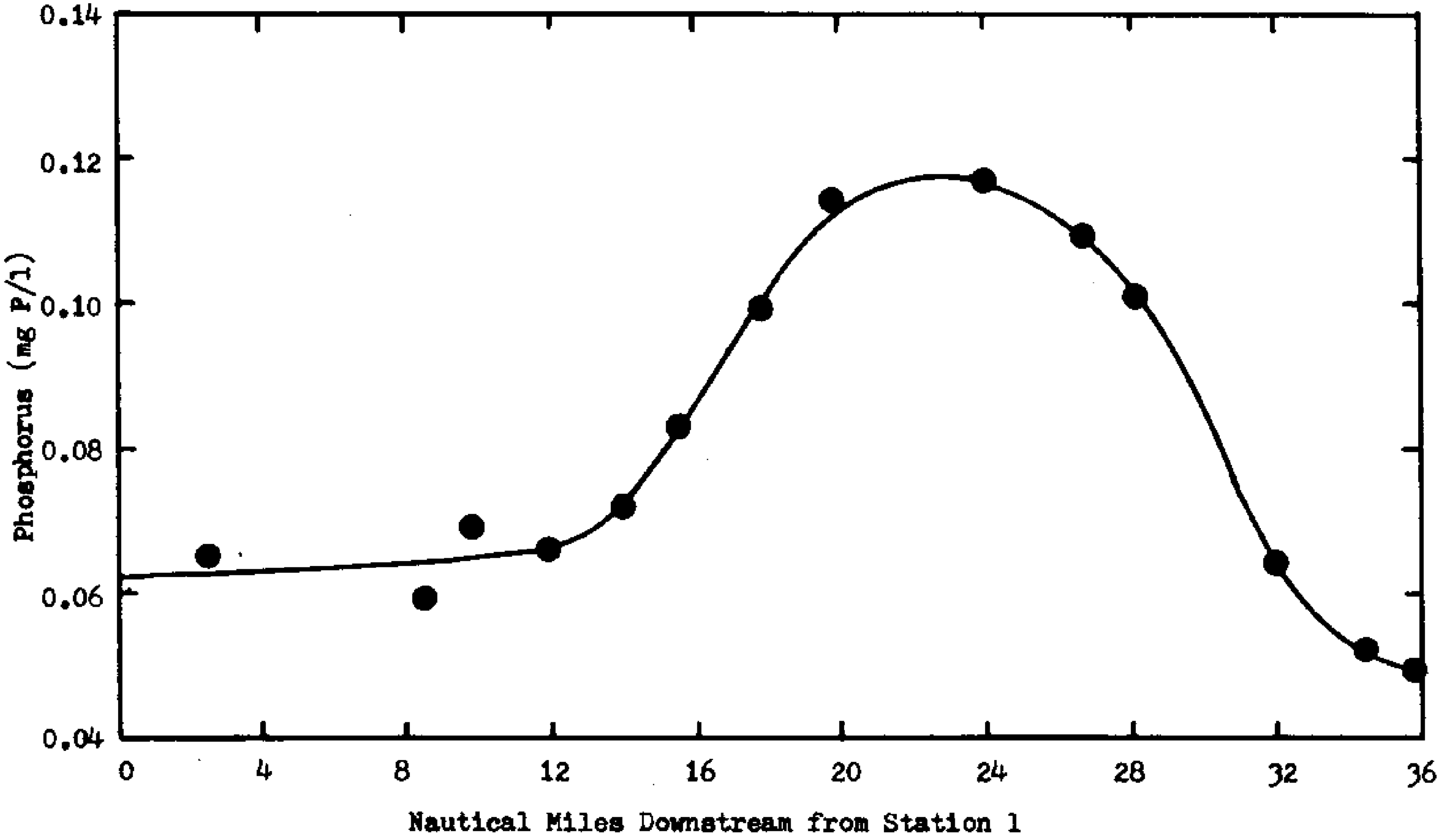

Figure 4: Concentration of reactive phosphorus in the surface waters of the Pamlico Estuary as a function of the distance downstream.

phosphorus in the bottom water might influence the phosphorus content of the sediments. No data are available on the former. However, vertical gradients of temperature and salinity in the estuary do not indicate extensive vertical stratifaction.

The gradual decrease in the phosphorus content of the sediments might also be related to the change in the clay mineral composition of the sediments along the length of the estuary. Edzwald (23) examined the clay-sized fraction of sample numbers 7, 12, 15, 18 and 22 by X-ray diffraction. The results of this analysis appear in Figure 5 and indicate a decrease in kaolinite from 60 to 30 percent and an increase in illite from 5 to 25 percent along the length of the estuary. Chlorite plus 14 Å intergrade clay average about 40 percent along the entire length of the estuary. A direct relation between the clay composition and phosphorus content of the sediments is difficult to establish since various forms of clay minerals, such as Fe-kaolinite and K-kaolinite, may have different adsorption capacities for phosphorus (24).

The phosphorus in both the water and the sediment is lowest where the estuary enters the Pamlico Sound. This is probably due to the high salinity and to dilution by water from the Pungo River and the Pamlico Sound. The Pamlico Sound is characteristically low in reactive phosphorus, averaging around 0.05 mg/l.

B. Iron in the Sediments

The amounts of iron (mg Fe/gm sed.) extracted by the acid and oxalate procedure are listed in Appendix B, and are plotted as a function of distance downstream in Figure 6. In the upper and middle

