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Relationships Between Phosphate and Other Chemicals at the Water-Substrate Interface in Lake Erie

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By
N. Wilson Britt
and
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Kenneth R. Smith
1970

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MONTHLY VARIATION IN PHOSPHATE AND RELATED CHEMICALS FOUND IN THE SEDIMENT IN THE ISLAND AREA OF LAKE ERIE, 1967-68, WITH REFERENCE TO SAMPLES COLLECTED IN 1964, 1965, AND 1966

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ABSTRACT

Samples of sediment collected in 1964, 1965, 1966, and on a monthly basis from May, 1967 through November, 1968, were analyzed for total phosphate, iron and organic carbon. Samples were collected by means of an Ekman Dredge and by means of a core technique developed by Dr. Skoch. The cores were sectioned at 2.5 cm intervals and each of the six sections was analyzed for the same factor.

Results of the analyses showed only a slight increase in phosphate since 1964. However all three factors showed a definite increase from May, 1967 through November, 1968. The two sampling methods yielded slightly different results. The sediment was found to consist of two distinct layers, with the upper 5 cm of sediment being usually higher in concentrations of materials than the lower portions.

MONTHLY VARIATION IN PHOSPHATE AND RELATED CHEMICALS FOUND IN THE SEDIMENT IN THE ISLAND AREA OF LAKE ERIE, 1967-68, WITH REFERENCE TO SAMPLES COLLECTED IN 1964, 1965, AND 1966[1]

INTRODUCTION

The normal change of a lake from oligotrophic to eutrophic proceeds slowly. However, increasing the amounts of allochthonous materials entering the water, will increase the rate of change. Perhaps the most influential of these materials are the nutrients. Many investigators (Ohle, 1953) assume that of all the nutrients, phosphorus may well be the initial factor in the development of eutrophic conditions. This assumes that all other factors are at least at minimal levels for productivity.

Studies conducted over the years have shown that the varying amounts of phosphorus entering Lake Erie are seemingly governed by season and rainfall. Thus data collected in the spring of the year should show higher amounts present than in the late summer or fall. Curl (1959) reported that in 1951 the Detroit River was carrying 0.0 to 4.6 μg/PO_4-P, with a mean of 2.6 μg/l. He further reported an average of 10.8 μg/l PO_4-P dissolved in the waters around the islands of Lake Erie during 1951-52. He reported 49.5 mg/g dry wt P in the sediment of the same area. In his 1957 paper he listed an average of 43.0 μg/l PO_4-P in Maumee Bay water and 25.0 μg/l PO_4-P in the Muamee River water, above Toledo, during 1945-46.

At the Tenth Conference on Great Lakes Research in 1966, Heinke (1967) reported that the average soluble phosphate for Lake Erie in 1965 was 35.5 µg/l PO_4. The Report on the Pollution of Lake Erie and its Tributaries (U. S. Department of Health, Education and Welfare, 1965) listed an average input of soluble phosphate for the total drainage basin of the Lake in 1962, as 174,000 lb/day, and an output at Niagara of 24,000 lb/day. The Detroit River contributed 91,000 lb/day of the input and the Maumee about 20,000. If these values are converted to tons per year the results are 32,000 tons/year entering the entire Lake and 3650 tons/year from the Maumee River alone. Curl (1959) calculated that 510 tons/year entered the western basin of the Lake of which 112 tons/year was from the Maumee River, in 1950-51. Comparison of these two reports for the Maumee River, shows an increase in phosphorus by a factor of 30 between 1950-51 and 1962. Verduin (1964) showed an increase by only a factor of 4 from 1945-46 to 1962 in Maumee Bay. He reported 105 µg/l PO_4 in Maumee Bay before 1945-46 and 450 in 1960-61. The samples from which his data were obtained, were collected during the same months each year. He attributed the increase in phosphate to the increased use of fertilizers during this period of 1946 to 1961. Curl (1957) also attributed increased phosphorus loads in the Maumee to non-urban land run-off, rather than to urban sewage.

Although it is evident that the amount of phosphorus entering the Lake since 1945 has increased, an accurate comparison of the figures is impossible. Unfortunately, only one report (U. S. Department of Health, Education and Welfare, 1965) gave any information as to the amount of phosphorus that leaves the Lake over the falls. How much the increased phosphorus load is affecting the enrichment of the Lake is difficult to determine. This is due to several factors; first, because the form of phosphorus tested for is expressed in different ways, second, because with the exception of Verduin's data, there is a probable difference as to the time of year when the samples were collected, and third, because of the instability of solubel phosphates. The latter makes necessary the preservation of the sample by some method before analysis, and that the time between collection and analysis be as brief as possible.

Changes in dissolved oxygen (DO) and pH appear to regulate the chemical equilibrium of the phosphorus cycle by precipitation of soluble forms of phosphates at high concentration of DO and the release of these forms from the sediment at low concentration of DO.

Bacteria and phytoplankton compete for the available forms of phosphorus (Reid, 1961). Hayes (1955) and Rigler (1956) have shown that the bacteria in the mud and water are quite important in converting phosphorus compounds from one form to another. As the organisms die, they settle into the sediments carrying with them their accumulations of phosphorus. The sediment bacteria probably use some of this material and release the rest into the sediment.

As mentioned earlier, pH and DO in some way regulate the chemical equilibrium of the phosphorus cycle. This often can be a purely chemical reaction, for it has been demonstrated that in the presence of DO and alkaline pH, ferrous iron will unite with phosphate to form an insoluble complex which settles into the mud. The reverse conditions of low or no DO and slightly acid pH, which frequently exist at the mud-water interface of the sediment, will break up this complex and release both ions into the overlying water. Reactions of this nature have been demonstrated that phosphorus 10 to 15 mm below the sediment surface will not respond to changes in the DO of water above the sediments. However, he pointed out that this depth may vary due to the activity of burrowing organisms.

The work of Zicker, et al. (1956) showed that the addition of calcium carbonate to water containing phosphate will precipitate a phosphate-carbonate complex. This complex is much less reactive to the minor pH changes and DO changes than the iron complex, and would ordinarily release the phosphate back into the water. It is also theoretically possible that the formation of insoluble Hydroxyapatite might remove phosphates from the cycle.

Research by Hayes, et al. (1952) demonstrated that there is a decrease in the total phosphorus content of the water during periods of ice cover. Both the zooplankton and phytoplankton populations are lower during such periods. The turbidity of Lake Erie water decreases during the winter period of ice cover (personal observation), probably because of a lack of wave action. The combination of these possibly would account for a decrease in total phosphorus such as that reported by Hayes. Hutchinson (1957) pointed out the close relationships between phosphates and iron in natural waters.

Because of the variation in reported phosphorus concentrations in Lake Erie, we planned to study the phosphates and iron occurring in the sediments. Due to the instability of the soluble form of these elements, we decided to determine the total amounts of both and to try to relate these to the dissolved oxygen and pH of the water. The total organic carbon was also determined, since the iron and phosphorus are often complexed with organic compounds (Hutchinson, 1957).

