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# VARIATIONS IN THE PHOSPHORUS CONTENT OF ESTUARINE WATERS OF THE CHESAPEAKE BAY NEAR SOLOMONS ISLAND, MARYLAND\*

By

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Studies by Cowles and Brambel (1938), Newcombe and Lang (1939), and Newcombe, Horne and Shepherd (1939) have provided information on the quantitative methods for estimating inorganic phosphorus and, also, on the vertical and horizontal distribution of this nutrient substance in the waters of the Chesapeake Bay. A continuation of distributional work has provided definite information on the magnitude of diurnal, daily and horizontal variations in estuarine waters, and certain points are developed that concern the handling of phosphate samples. Most significant, perhaps, is the evidence pointing to exceedingly rapid utilization and regeneration of inorganic phosphorus under natural conditions. It should be pointed out that the quantity of phosphorus present has been measured in the form of inorganic phosphorus (PO<sub>4</sub>) only. Were additional data available bearing on the amounts of dissolved organic phosphorus as well as particulate organic phosphorus, then more positive explanations might be offered for the variations that obtain. It is well-known that phosphorus assimilated by phytoplankton is again set free by processes of decay and digestion by other organisms. The precise location of this transformation and the rate at which it takes place are not clearly understood. Under certain conditions, phosphorus may be removed from active participation in the cycle or it may be conceived as existing predominantly in one particular form during specific intervals of time or space. Atkins (1930) and Cooper (1938) have attributed high phosphate concentrations to regeneration of phosphorus from decomposing floating organic material. The rapid utilization and regeneration of inorganic phosphorus observed in the Chesapeake waters has been interpreted on a basis of light available to the phytoplankton. The method of analysis employed is the variation of Deniges' ceruleomolybdate method described by Newcombe and Lang (1939).

#### RESULTS

The results of intermittent observations since 1936 on the distribution of nutrient salts in the Chesapeake Bay have clearly shown that these basic

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substances do not follow any particular predescribed rule with respect to hourly, daily or seasonal changes. The physical and chemical properties of the Bay waters are essentially estuarine in character and, in the present



Figure 23. Showing the change in concentration of phosphorus accompanying storage with and without  $CS_2$  preservative. ---- preserved; ------ unpreserved. Each point represents an average of two or three sample bottles. A. Initial concentration, high; B. Initial concentration, low.

state of knowledge, they are not particularly well understood. The characteristics treated here are: (1) effect of storage, (2) close interval changes with respect to space and time, (3) daily changes, (4) horizontal and vertical gradients.

Experiments designed to determine the stability of phosphate samples accompanying storage have shown that under the high summer tempera-



Figure 24. Variations at close time intervals of phosphate as mg. atoms P/m<sup>3</sup> off the laboratory pier. ----June 16-17; \_\_\_\_\_\_ Sept. 5-6; Sept. 14-15, 1939, \_\_\_\_\_

[III, 1

### JOURNAL OF MARINE RESEARCH

ture conditions characteristic of the waters in this latitude, namely  $25^{\circ}-30^{\circ}$  C., the phosphorus concentration may change significantly within a period of one hour. The character of this change is dependent, among other factors, on the light and temperature conditions during storage. In an effort to preserve samples so as to permit storage, the following preservatives were tested: chloroform, sodium fluoride and carbon disulphide.



Figure 25. Daily concentrations of phosphorus at the end of the laboratory pier taken during period June 20-Sept. 25, 1939. Samples were collected in dark green bottles and analyzed immediately.

Chloroform and sodium fluoride are not satisfactory preservatives. Carbon disulphide has been tried frequently and in most instances significantly retards the rate of change that normally accompanies storage during the first fifteen hours. (Figure 23.)

Close Interval Changes.—The results obtained by Newcombe and Lang (1939) showing pronounced diurnal changes in concentration of phosphorus have been confirmed (Figure 24). During the periods of these experiments, the weather was clear and the wind movement light and moderate. The tidal amplitude and the accompanying chlorinity concentrations are presented in Figure 24. The results indicate a characteristic increase during

#### 1940]

and following the hours of sunset and a corresponding decrease during the morning hours. Although considerable variations are known to exist between the different series that have been taken, nevertheless, there seems to be a general agreement with respect to the occurrence of higher concentrations during the hours of darkness. These findings are supported by random samples taken throughout the summer season.



Figure 26. Location of principal sampling stations (numbered points) in the Patuxent River (2 is equivalent to 102 and 108 is about 7 miles south of this station).

Day and night time samplings in the shallow waters between the end of the pier and shore have indicated that a decrease or increase may exist in the direction of the shore. These observations are important because of the possible significance they might be considered to possess in connection with the abrupt increase in concentration of P during the early hours of darkness. The changes are not considered to be greater than the normal variation obtained over this range of distance in the general region.