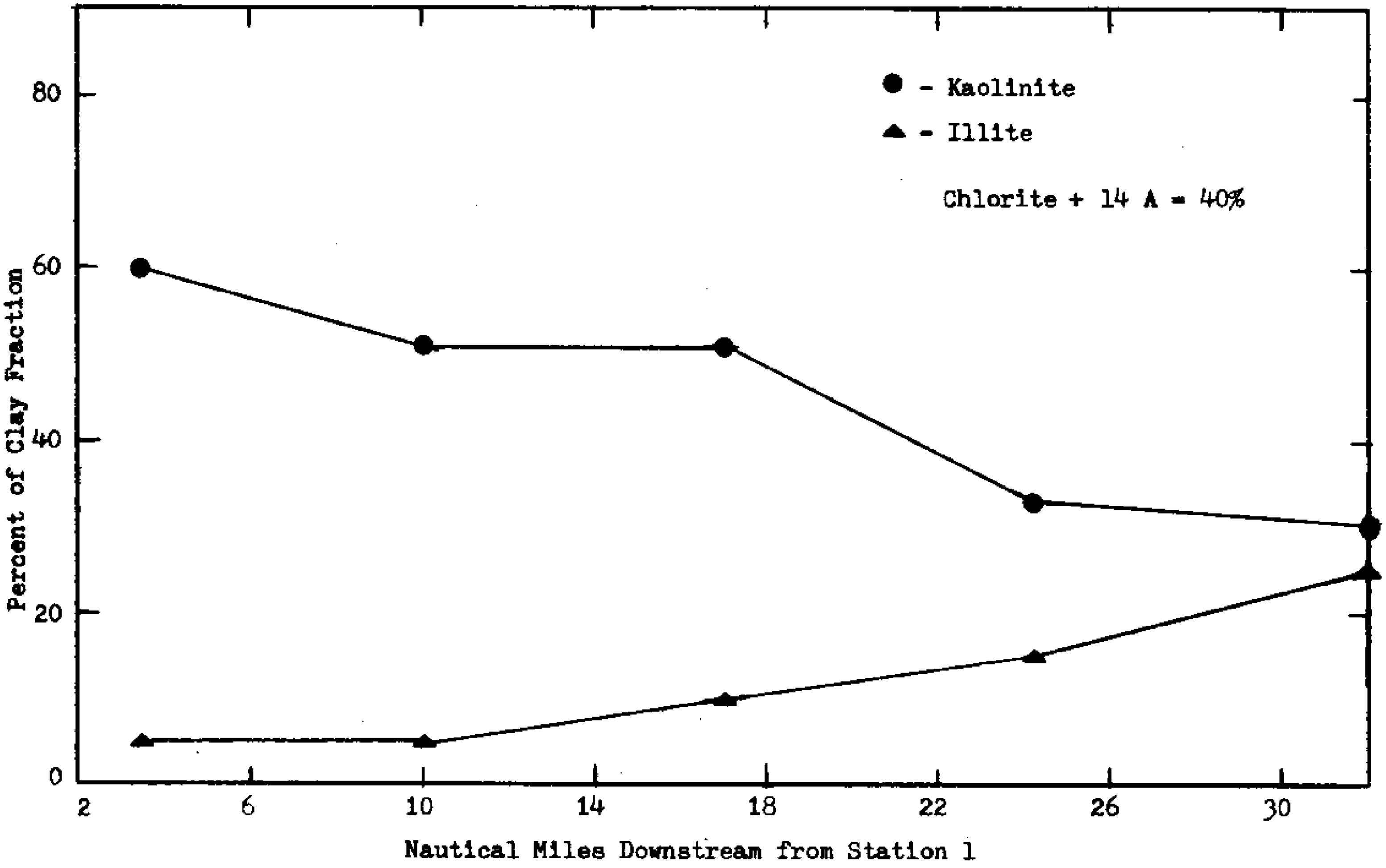

Figure 5: Mineral composition of the clay-sized fraction as a function of the distance downstream.

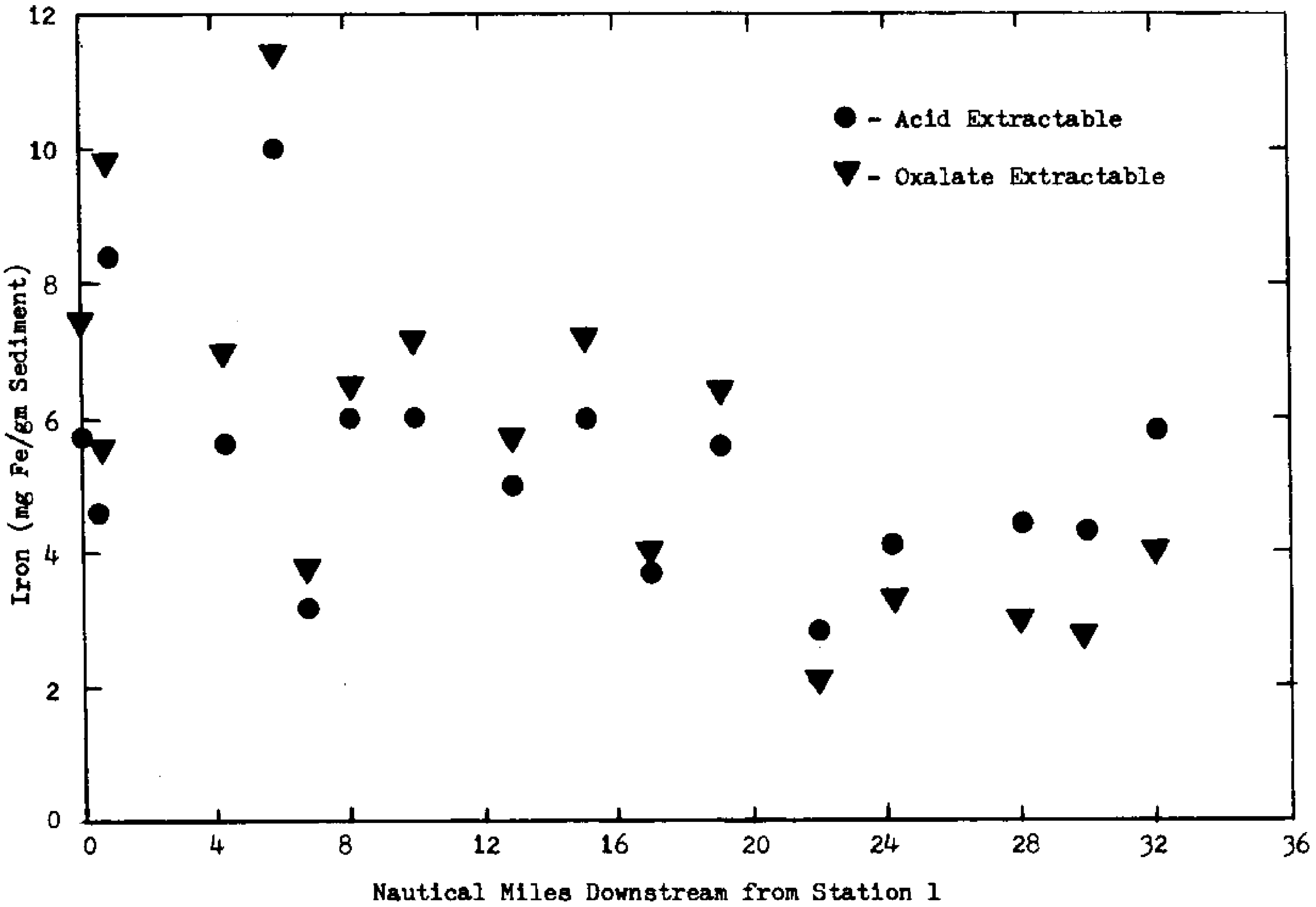

Figure 6: The amount of acid and oxalate-extractable iron in the sediments as a function of the distance downstream.

portion of the estuary, down to mile 20, there is a strong correlation (r = 0.99) between the amount of iron extracted by the acid and the amount extracted by the oxalate. The amount of iron extracted by the oxalate is generally 15-20% higher than that extracted by the acid. Studies by Schwertmann (25), McKeague and Day (26), and McKeague, Brydon, and Miles (27) have shown that oxalate extracts amorphous forms of iron almost completely and crystalline oxides only slightly. Therefore, it seems likely that both the oxalate and the acid are extracting an amorphous form of iron from the sediments and that the oxalate extracts this form of the iron slightly better than the acid.