A single sampling station, in the island area of Lake Erie, was chosen for the study. The site (82°50' W 41°40' N) is located approximately 1 km south of Rattlesnake Island and 3 km west of South Bass Island. The depth of the water is 11 m and the bottom is mud-silt. Besides being in one of the deeper areas of the western basin, the site is located in one of the major bottom current pathways through which water flows to and from the central basin. The particular site was chosen first, because the area has long been used as a collecting site for bottom fauna and for the monitoring of DO (Britt, 1955a, 1955b, 1966; Wright, 1955; Britt, Skoch, and Smith, 1968), and has proven to be an excellent station to illustrate bottom fauna changes which have occurred throughout the western basin of the Lake. Second, the site is easily reached even during ice cover which facilitated a monthly pattern of sampling throughout the year. We believe that this station will indicate some of the changes in the phosphorus chemistry of the sediment which occurs throughout the western basin.

Procedures

Sediments and water samples were collected once each month for July, August, and September, 1966. The following May, 1967, a once monthly program of sampling that continued through November, 1968, was initiated. The only two exceptions were the months of November, 1967 and March, 1968, when the Lake and weather conditions prevented sample collection. A buoy was used to mark the collecting site during the summer months.

Water samples were collected at the surface and from within 20 to 30 cm of the sediment by means of a three-liter Kemmerer Water Bottle (according to the method of Britt, Skoch, and Smith, 1968). The temperature and pH of the water were recorded and the DO determined by the azide modification of the Winkler method (A.P.H.A. 1965).

Sediment samples were collected in two ways: (1) Two or more large Ekman dredge (9'' by 9'') hauls were thoroughly mixed in a large tub and two 1 quart jars were filled with sediment. This material was oven dried at 60°C in the laboratory and stored for later chemical analysis. This type of sample will be referred to as an Ekman sample. (2) Core type samples were taken by the use of plexiglas tubes (6.2 cm inside diameter and 22.2 cm long) which were used to obtain sub-samples of the sediment from a large (9'' by 9'') Ekman dredge. The texture of the sediment at the site is such that a carefully handled dredge will retrieve a sample which is relatively undisturbed and in which the interface layer of the mud is not destroyed. Each plastic tube was capped by a rubber stopper which had a 5 cm length of tygon tubing cemented through a 1.3 cm hole in the stopper. The core tube was driven by hand into the sediment contained in the dredge and the bottom of the tube was then closed by a solid rubber stopper. Cores taken in this manner show a layering of the sediment and the thickness of the interface layer. Two such core samples may be obtained from a single dredge haul. The average length of the sediment cores obtained was 17 cm.

The stoppered tubes, containing the sediment, were immediately placed in ice and were thus transported to the laboratory. The sediment column was then sliced into sections 2.5 cm thick. The sections were sliced from the top of the tube by a spatula as the fresh sediment was pushed out of the tube from the bottom. An attempt was made to first freeze the core in the tube and then to remove it and saw it into the required slices. However, more accurate sections could be made while the sediment was fresh. The sections were placed in acid-washed glass petri dishes and weighed. They were then oven dried at 60°C for at least one week and reweighed; from the weight difference the percent water content was determined. The dried material was stored in inert plastic containers for later chemical analysis.

The dried sediment samples were analyzed in replicate (two or more samples) for total phosphate (expressed as PO_4), total iron, total carbon, and total oxidizable material. The Ekman samples were assayed by the mechanical soil analysis method of Bouyoucos (1936).

Total phosphate was determined by a modification (Skoch, 1968) of the extraction method suggested by the American Association of Soap and Glycerin Producers' Special Technical Committee Report (1958) which employs a benzeneisobutanol extraction and the development of color by the stannous chloride-ammonium molybdate reaction.

The total iron in the sediment was determined by a modification (Skoch, 1968) of the Trypyridine method in Standard Methods (A.P.H.A., 1965).

Total organic carbon and total oxidizable material assays were carried out by the dichromate oxidation procedure (Maciolek, 1962). The sample was pretreated with 2% sulfuric acid, to remove carbonates before oxidation. During oxidation, evolved carbon dioxide was absorbed by a sodium hydroxide solution; this was then titrated with standard hydrochloric acid to determine the total organic carbon. The dicromate solution was titrated with standard ferrous sulfate solution to determine the amount of oxygen consumed by the sediment.

Results

Analyses of Ekman samples. Total phosphate: The results of the chemical analysis for the total phosphate (PO_4) content of the sediment are found in Figure 1. The numerical values expressed as mg/g dry wt PO_4 are listed in Table 1. Figure 1 shows a fluctuating, yet steady increase in the phosphate load, in the Ekman samples of sediment each month from May, 1968 through November, 1968. The mean phosphate during the 19 months of 1967-68 was 2.30 mg/g dry wt PO_4, which ranged from a low in August, 1968 of 1.58 mg/g dry wt PO_4 to the high of 3.14 mg/g dry wt PO_4 in May, 1968.

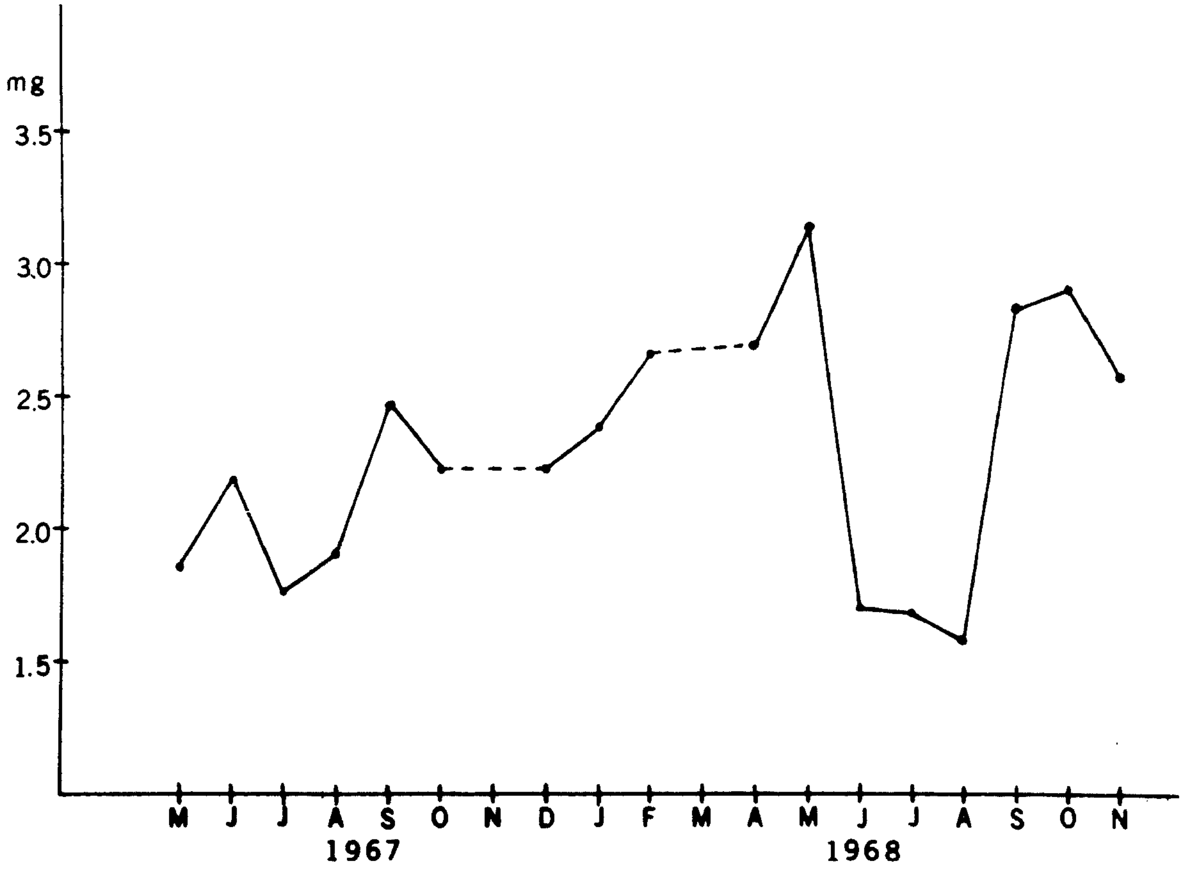

FIGURE 1. TOTAL PHOSPHATE (mg/g dwt) FROM EKMAN SAMPLES.