#### JOURNAL OF MARINE RESEARCH

Daily Changes.—The results of daily analyses of water from off the laboratory pier during the period June 20-September 25 are shown in Figure 25. The highest values obtain during August with a slightly lower average during July. That a pronounced decrease takes place in September when turbidity is significantly reduced is clearly shown. This condition of





low phosphorus content and high transparency has continued during the fall period. The highest concentration recorded during summer is 1.48 mg. atoms per m.<sup>3</sup> It is not unusual to get mere traces in the pier samples, as is shown in Figure 25. The existence of marked daily variations in summer is quite evident.

Horizontal and Vertical Gradients.-Numerous horizontal sections taken during the different seasons of the year have indicated a conspicuous in-

1940]

#### TABLE I

Vertical and Horizontal Gradients of Phosphorus and Chlorinity in the River-Bay Section. Time, August 15, 1939. Phosphorus, mg. Atoms per m<sup>3</sup>. Chlorinity, Parts per Thousand by Weight

Station	1		4		7		9		14		25		35		<b>m</b> •3
	<i>P</i> .	Chlor.	Ρ.	Chlor.	Tide										
21	1.59	4.54	1.60	4.69	1.56	4.77									
18	1.52	6.39	1.54	6.27											Ebb
16	1.79	6.31	1.85	6.63	1.42	7.01									
14	1.29	6.82	1.15	6.96	1.21	7.84									
12	0.54	7.44	0.50	7.38	0.58	7.70									
10	0.05	7.27	0.51	7.64			0.67	8.09	0.60	8.48					
8	0.39	7.82	0.55	7.94			0.43	8.02	0.71	8.20	0.72	8.41	0.62	8.43	
5	0.05	8.22	0.11	8.26			0.32	8.50	0.38	9.44					
102A	Trace	7.99	Trace	8.01	C. Berlin		0.54	11.81	0.73	12.30	1.11	12.96	1.65	13.22	Flood
110	Trace	8.23	Trace	8.25			Trace	8.52	Trace	11.09					

Depth in Meters

SEARS FOUNDATION

crease in phosphorus accompanying the decrease in chlorinity in the direction of Station 21 (Figure 26). The characteristic trend at the several levels studied is shown in Figure 27 and Table I. The horizontal gradients are subject to pronounced variations produced by mixing processes that may be influenced by tidal forces, wind movements, or excess drainage operating as single factors or in combination.

Table II shows the character of the horizontal gradient that may occur in the Bay waters during summer. This by no means represents a constant condition since hourly sampling in these waters has indicated that the changing position of water masses results in pronounced changes in the concentration of phosphorus at a given point (Figures 24 and 28). The table, therefore, simply represents normal expectancy for this region under prevailing chlorinity, temperature and light conditions.

The vertical gradients are conspicuously developed during the summer season. It is shown in Table I and Figure 27 that the subsurface levels may be expected to contain higher concentrations of phosphorus. Occasionally, low values have been obtained near the bottom, but usually there is evidence that this water had a recent origin near the surface. Concentrations above 1 mg. atom of P per cubic meter may be expected in the deeper waters whereas, in summer, but mere traces of phosphorus sometimes obtain in the surface level. The surface concentrations in the river waters are usually higher than those of the Bay and this is particularly evident following a period of rainfall.

#### DISCUSSION

Earlier studies at this Laboratory have provided considerable evidence of the existence of atypical phosphate conditions which seem to possess more than local interest (Newcombe, Horne and Shepherd, 1939; Newcombe and Lang, 1939). A continuation of these observations has brought to light certain basic facts that may not be universally recognized and has also contributed toward a more accurate picture of the variations in the concentration of phosphorus that characterize estuarine waters.

Little attention seems to have been given to the preservation of phosphate samples. When difficulty is experienced in running samples immediately on board boat, a definite problem arises in respect to the preservation of samples having a temperature around 26° C. at the time of collection. Ibanez (1933) favors the use of sodium fluoride as a satisfactory preservative. In several experiments, chloroform and sodium fluoride were employed without success. Carbon bisulfide reduces the change significantly for a short period and in past studies has been used (Figure 24). Recent experiments, however, strengthen the opinion that wherever possible phosphate samples should be run immediately, though collected in dark bottles and held in a cool place. Significant change may take place within

1940]

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#### TABLE II

#### CHESAPEAKE BAY CROSS-SECTION AT STATION 108 SHOWING HORIZONTAL AND VERTICAL GRADIENTS OF PHOSPHORUS AND CHLORINITY. TIME, JULY 17, 1939. PHOSPHORUS, MG. ATOMS PER M.<sup>3</sup> CHLORINITY, PARTS PER THOUSAND BY WEIGHT