It is possible that the difference in the acid and oxalate extraction should be larger than observed. One of the reasons for this is that the sediments were extracted with the acid for two hours, and with the oxalate for only one hour. Several samples were extracted with oxalate for two hours and the iron recovery increased by about 5%.

In the lower portion of the estuary, after mile 22, the amount of iron extracted by the acid was higher than that extracted by the oxalate. The cause of this is possibly due to the presence of some form of iron that is extracted strongly by the acid and poorly by the oxalate. This form of iron might be closely associated with the clay mineral composition of the sediments.

A factor that could possibly influence the amount of iron found in both the acid and oxalate extraction involves the sample pretreatment procedure that was used. All of the sediments were dried at 100°C prior to analysis. It is possible that some of the amorphous forms of iron were converted to crystalline forms during this procedure. These crystalline forms would be less available to extraction by acid and oxalate. To determine the effect of oven drying, sediment samples from the upper, middle and lower portions of the estuary were air-dried and the iron extracted with oxalate for one hour. The amount of iron extracted from the upper and middle samples was essentially equal to that extracted from the oven-dried sample. The amount of iron extracted from the air-dried sample from the lower portion of the estuary was about 30 percent higher than that extracted from the oven-dried sediment.

C. Correlation between Iron and Phosphorus

As mentioned previously, several investigators have found a correlation between phosphorus and iron in lake sediments. The iron and phosphorus data from this study were examined to determine if a similiar correlation might exist with estuarine sediments. First, the available phosphorus was plotted as a function of the acid-extractable iron in Figure 7 and as a function of the oxalate-extractable iron in Figure 8. A linear regression analysis of the data in Figures 7 and 8 was performed using an IBM 360/75 computer.

Next, the samples were placed into two groups. Group A included samples 1 through 9 and contained samples for which the average salinity in the overlying water was low and for which there was little change in the average phosphate concentration of the overlying water between samples. Group B consisted of samples 10 through 23 and contained samples for which the average phosphate and salinity of the overlying water were not constant between samples. The available phosphorus was plotted as a function of the acid-extractable iron for

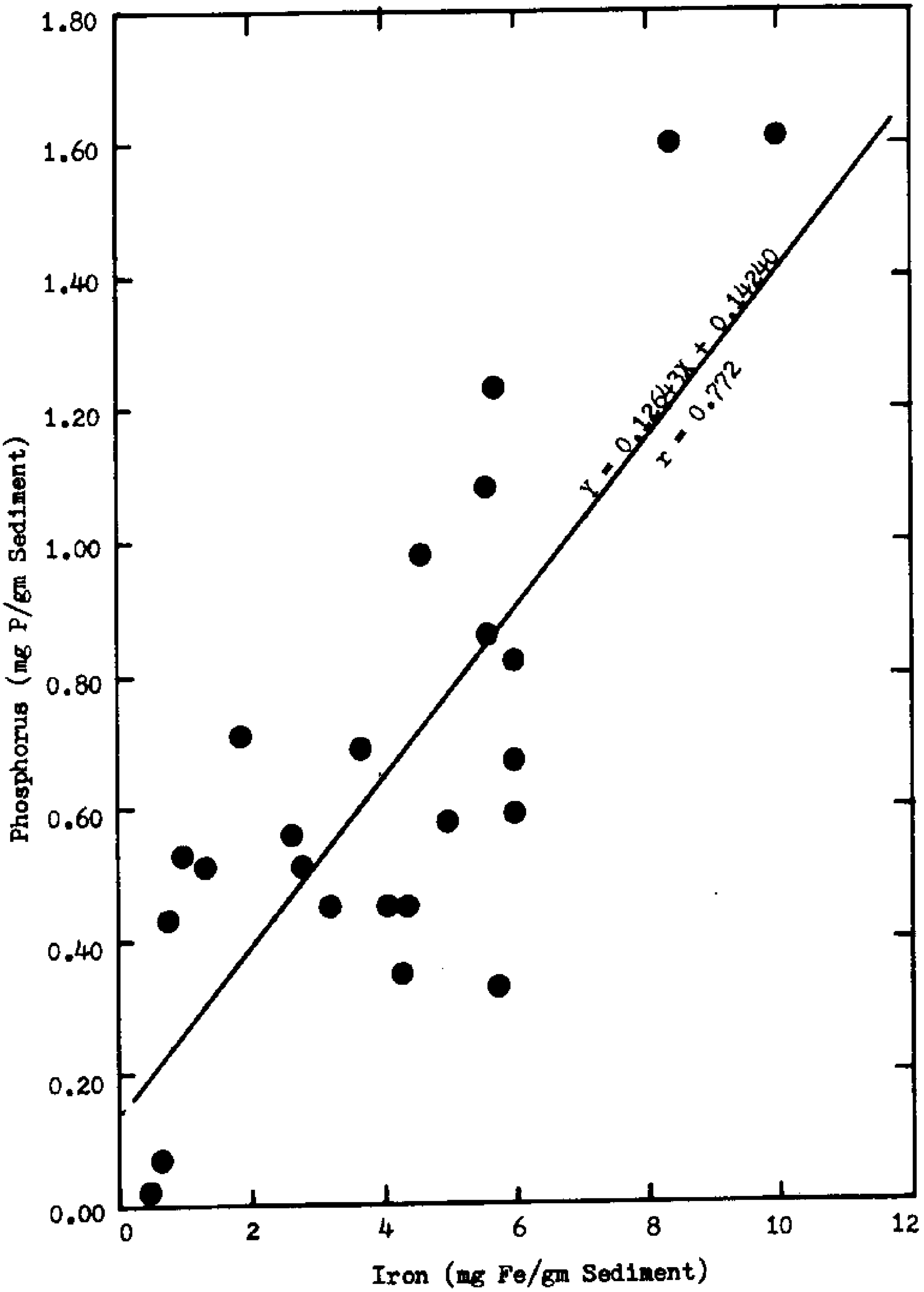

Figure 7: Correlation between the amount of available phosphorus and acid-extractable iron in the sediments.