TABLE 1. DATA FROM THE ANALYSES OF EKMAN SAMPLES

Date	Total PO_4 mg/g	Total Fe mg/g	Total C mg/g	Oxygen Consumed mg/g	Sand %	Silt %	Fine Clay %
Aug. '64	1.94	26.62	1.30	52.6	20.0	45.6	41.6
Aug. '65	2.22	28.96	1.34	54.2	13.8	29.7	57.2
July '66	2.16	27.77	1.39	56.0	21.5	47.0	46.0
Aug. '66	1.98	27.50	1.26	51.0	32.4	58.4	37.6
Sept.'66	2.01	29.00	1.28	51.8	26.0	34.4	49.2
May '67	1.85	26.70	1.30	52.4	15.0	43.2	45.2
June '67	2.17	29.30	1.24	50.0	15.6	38.6	46.6
July '67	1.76	28.17	1.30	52.5	16.4	36.8	53.0
Aug. '67	1.89	30.93	1.38	55.6	15.5	38.5	45.9
Sept.'67	2.46	30.05	1.35	54.6	23.0	36.8	52.6
Oct. '67	2.22	28.72	1.44	58.1	19.0	37.8	49.2
Dec. '67	2.22	28.88	1.30	52.5	20.2	34.7	53.6
Jan. '68	2.38	27.15	1.42	57.4	18.2	39.1	50.7
Feb. '68	2.65	27.13	1.46	58.9	15.2	39.0	51.6
Apr. '68	2.69	27.57	1.48	59.5	17.2	44.0	55.2
May '68	3.14	30.39	1.52	61.3	23.0	34.2	55.6
June '68	1.70	32.49	6.60	56.8	11.7	24.4	57.0
July '68	1.68	31.42	5.52	56.0	12.3	23.8	54.6
Aug. '68	1.58	29.64	3.60	56.4	15.3	20.8	54.6
Sept.'68	2.83	32.49	4.20	56.9	14.5	23.6	54.1
Oct. '68	2.90	31.33	3.24	64.4	13.2	18.8	52.7
Nov. '68	2.57	32.28	3.42	64.0	15.2	19.8	53.7

Samples taken in August of the 5 years 1964 through 1968 show a variation of about 2 mg/g dry wt PO_4 with the years 1964, 1966, and 1967, being quite close (Table 1). The August, 1965, sample, although high, is below the mean concentration of the 1967-68 samples.

Total iron. Determination of the total iron (Fe) in the samples, resulted in Figure 2 with the data presented in Table 1. Figure 2 does not have the same magnitude of increase in iron load as the phosphate in Figure 1. Although the early months of the study are similar, the highest peak occurs in August of 1968. August samples from the 5 years, show an alternating rise and fall in the amounts of iron, but does indicate a slight increase. The mean of the 19 months sampling in 1967-68 is 29.69 mg/g dry wt Fe. The drop of iron occurring in December, 1967 through February, 1968 does not have an equivalent in the phosphate load. However, the period June through August in both years shows a drop in both the phosphate and iron concentrations. In general, there is no close similarity between the iron and phosphate graphs (Figures 1 and 2).

Total organic carbon and oxygen consumed. Figure 3 illustrates the relationship between oxygen consumption and the amount of organic carbon in the sediment. As in Figure 1, we see a steady increase in the amount of organic carbon from May, 1967 through November, 1968. As in the phosphate data, the peaks are similar although the higher peaks are during October, 1967, January, 1968, and May, 1968. The sharp rise in total organic carbon which occurred after May, 1968 and the variation during the following months is very similar to the fluctuation in iron

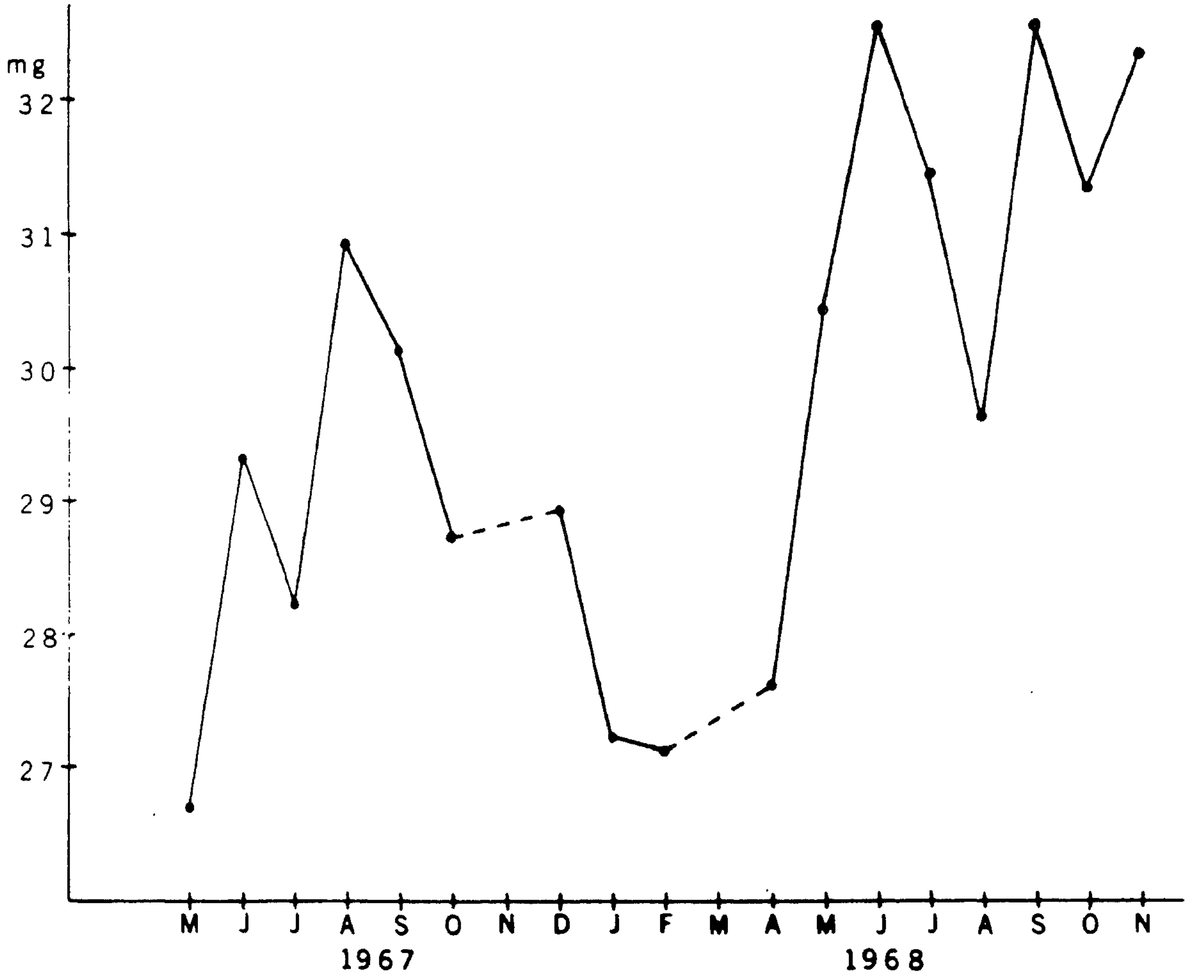

FIGURE 2. TOTAL IRON (mg/g dwt) FROM EKMAN SAMPLES.

(Figure 2). The lowered oxygen consumption during the same period reflects the lowered phosphate levels (Figure 1). Total organic carbon concentrations averaged 2.29 mg/g dry wt C, while the oxygen consumption had a mean of 57.1 mg/g dry wt O_2 for the 19 months. (Refer to Table 1 for actual data.) Note that the values for oxygen consumption, plotted in Figure 3, are reduced by a factor of 0.1.

Mechanical soils analyses. Comparison of Figure 3 with the results of the soil analyses (Figure 4) shows a close similarity in the changes from month to month during 1967-68. This is most clearly shown in the fluctuation of the silt load in the sediment. The data from July, August, and September, 1966, as well as those from August, 1964, and August, 1965, are presented in Table 1, but are not portrayed in Figure 1 because of the confusion of points. However, the variation in the silt load during the 3 months of 1966 is quite similar to the variation in iron during the same months (Figure 2). The average composition of the sediment samples from May, 1967 through November, 1968 was: silt 32.7%, sand 16.5, and fine clays 52.1.

Physical-chemical data at time of sample collection. The DO, temperature (°C), and pH recorded at the time the samples were collected are found in Table 2. The pH of the water, taken both at the surface and near the bottom, ranged from a low of 7.6 to a high of 8.4 with a mean of 8.0 during the 13 months of 1967-68. The lowest pH of 7.6 occurred in August of 1967 and the highest pH of 8.4 occurred in July, 1967, January, 1968, and February, 1968. The temperature and DO are graphed in Figure 5 to show the variation as the seasons progressed.

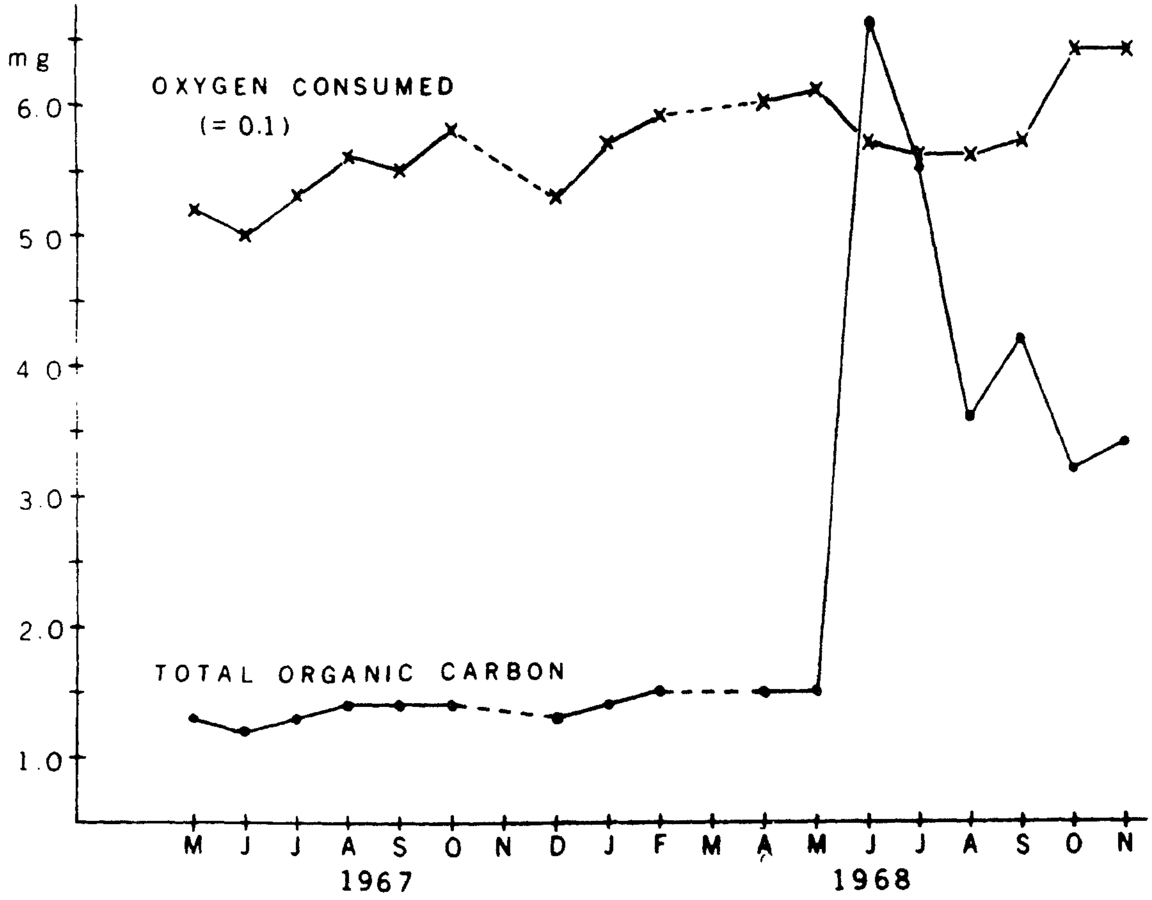

FIGURE 3. TOTAL CARBON (mg/g dwt) AND OXYGEN CONSUMED BY SEDIMENT DURING OXIDATION (mg/g dwt). AMOUNT OF OXYGEN PRESENTED IN FIGURE IS ONE-TENTH ACTUAL VALUES IN TABLES..