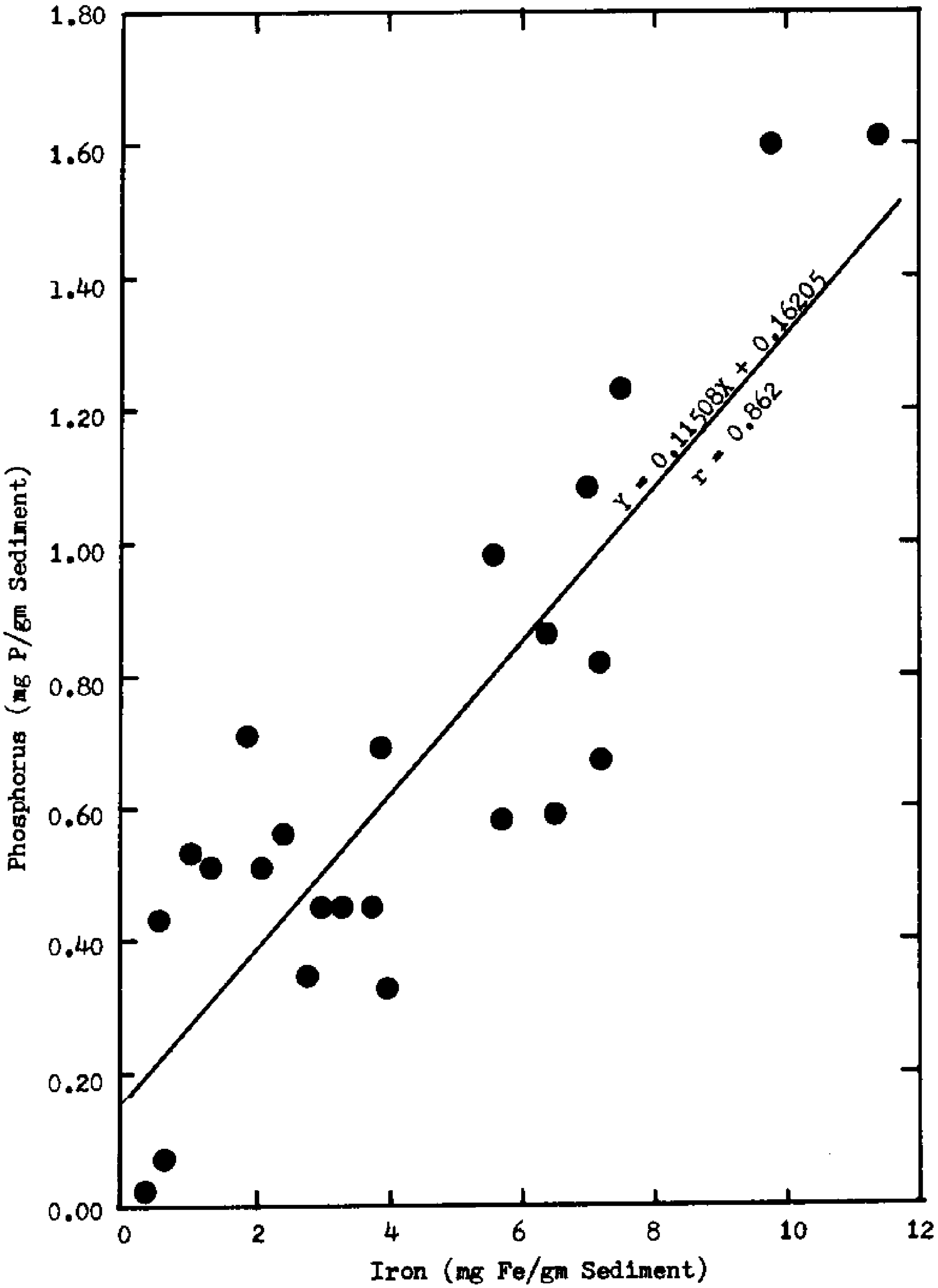

Figure 8: Correlation between the amount of available phosphorus and oxalate-extractable iron in the sediments.

group A and B samples in Figure 9 and as a function of the oxalate-extractable iron for group A and B samples in Figure 10. In each of these figures, a separate linear regression analysis was performed on the group A and B samples. Table 1 summarizes the phosphorus-iron correlation coefficients obtained for all samples and for group A and B samples.

TABLE 1

	Correlation Coefficient (r)	
	P & Acid-Extr. Fe	P & Ox-Extr. Fe
All Samples	0.772	0.862
Group A Samples	0.981	0.988
Group B Samples	0.771	0.863

As indicated in Table 1, the best correlation obtained was for the group A sediments with correlation coefficients for acid and oxalate extractable iron equal to 0.981 and 0.988 respectively. These correlation coefficients indicate that in the upper part of the estuary a substantial portion of the available phosphorus might be bound to some type of amorphous iron complex. The y intercept of the linear regression lines for the group A samples was 0.352 for acid-extractable iron and 0.369 for oxalate-extractable iron. These values perhaps represent an estimate of the amount of available phosphorus in these samples not associated with the iron complex. This phosphorus could be associated with some mineral form of phosphate such as apatite or phosphorite or might be adsorbed directly to clay particles.