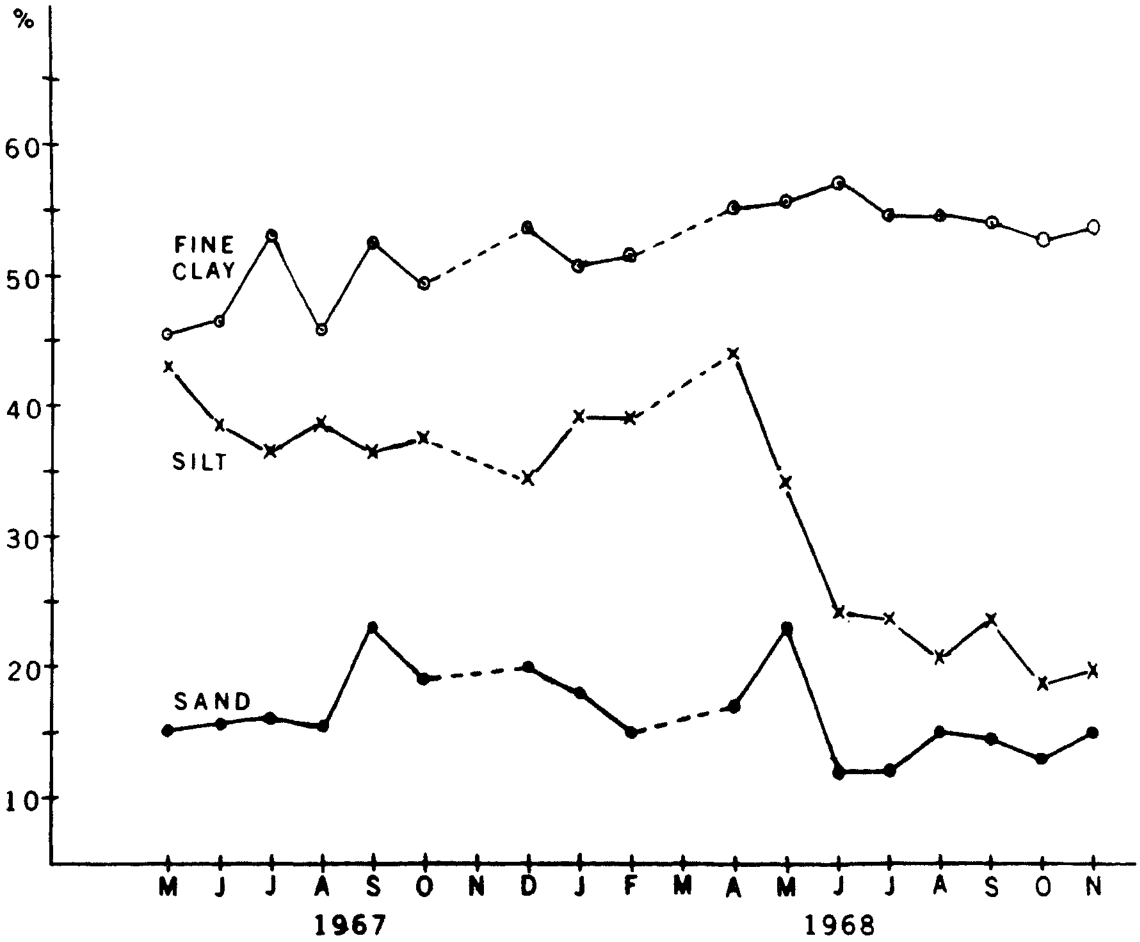

FIGURE 4. MECHANICAL SOILS ANALYSIS BY THE BOUYOUCOS METHOD WHICH PRESENTS THE RELATIVE PERCENT OF SAND, SILT, AND FINE CLAYS.

TABLE 2. PHYSICAL-CHEMICAL DATA FROM DAY OF SAMPLE COLLECTION

Date	Dissolved Oxygen ppm		Temperature °C		pH	
	surface	bottom	surface	bottom	surface	bottom
July '66	10.5	9.6	25.0	24.0	-	-
Aug. '66	9.9	8.3	23.3	23.8	-	-
Sept. '66	8.8	8.4	-	-	-	-
May '67	11.1	11.1	12.0	12.0	-	-
June '67	-	-	22.0	20.6	8.0	8.1
July '67	8.4	8.2	22.0	21.5	8.4	8.4
Aug. '67	8.4	8.3	22.0	22.0	7.6	7.8
Sept. '67	8.7	8.2	21.0	20.0	7.9	8.1
Oct. '67	9.7	9.5	13.0	13.0	7.9	8.0
Dec. '67	13.4	13.4	3.0	3.0	7.8	7.8
Jan. '68	14.2	14.1	0.0	0.3	8.4	8.4
Feb. '68	14.9	14.9	0.0	0.3	8.4	8.4
Apr. '68	12.6	12.3	9.0	8.0	8.0	8.0
May '68	9.6	9.6	14.5	14.5	8.1	8.1
June '68	9.5	6.5	20.5	19.5	8.2	7.9
July '68	9.6	6.8	22.8	21.8	8.4	7.8
Aug. '68	-	-	-	-	-	-
Sept. '68	8.9	7.9	21.8	21.0	8.0	8.0
Oct. '68	8.9	8.9	17.5	17.0	7.6	7.6
Nov. '68	11.5	11.3	8.1	8.0	7.9	7.9

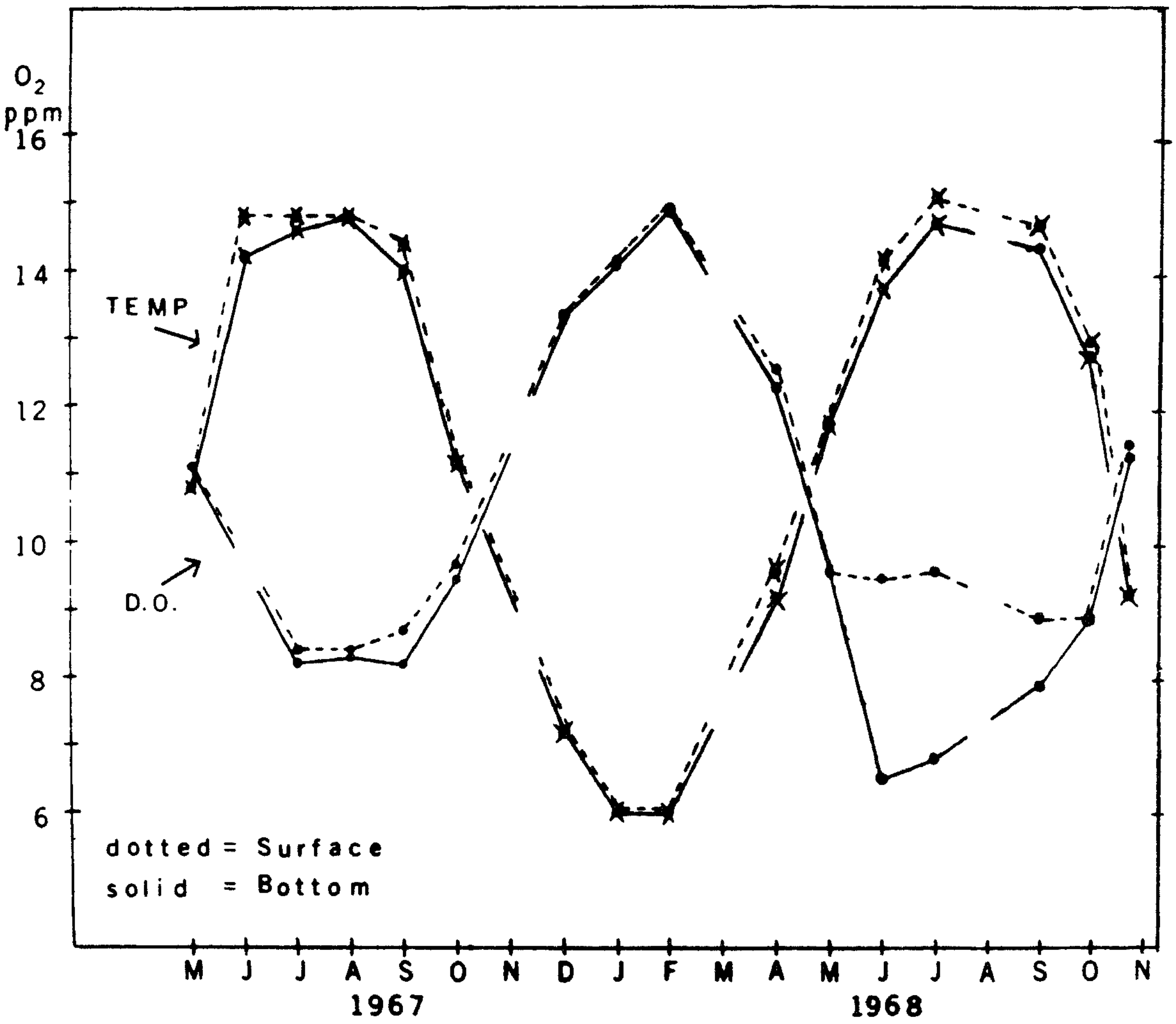

FIGURE 5. DISSOLVED OXYGEN AND TEMPERATURES OF WATER AT TIME OF COLLECTIONS. DOTTED LINES INDICATE SURFACE DATA AND SOLID LINES INDICATE BOTTOM DATA.

During the 19 months of sampling, the DO was not recorded below 70% saturation and was often near 100%. The lowest DO recorded in this study, occurred during June, 1968 along with high temperatures. Of special interest is that the warming trend of the water, and subsequent drop in DO occurred after 18 May, 1967 and before 18 May, 1968.

Analyses of core sample. The results of the chemical analyses of the sections from the core samples are presented in Figure 6. Each successive section represents a layer approximately 2.5 cm deeper into the sediment. The numerical data are presented in Table 3. The two sections closest to the surface of the sediment (section 1 and 2) contain approximately the same concentrations of each of the materials for which they were analyzed. Sections 4, 5, and 6 compose a second, distinct layer of sediment. The monthly variation in concentrations, which have been shown in Figures 1 through 4, are seen again in the surface layers of sediment from the core samples. The values obtained from the analysis of the Ekman samples were lower than the mean values from the core samples.

The average phosphate concentration for 1967-68, obtained by the analysis of the core samples was 2.50 mg/g dry wt PO_4. The iron averaged 31.10 mg/g dry wt Fe during the same period and the average total organic carbon was 1.31 mg/g dry wt C. The core samples averaged 6.07 mg/g dry wt O_2 upon oxidation.

In 1966 the core samples averaged 2.27 mg/g dry wt PO_4, 29.05 mg/g dry wt Fe, 1.45 mg/g dry wt C, and used 5.71 mg/g dry wt O_2.

TABLE 3. DATA FROM THE ANALYSES OF CORE SAMPLES EXPRESSED AS MG/g DRY WT

Date	Section 1	Section 2	Section 3	Section 4	Section 5	Section 6
July '66						
PO_4	2.40	2.57	2.49	2.25	1.86	2.19
Fe	29.39	30.56	29.74	29.03	29.95	28.31
O.C.	61.9	60.4	56.1	53.1	49.9	54.5
C	1.54	1.50	1.45	1.46	0.79	1.57
Aug. '66						
PO_4	2.42	2.61	2.19	1.69	1.94	1.74
Fe	28.02	27.68	27.02	27.70	27.08	27.74
O.C.	62.9	61.6	59.0	56.9	53.5	46.5
C	1.48	1.71	1.59	1.35	2.42	1.39
Sept. '66						
PO_4	2.92	2.53	2.69	2.29	1.80	2.22
Fe	31.24	29.60	30.81	28.92	28.98	31.12
O.C.	60.8	62.4	57.5	65.4	54.2	51.5
C	1.49	1.51	0.73	0.97	1.40	1.69
May '67						
PO_4	2.74	2.87	2.55	2.55	2.32	2.47
Fe	34.32	32.62	31.62	30.92	31.38	30.19
O.C.	64.3	64.1	57.1	60.8	57.8	54.4
C	1.09	1.94	0.73	1.33	1.29	1.12
June '67						
PO_4	2.92	2.77	2.14	2.95	2.68	1.96
Fe	30.95	31.29	29.82	28.75	31.19	27.28
O.C.	65.2	63.5	61.6	63.7	61.1	56.0
C	1.65	1.79	1.51	0.72	1.21	0.61
July '67						
PO_4	3.09	3.00	2.99	2.71	2.68	2.38
Fe	37.01	35.78	35.14	33.11	32.71	32.91
O.C.	70.7	70.5	62.5	60.5	61.3	61.3
C	1.24	1.21	0.73	0.73	1.52	1.12
Aug. '67						
PO_4	2.36	2.71	2.60	1.80	2.87	2.29
Fe	32.10	32.03	30.24	25.20	31.27	31.59
O.C.	66.5	66.4	60.0	61.9	60.3	55.4
C	1.65	0.97	0.97	1.81	1.50	1.21
Sept. '67						
PO_4	2.52	2.64	2.65	2.57	2.89	2.13
Fe	32.44	32.24	32.93	31.03	32.03	28.12
O.C.	63.1	67.1	67.0	66.0	65.3	61.4
C	0.85	1.21	0.85	1.64	1.62	1.20
Oct. '67						
PO_4	2.43	2.19	2.43	2.31	2.29	2.17
Fe	29.13	32.24	30.63	29.35	26.67	29.26
O.C.	64.5	67.6	65.9	67.6	65.1	53.7
C	0.97	1.60	1.70	2.29	0.73	0.73
Dec. '67						
PO_4	2.36	2.67	1.99	1.97	2.07	2.94
Fe	30.43	31.02	33.26	31.21	30.60	29.80
O.C.	63.0	63.1	62.9	58.9	59.1	53.7
C	1.21	1.33	0.85	1.45	1.33	1.09
Jan. '68						
PO_4	2.65	2.61	2.58	1.95	2.09	2.06
Fe	28.85	30.33	29.91	28.87	27.39	27.85
O.C.	61.8	65.0	62.2	58.9	58.3	58.6
C	1.21	1.70	1.45	1.21	1.33	1.33
Feb. '68						
PO_4	2.98	2.77	2.55	2.21	2.50	2.02
Fe	29.47	30.78	29.34	25.45	25.40	26.23
O.C.	61.3	65.2	60.1	53.9	53.9	53.8
C	0.73	1.81	0.97	1.94	1.33	1.17
Apr. '68						
PO_4	3.24	2.31	2.85	2.56	2.14	2.02
Fe	27.17	25.64	26.09	29.51	29.56	27.68
O.C.	63.6	64.2	64.2	62.5	61.0	63.9
C	1.82	1.58	1.21	1.55	1.82	0.85
May '68						
PO_4	3.21	2.83	2.76	2.60	2.47	2.07
Fe	27.82	30.09	27.94	28.60	29.54	25.61
O.C.	56.8	56.4	59.1	60.1	53.8	54.9
C	1.57	1.47	1.22	0.98	1.96	1.96
June '68						
PO_4	2.82	3.04	3.00	3.33	2.34	2.12
Fe	33.04	34.05	31.39	31.41	33.40	28.51
O.C.	68.0	64.0	60.0	61.6	58.4	56.8
C	7.92	3.12	2.28	2.40	3.60	4.60
July '68						
PO_4	2.49	1.24	2.14	2.37	2.31	1.96
Fe	34.19	32.22	32.24	32.55	31.57	32.28
O.C.	61.2	68.8	69.6	68.0	68.0	69.2
C	3.36	3.60	3.48	2.28	2.46	2.52
Aug. '68						
PO_4	3.09	2.51	2.77	2.53	2.02	2.36
Fe	36.15	33.15	33.22	31.90	33.02	31.89
O.C.	67.6	60.8	60.0	57.6	56.8	58.0
C	2.70	1.62	1.80	0.84	0.72	3.32
Sept. '68						
PO_4	2.55	2.47	2.46	2.47	2.01	1.96
Fe	34.08	35.26	33.42	35.78	32.40	31.86
O.C.	68.4	70.0	64.8	64.8	62.4	60.0
C	2.94	3.30	4.98	3.48	3.18	3.66
Oct. '68						
PO_4	2.89	2.63	2.37	2.43	2.22	2.24
Fe	33.78	33.01	34.88	33.04	33.60	33.94
O.C.	66.8	69.2	69.6	69.2	66.8	63.2
C	1.14	1.08	3.18	3.72	1.44	2.16
Nov. '68						
PO_4	2.51	2.78	2.64	2.65	2.46	2.23
Fe	32.47	31.00	33.47	31.86	33.47	31.87
O.C.	68.0	66.8	69.6	68.0	68.0	67.2
C	2.16	2.48	2.28	2.31	2.04	2.82