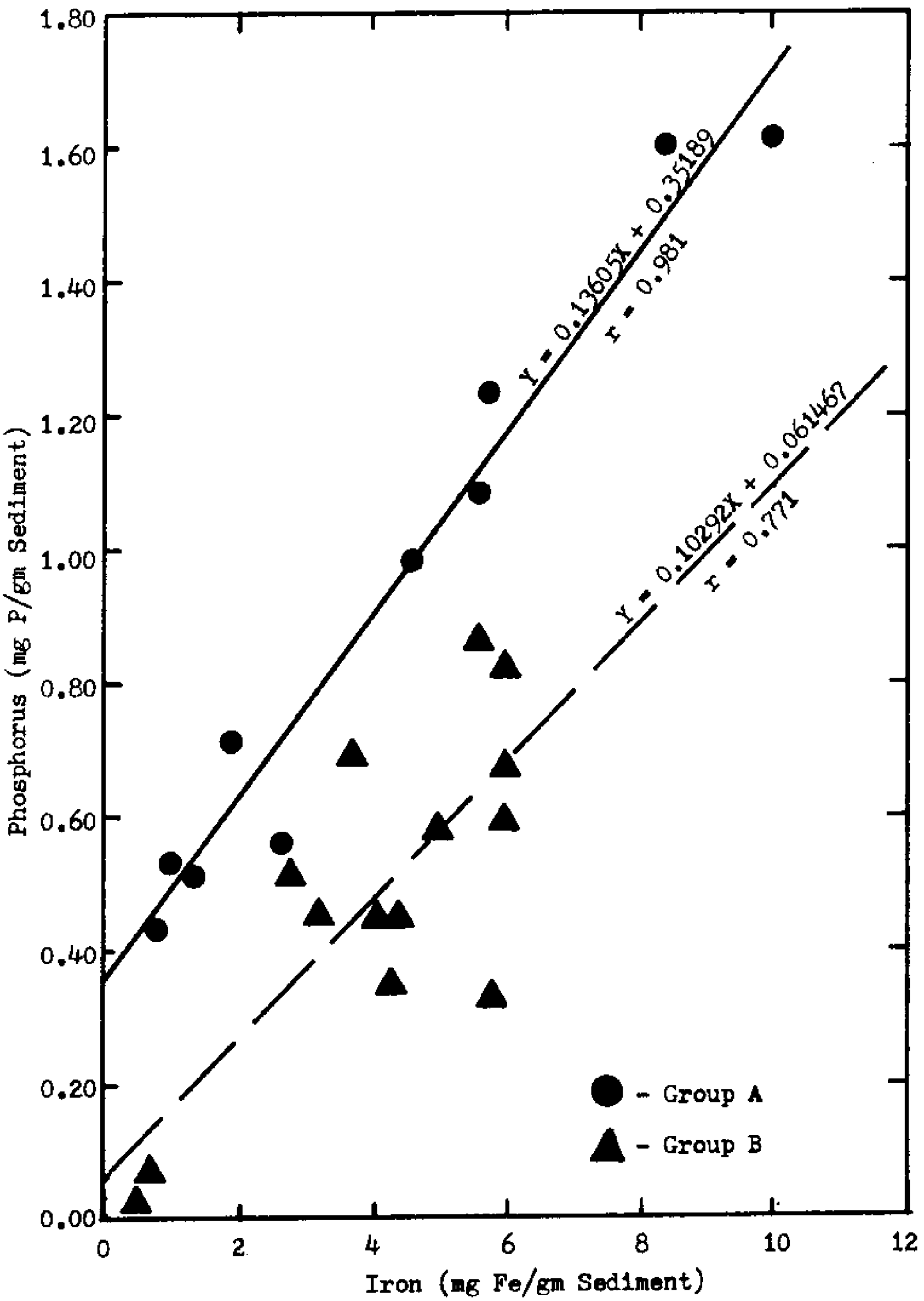

Figure 9: Correlation between the amount of available phosphorus and acid-extractable iron in group A and B sediments.

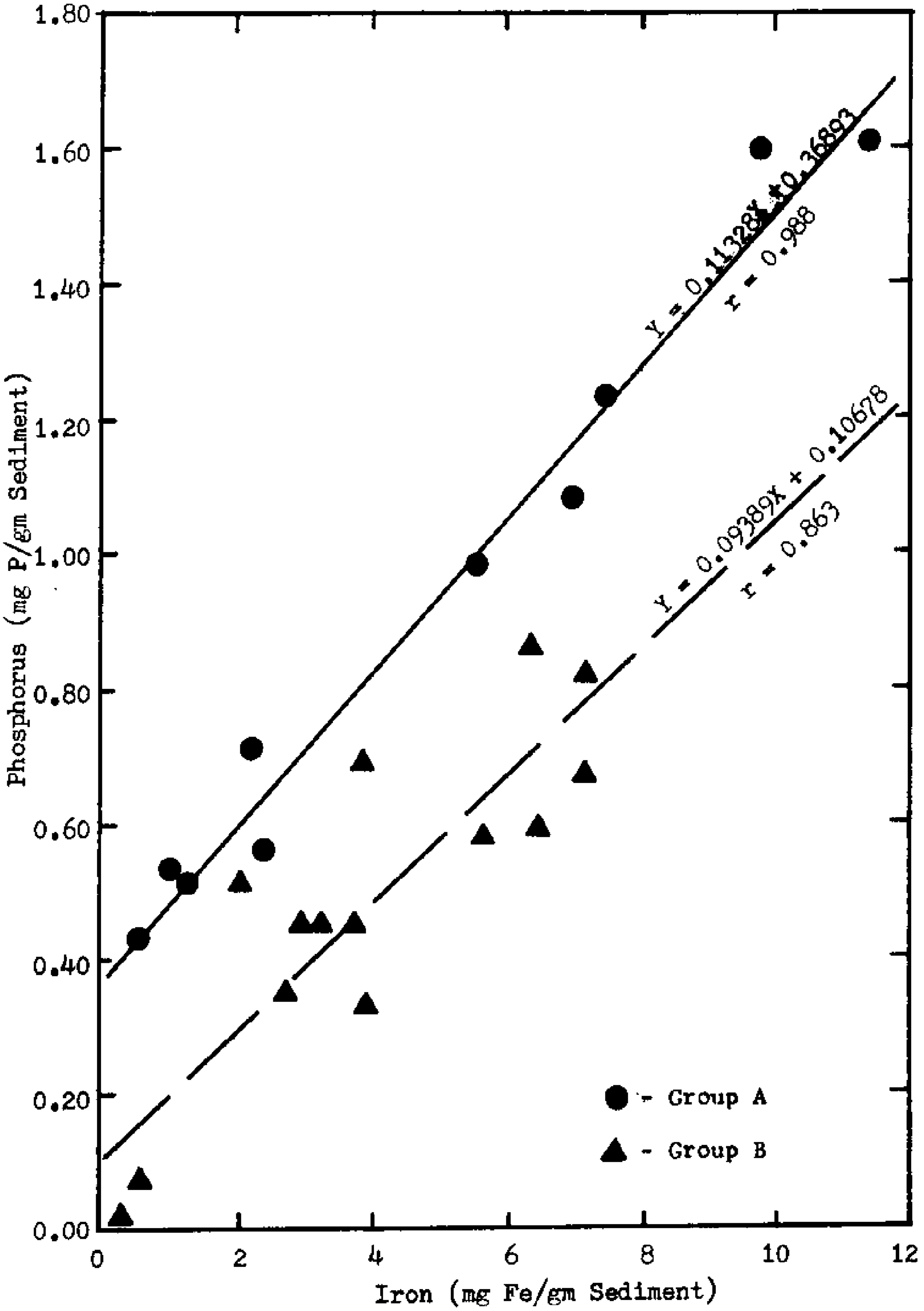

Figure 10: Correlation between the amount of available phosphorus and oxalate-extractable iron in group A and B sediments.

The correlation for the group B samples was significantly less than the group A samples with correlation coefficients for acid and oxalate-extractable iron equal to 0.771 and 0.863 respectively. The decrease in correlation is thought to be due to two major factors; the increase in salinity and the changes in the clay mineral composition of the sediments. These two factors will be discussed in more detail in the following section.

The correlation coefficients for all samples considered together, as in Figures 7 and 8, were essentially equal to the coefficients for the group B samples.

The slope of each of the linear regression lines was tested using an analysis of variance and the F distribution. All of the slopes were found to be significant at the $F_{0.95}$ level. In all cases the p value was less than 0.001, except for the group B acid-extractable iron for which it was less than 0.005.

D. Variations in the Phosphorus-Iron Ratio

Since there was a fairly good correlation between the amount of available phosphorus and the amount of oxalate-extractable iron it was felt that the ratio of these two values might be related to the changing chemical parameters in the estuary. In Figure 11 the ratio of available phosphorus (mg P/gm sed.) to oxalate-extractable iron (mg Fe/gm sed.) is plotted as a function of the distance downstream. Only those samples composed predominantly of clay and silt are plotted.