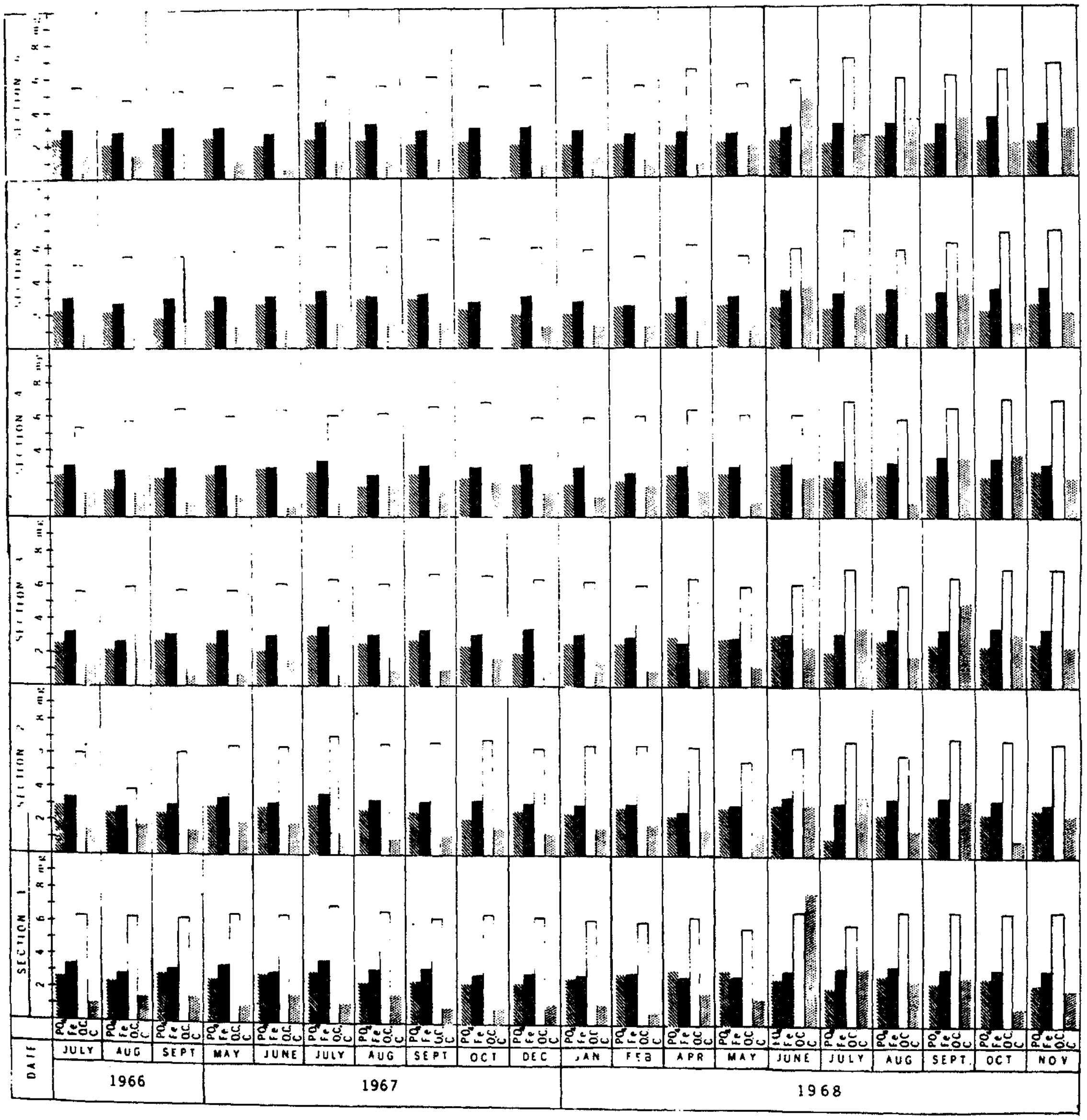

FIGURE 6. RESULTS FROM THE ANALYSES OF CORE SAMPLES. SECTION 1 THROUGH 6 INDICATE DEPTHS OF CORE SLICES FROM SURFACE OF SEDIMENT TO 18 cm IN DEPTH.

The iron and oxygen consumption values plotted in Figure 6 have been reduced by a factor of 0.1 to facilitate their presentation in the figure.

Discussion

The close relationships between iron, phosphorus, carbon, and oxygen consumption are shown in Figures 1, 2, and 3 of this report. Figure 4 can be compared to the other three to show a relation between the percentage of silt and the other factors. The Ekman samples taken at monthly intervals in 1967-68 show wide variation between the seasons of the year and even between months of the year. The decrease in the concentrations of both iron and phosphate found in the sediment between June and July, 1967 samples is interesting. Although there is no record of low DO during this time, I have been informed by Mr. Tim Luecke, pilot of the research boat, that there was a several-day period of calm weather and extreme clarity of the water following the June, 1967 sample. Based on my experience in 1966, and the record low DO recorded (Britt, _et al_., 1968) under similar conditions, I infer that low DO occurred. This may account for the lowered concentrations of iron and phosphate. This is further borne out by the drop in phosphate and iron during July-August, 1966 which was accompanied by a drop in the DO (Britt, _et al_, 1968).

Kishler (1967) found that Cladophora glomerata, collected from the island area of Lake Erie in 1966, contained an average of 1942 ppm total iron and 0.13 ppm total phosphate. He believes (personal communication) that as the dying masses of Cladophora detach from the rocky areas around the islands, they move out into the deeper waters where they decay and settle on to the sediment. The high iron content found at the present study site is quite similar to the amount in the algal cells and thus may indicate that his theory is correct. The difference between the results of this study and the figures given by Kishler may be accounted for by the plankton which add to the detritus of the sediment. The similarity between the total iron, and total organic carbon curves in 1968, (Figures 2 and 3) might be accounted for by a mass of Cladophora or other algae washing into the sampling area after April, 1968.

From the results of the analyses, very little increase in phosphate, iron, and carbon was found by a comparison of the samples from August of the five years (Table 1), with the exception of carbon content in August, 1968. However changes between months are often quite distinct and greater than any changes noted between years (Figures 1, 2, and 3).

Comparison of the Ekman samples of July, August, and September, 1966 with the samples from the same months in 1967 (Table 1), show an increase in phosphate and perhaps more significantly, if graphed, a similar pattern for both years. The averages of the data for the three months of each year show the increased amount. However, this increase is less than the differences in values between months. Furthermore, Figures 1, 2, and 3 show a slight yet definite increase in the amounts of iron, phosphate and carbon from May, 1967 through November, 1968.

Curl (1951) reported 49.4 mg/g dry wt PO_4 in the sediment off the west shore of South Bass Island, during the month of May, 1951. In 1967-68 the average total phosphate at my station, which is close to his sampling area was 2.31 mg/g dry wt PO_4 in the Ekman samples. This gives an apparent decrease, since 1951, by a factor of approximately 20. The magnitude of this decrease is such that the different methods of analysis for phosphate used or the type of sediment analyzed might account for the difference. He further reported that samples obtained during 1944, from January through December, gave an average of 5.9 μg/l PO_4, soluble phosphate, in the waters between Rattlesnake Island and South Bass Island. His lowest values of soluble phosphate were obtained during the months of July, 1944 (1.4 μg/l PO_4 - P) and August, 1944 (0.8 μg/l PO_4 - P). Peaks in phosphate in the water occurred in March, June, September, and December, 1944. If the data in Curl's paper are plotted, as in Figure 1 of this report, a quite similar curve results.

Figure 2 shows a decrease in the iron content of the sediment from December, 1967, to a fairly constant level during the period of ice cover on the Lake, and then a rise in April to July, 1968. This does not correspond to any similar change in phosphates or soils analysis. However, it does match the change in total organic carbon content. Sullivan (1967) showed similar changes in iron content in Lake Bloomington in Illinois. He found that both the phosphate and iron decreased in concentration in the sediments during the winter, but as in this study, the severity of iron depletion was more pronounced. During the winter of 1967-68 there was a drop in the amount of silt and a corresponding rise in the percentages of sand and fine clays. Possible currents under the ice may have shifted or washed away some of the iron bearing materials.

The core sampling technique was used during the 3 months of 1966 as well as the 1967-68 sampling period. The results show a definite layering of the sediment. The results of the analyses for phosphate, iron, carbon, and oxygen consumed show the same monthly pattern as that observed from the analyses of the Ekman samples. However, there is one major difference. In all cases the values from the core samples are higher than the values obtained from the Ekman samples.

Two distinct portions of sediment can be distinguished in a core. The first portion consists of sections 1 and 2 (Figure 5) which compose the upper 5 cm of sediment and have higher concentrations of the materials than the lower portion, sections 4 to 6. The top 5 cm of the mud reflect the same monthly changes in concentration as seen in the Figures 1 through 4. Figure 5 (core samples) and Table 3 show that the upper 5 cm of mud contain almost the same concentration of materials while the other sections in general are more variable.

Both Figure 5 and Table 3 show an apparent monthly variation in the concentration of the materials in a particular section. This can be explained by the fact that the upper portion of the sediment is directly affected by currents, wave action, and seiches and probably is shifted from one place to another. The rate of deposition or removal of sediment also appears to be quite variable and thus accounts for the seeming movement of a layer within the lower portion of the sediment.

A further possible explanation for the changes in concentrations and the homogeneous character of the top 5 cm of sediment may be the activity of the burrowing bottom organisms. The more prominent of the benthic fauna at present are the Tubificidae (standing crops ranging up to 50,000/m^2) and Chironomidae (standing crops ranging up to 3,000/m^2). Both types of organisms are known to burrow and mix materials from layer to layer in the sediment (Ruttner, 1963).

The activity, both chemical and physical, of the upper layer of sediment or mud has been demonstrated by the research of Mortimer (1941, 1942), Gorham (1958), Hayes and Phillips (1958), and Sullivan (1967). They have shown that the upper layer the major reactions in response to changes in DO and pH occur. The layer can be distinguished by its high water content and almost floccuent reaction to stirring. As mentioned, the action of waves, currents, and seiches would probably affect this layer. One would suspect that the activity of this layer will be, to some extent, governed by the depth of the water. By this is meant the reaction of the mud to wave action or stirring of the water mass. In western Lake Erie, and probably much of the central basin, the depth is sufficiently shallow to allow stirring of the bottom material during heavy storms. During periods of ice cover the bottom currents are quite strong and probably mix the sediments thoroughly.

The difference in concentration of materials, found between the results from the Ekman samples and core samples, can be attributed to the depth of sediment sampled. The Ekman dredge used in this study obtained a sample of mud approximately 25 cm thick and this material was thoroughly mixed before being sub-sampled and analyzed. The core sample contained only a 17 cm core and thus less of the lower portion of the sediment mentioned above.

Since the upper portion of the sediment is the active layer, samples of it should present a more accurate record of the changes occurring in the sediment with changes in DO and with the seasons.

The study demonstrates that a core sampler may be a more valuable tool than the Ekman dredge for sediment studies. The data accumulated on the total organic carbon and the oxygen consumed are new to the mass of data on Lake Erie. The variation in iron and phosphate in the sediment shown in this report indicates that samples must be collected seasonally rather than once a year.

Summary

In conclusion, we feel that the results of this project show several important points.

(1) The use of the Ekman dredge for sampling soft sediments, such as those found in the island area of Lake Erie, does not obtain as accurate a sample of the active layers of sediment as does the use of a core sampler.

(2) The phosphate present in the sediment varies greatly with the seasons of the year and thus a report of the amount of phosphate present, must be based on at least three consecutive months of sampling.

(3) The amounts of organic carbon and phosphate are quite similar, while iron is 10 times greater.

(4) The use of a core sampler shows that the top 5 to 7.5 cm of sediment, at this particular site, are affected by wave action and currents, and become well mixed. Possibly this portion of the mud becomes redistributed during each period of severe wave action, or as the result of bottom currents influenced by seiches.

(5) Because the site of sampling is one of the deeper portions of the western basin, similar results might be expected throughout the western basin wherever a soft type of sediment exists.

(6) The results obtained from this study are not intended as totally applicable throughout Lake Erie. However, similar changes in the sediment may occur and may be shown by future studies on the Lake.

(7) The amounts of total phosphate, total iron, and total organic carbon do not appear to have increased greatly in the sediments since 1964. Although there is a definite but slight increase in these factors from May, 1967 through November, 1968.

(8) The use of a shallow core sampler for the determination of the concentrations of materials such as phosphate and iron is new to the study of eutrophication in Lake Erie and should be of value for future investigators.

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