From mile 0 to mile 10 the P/Fe ratio decreases from around 0.17 to 0.10. This decrease is possibly due to the increase in salinity mentioned earlier. If the phosphorus is held by some type of iron-

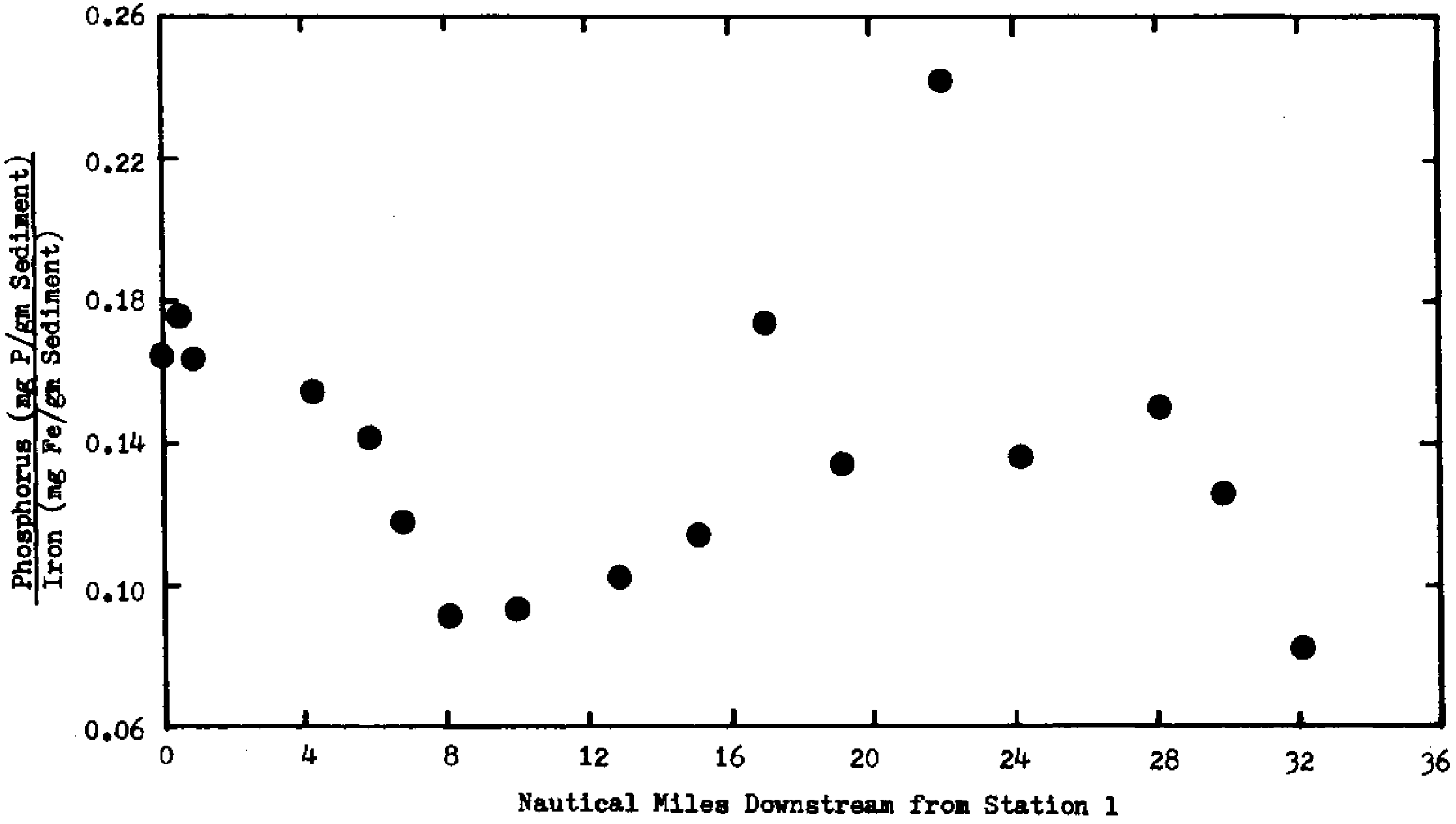

Figure 11: The ratio of available phosphorus to oxalate-extractable iron as a function of the distance downstream.

inorganic P complex of limited stability, then an increase in the ionic strength of the overlying and interstitial waters could result in displacement of the phosphorus by competing ions such as chloride or sulfate. The iron, however, if present as an amorphous hydrous oxide, would not be appreciably affected by the increase in ionic strength.

After mile 10, the P/Fe ratio begins to increase and becomes somewhat erratic throughout the remainder of the estuary. There are several possible explanations for this behavior. The increasing salinity might be having a greater effect on the correlation between phosphorus and iron. In addition, the mining operation of Texas Gulf Sulfur may have introduced small quantities of apatite into the sediments. This apatite would have been dissolved in the laboratory analysis since an acid extraction was used.

E. Manganese in the Sediments

The amounts of manganese in the acid extracts are plotted as a function of distance downriver in Figure 12. The values obtained were relatively low, the highest value of 0.41 mg Mn/gm sed. occuring near the end of the estuary at mile 32. No correlation was found between the manganese and phosphorus content of the sediments. In the upper and middle portion of the estuary there was a fair correlation between the amount of iron and manganese in the sediments. The increase in the manganese content of the sediments in the lower portion of the estuary is possibly related to changing mineral composition due to differential sedimentation. The increase could also be due to the influx of manganese rich sediments from the Pamlico Sound.

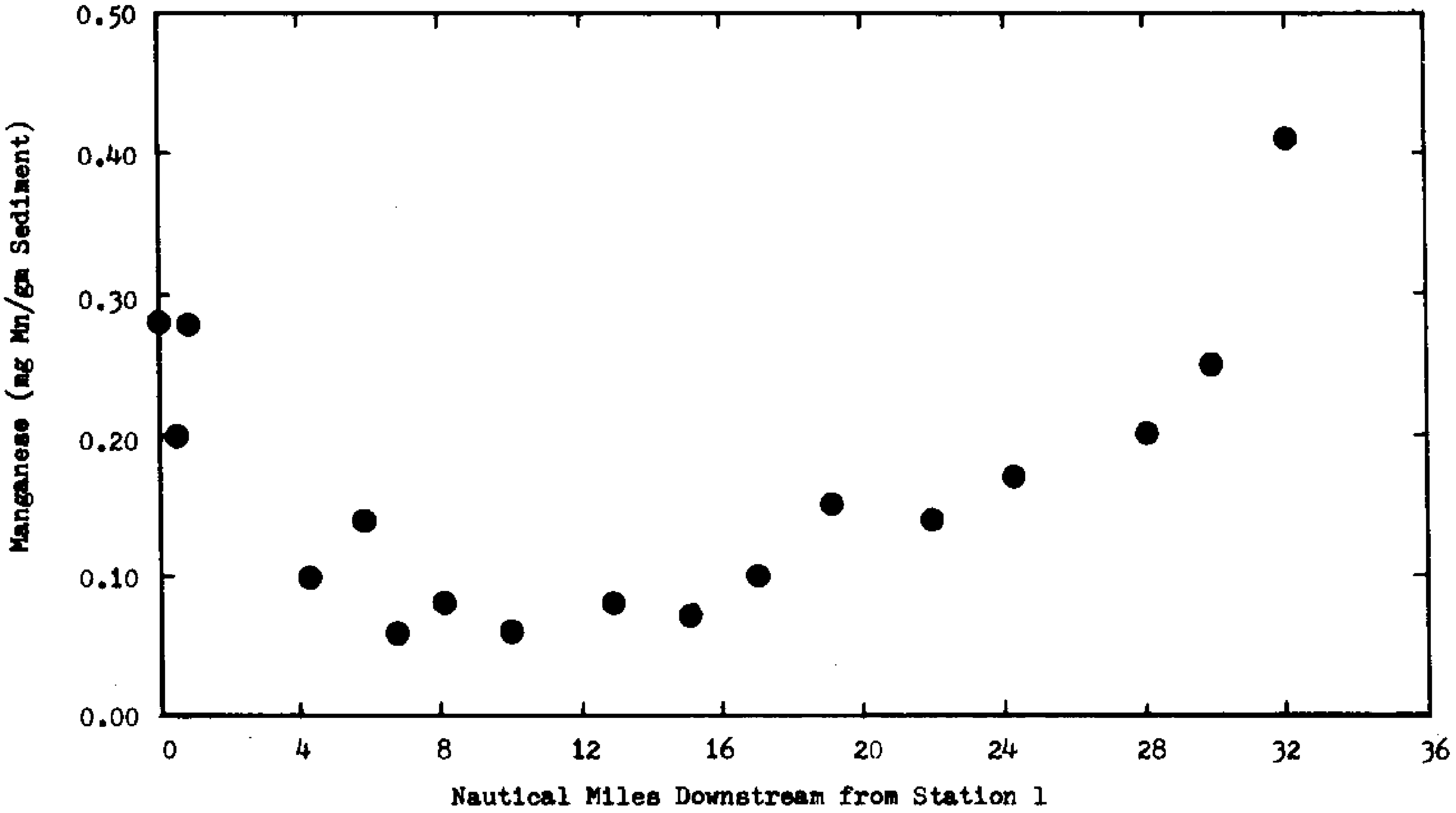

Figure 12: The amount of acid-extractable manganese in the sediments as a function of the distance downstream.

CHAPTER IV

CONCLUSION

The results obtained in this study give insight to some of the properties of phosphate in estuarine sediments. The conclusions can be summarized as follows:

(1) The sediments contain a large amount of phosphorus when compared to the phosphorus concentration in the overlying waters. On the average, one gram of dried sediment contained as much phosphorus as 10 liters of the overlying water.

(2) Under conditions of low salinity, there is strong correlation between the amount of available phosphorus and the amount of acid and oxalate-extractable iron in the sediments. The correlation decreases as the ionic strength increases.

(3) The phosphorus-iron correlation suggests the existence of an Fe-inorganic P complex similar to that proposed by Williams (14). This complex is destabilized by increasing ionic strength. Working with lake sediments, Williams found that the Fe/P atomic ratio of the complex varied between 5 and 10 for most sediments. In the Pamlico estuary the range of the Fe/P atomic ratio was somewhat lower, ranging between 3 and 7 for most of the sediments studied.

This study did not attempt to examine the transport of deposition of phosphorus. It is interesting, however, that the results are generally consistent with a transport system proposed by Carritt and Goodgal (5). In the Tar River the low salinity, neutral pH, and high turbidity could favor the formation of a phosphorus-solids sorption complex. This complex might consist of phosphate sorbed to suspended particles of clay or hydrous ferric oxide, or phosphate sorbed to clay particles coated with a hydrous ferric oxide. Clays of this type could be supplied by erosion of red clays which occur throughout Piedmont North Carolina. Phosphate is furnished by run off from land that is cultivated and fertilized, and from the effluent of sewage treatment plant. A recent committee report concluded that sediments are a prime carrier of phosphates from cropland to streams (28). The settling of these suspended solids would result in sediments with a high phosphorus content such as those observed in the upper portion of the estuary. Wang and Brabec (29) measured the particulate phosphorus and particulate iron in the suspended solids of the Illinois River. The overall averages for phosphorus and iron were 0.42 and 2.48 mg/l respectively. These values yield a P/Fe ratio of 0.17, the same as that obtained in this study for the sediments around mile 0 (Figure 11).

As the water and suspended solids move further down the estuary, there is an increase in the salinity, pH, and a decrease in stream velocity. These conditions would favor the settling of the suspended solids and the regeneration of the phosphate. Based on Figure 2, about 0.8 mg of phosphorus might be released per gram of dried sediment.

Using an average suspended solids load of 243 tons/day and an average flow of 2000 cfs, the increase in the phosphorus concentration of the estuary due to release from the suspended solids would be 0.036 mg P/l. This calculation assumes that the phosphorus content of the suspended solids is the same as that of the bottom sediments. Thus, the suspended solids that settle would contain less phosphate, the phosphate having been released to the water.

The results of this study are far from conclusive, and are probably applicable to a limited number of estuaries. The effect of organic material in the sediments may be quite significant with regard to phosphorus and iron in the water and sediments of the estuary. Additionally, there is a need for more research before any firm conclusions can be reached about phosphate interreactions in an estuary. This research might include the influence of various chemical factors of suspended solids and laboratory studies on the effects of ionic strength and competing ions on phosphate sorbed to clay and hydrous ferric oxides.

REFERENCES

1. Wentz, D.A. and Lee, G.F., "Sedimentary Phosphorus in Lake Cores - Analytical Procedure", Environ. Sci. & Tech., 3:750-754 (1969).

2. Porcella, D.B., "Biological Effects of Sediment - Water Nutrient Interchange", Jour. San. Eng. Div., Proc. Amer. Soc. Civil Eng. 96, SA4, 911 (1970).

3. North Carolina Dept. of Water and Air Resources, Water Pollution Division, "Chemical and Physical Character of Surface Waters of North Carolina", Raleigh, N.C., Bull. 1, vols. 7-11.

4. Hobbie, J.E., "Hydrography of the Pamlico River Estuary", Water Resources Research Inst. of the University of N.C., Report No. 39, Aug. 1970.

5. Carritt, D.E. and Goodgal, S., "Sorption Reactions and Some Ecological Implications", Deep-Sea Research, 1:224-243 (1954).

6. Pomeroy, L.R., Smith E.E. and Grant, C.M., "The exchange of Phosphate Between Estuarine Water and Sediments", Limnology and Oceanography, 10:167-172 (1965)

7. Olsen, S., "Phosphate Adsorption and Isotopic Exchange in Lake Muds, Experiments with P32 Preliminary Rep.", Verh. int. Ver. Limnol., 13:915-922 (1958)

8. Olsen, S., "Phosphate Equilibrium Between Reduced Sediments and Water: Laboratory Experiments with Radioactive Phosphorus", Verh. int. Ver. Limnol., 15:333-341 (1964)

9. Olsen, S., "Introduction to the Phosphate Equilibrium between Mud and Water in Lake Fures", Report from Laboratory of Radioactive Biology, University of Washington, Seattle, Wash. (1965)

10. Mackereth, F.J.H., "Chemical Investigations of Lake Sediments and Their Interpretations", Proc. Royal Soc., B161, pp. 295-309 (1965)

11. Mackereth, F.J.H., "Some Chemical Observations of Post-Glacial Lake Sediments", Phil. Trans. Royal Soc. London, B250, pp. 165-213 (1966)

12. Schleicher, J.A. and Kuhn, J.K., "Phosphorus Content in Unconsolidated Sediments from Southern Lake Michigan", Environmental Geology Notes, No. 39, Nov. 1970, Illinois State Geological Survey, Urbana, Illinois.

13. Shukla, S.S., Syers, J.K., Williams, J.D.H., Armstrong, D.E., and Harris, R.F., "Sorption of Inorganic Phosphate by Lake Sediments", Soil Sci. Soc. Amer. Proc., 35:244-249 (1971)

14. Williams, J.D.H., Syers, J.K., Shukla, S.S., Harris, R.F., and Armstrong, D.E., "Levels of Inorganic and Total Phosphorus in Lake Sediments as Related to Other Sediment Parameters", Environ. Sci. and Tech., 5:1113-1120 (1971)

15. Am. Public Health Assoc., Standard Methods for Examination of Water and Wastewater, APHA, AWWA, WPCP, pp. 527-530, 13th Ed. (1971)

16. Yuan, T.L. and Breland, H.L., "Evaluation of Atomic Adsorption Methods for Determination of Aluminum, Iron, and Silicon in Clay and Soil Extracts", Soil Sci. Soc. Amer. Proc., 33:868-872 (1969)

17. Saunders, W.M., "Phosphate Retention by New Zealand Soils and Its Relationship to Free Sesquioxides, Organic Matter, and Other Soil Properties", New Zealand J. Agr. Res., 8:30-57 (1965).

18. Ingram, R.L., Procedures in Sedimentary Petrology, R.E. Carver, Ed., John Wiley & Sons, New York 1971

19. Stumm, W. and Leckie, J.O., "Phosphate Exchange with Sediments", Presented at the 5th International Water Pollution Research Conference, San Francisco, Calif., July 1970.

20. Hobbie, J.E., N.C. State University, Raleigh, N.C., unpublished data.

21. Water Resources Data for North Carolina, Part 2, Water Quality Records, U.S. Dept. of Interior, Geological Survey, 1965-69.

22. Hobbie, J.E., "Phosphorus Concentrations in the Pamlico River Estuary of North Carolina", Water Resourses Research Institute of the University of North Carolina, Report no. 33, Mar. 1970

23. Edzwald, J.K., ""Coagulation in Estuaries", Ph. D. Thesis, in progress, School of Public Health, University of North Carolina, Chapel Hill.

24. Evans, L.T. and Russell, E.W., "The Adsorption of Humic and Fulvis Acids by Clays", J. Soil Sci., 10:119 (1959)

25. Schwertmann, V., "Die Fraktionierte Extraktion der Freien Eisenoxide in Boden, Ibre Mineralogischen Formen und Ibre Entstehungsweisen", Z. Pflanzenernahr. Dung. Bodenkunde, 84:194-204

26. McKeague, J.A. and Day, J.H., "Dithionite- and Oxalate-Estractable Fe and Al as Aids in Differentiating Various Classes of Soils", Can. J. Soil Sci., 46:13-22 (1966)

27. McKeague, J.A., Bydon, J.E., and Miles, N.M., "Differentiation of Forms of Extractable Iron and Aluminum in Soils", Soil Sci. Soc. Amer. Proc., 35:33-38 (1971)

28. Wadleigh, C.H., "Soil Science in Relation to Water Resources Development: IV Responsibility of Soil Sciences in Water Quality Improvement." Committee Report Soil Sci. Soc. Amer. Proc. 34:542 (1970)

29. Wang, W.C. and Brabec, D.J., "Nature of Turbidity in the Illinois River", Jour. AWWA, 61:460 (1969)

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Appendix A. Location and Description of Samples

Sample Number	Distance Downstream (nautical miles)	Depth (ft.)	Lithology	Date Collected
1	0.0	7	mud	10/2/71
1A	0.0	6	mud & sand	"
2	0.5	5	mud	"
3	0.9	6	mud	"
4	1.4	7	mud & sand	"
5	2.5	6	mud & sand	" "
6	3.0	6	mud & sand	"
7	3.4	5	mud & sand	7/21/71
8	4.3	7	mud	"
9	5.9	7	mud	"
10	6.8	9	mud	"
11	8.1	11	mud	"
12	10.0	10	mud	"
13	12.9	12	mud	"
14	15.1	14	mud	"

Appendix A. Location and Description of Samples

Sample Number	Distance Downstream (nautical miles)	Depth (ft.)	Lithology	Date Collected
15	17.0	13	mud	7/21/71
16	19.1	15	mud	"
17	22.0	15	mud	"
18	24.2	15	mud	"
19	25.5	17	mud & sand	"
20	28.1	16	mud	"
21	29.9	17	mud	"
22	32.1	18	mud	"
23	33.6	13	mud & sand	"

Appendix B. Phosphorus and Iron Content of the Sediments*

Sample Number	Available Phosphorus (mg P/gm Sediment)	Acid-extractable Iron (mg Fe/gm Sediment)	Oxalate-extractable Iron (mg Fe/gm Sediment)
1	1.23	5.75	7.50
1A	0.43	0.80	0.60
2	0.98	4.60	5.60
3	1.60	8.40	9.80
4	0.53	1.00	1.05
5	0.56	2.65	2.45
6	0.51	1.35	1.35
7	0.71	1.90	2.25
8	1.08	5.60	7.00
9	1.61	10.00	11.40
10	0.45	3.20	3.80
11	0.59	6.00	6.50
12	0.67	6.00	7.20

* All values are based upon weight of oven dried sediments

Appendix B. Phosphorus and Iron Content of the Sediments*

Sample Number	Available Phosphorus (mg P/gm Sediment)	Acid-extractable Iron (mg Fe/gm Sediment)	Oxalate-extractable Iron (mg Fe/gm Sediment)
13	0.58	5.00	5.70
14	0.82	6.00	7.20
15	0.69	3.70	3.90
16	0.86	5.60	6.40
17	0.51	2.80	2.10
18	0.45	4.10	3.30
19	0.07	0.70	0.65
20	0.45	4.40	3.00
21	0.35	4.30	2.80
22	0.33	5.80	4.00
23	0.02	0.50	0.35

UNIVERSITY OF NORTH CAROLINA SEA GRANT PUBLICATIONS*

UNC-SG-72-01
Lyman, John and William Rickards. 1972. University of North Carolina Sea Grant Program, Annual Report, 1 July 1970 - 30 June 1971.

UNC-SG-72-02
Wurfel, Seymour W., ed. 1972. Attitudes regarding a law of the sea convention to establish an international seabed regime.

UNC-SG-72-03
Upchurch, Joseph B. 1972. Sedimentary phosphorus in the Pamlico estuary of North Carolina.

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