#### STATIONS

Depth in	V	Vest Sho	re			East Shore				
Meters	108a	108b	108c	108d	108e	108f	108g	108h	108i	
1 P	0.10	Trace	0.27	0.29	Trace	0.15	Trace	Trace	Trace	
Chlor.	7.23	7.23	7.29	7.35	7.64	7.56	7.51	7.51	7.62	
4P		0.13	0.01	0.07	0.01	0.37	0.05	0.54	Trace	
Chlor.		7.28	7.40	7.35	7.65	7.62	7.55	7.55		
9 P				0.06	0.14	0.15	0.20	Trace		
Chlor.				7.56	7.65	7.60	7.64	7.63		
14 P					0.21	0.23				
Chlor.					8.46	8.28				
19 P						0.08				
Chlor.						7.56				
25 P						0.53				
Chlor.						10.04				
30 P						0.57				
Chlor.						10.18				
Tide		Ebb						Slack	Flood	

less than thirty minutes under the high summer temperatures of Chesapeake Bay waters.

The character of the close interval changes shown in Figure 24 is thoughtprovoking. These data confirm the general picture suggested by Newcombe and Lang (1939). The present state of knowledge with respect to phosphorus metabolism in the sea does not permit an explanation of this diurnal change. Available evidence does not point in the direction of the inflow of adjacent water masses as a possible explanation of the night and morning changes. There does not seem to be any conclusive evidence that would permit an explanation based on actual phosphate liberation by the living organisms in sufficient quantities to account for the observed fluctuations.

The pronounced diurnal variations suggests an absence or greatly reduced phosphate utilization during darkness and a marked liberation of phosphorus at this time. In fact, Renn (1937) discussing regeneration experiments states "if autolyzing bacterial cells liberate phosphorus as phosphate there always exists the possibility that diatoms and other phytoplankton may similarly bring about direct regeneration." Although his attempts to demonstrate such regeneration gave negative results, it was his opinion that the possibility definitely exists. Granting such an hypothesis, how can such a large phosphorus transfer be rationalized? If, in the presence of JOURNAL OF MARINE RESEARCH



Figure 28. Chesapeake Bay cross section at Station 108 showing horizontal gradients of phosphorus at several depths. July 17, 1939.

an abundance of phosphorus, a diatom rapidly absorbed relatively large amounts of this element, it would seem reasonable to assume that a mechanism may exist within the cell whereby a speedy elimination of the phosphorus could be effected. Harvey (1937) has discussed the adsorption of phosphate on the surface of diatoms. He points out that colloidal and larger particles of phosphate can be utilized by and support the growth of diatoms. When more is known of the biochemical and biophysical processes involved in diatom metabolism, it may be possible to offer an explanation for the noticeably rapid utilization and regeneration of this important nutrient.

A conspicuous characteristic of the daily fluctuations indicated in Figure 25 is the sudden change that may occur within a short time interval. A careful examination of available data fails to offer an explanation. The highest average values are for August. Those determinations were all run immediately after collection on unpreserved samples. Some of those done during the summer of 1938 are on samples preserved by carbon disulphide which, it is believed, may account for the exceptionally high values obtained, on occasion, at that time. It is not uncommon to obtain concentrations of phosphorus above 0.2 mg. atoms per m.<sup>3</sup> in pier samples during late June, July and August. During the first part of September, 1939, an abrupt decline in concentration of phosphorus was observed in the waters off the laboratory pier. This change was accompanied by a marked reduction in turbidity as shown by Secchi disc readings. The increase in the transparency of the water is not explained by rainfall data nor by any other available observations. It is known that the condition of relatively low turbidity remains during the fall and winter seasons when the numbers of plankton organisms are greater. If an increase in phytoplankton occurs at this particular time when the stratum of photosynthetic activity is much deeper, then the decrease in inorganic phosphorus may be accounted for.

It seems desirable to point out the magnitude of the diurnal changes in concentration of phosphorus and the distinctive correspondence between its variations and those changes in submarine illumination referred to above. Results thus far seem to indicate that the light factor is of major importance in causing these variations as well as those horizontal differences that exist in the Chesapeake Bay waters (Newcombe and Lang, 1939). A conclusive answer to this problem must await information on (1) plankton abundance, (2) dissolved organic phosphorus, and (3) particulate organic phosphorus.

The horizontal sections of the Bay completed for the first time, show the normal expectancy in regard to stratification of chlorinity and phosphorus content (Table II). The highest concentrations in summer characterize the bottom waters whereas the smallest values are obtained in surface layers. Following periods of disturbance due to tidal action or winds or a combination of both, a fairly homogeneous condition is set up. It represents a temporary dislocation and the stratified condition returns after varying time intervals depending on the particular condition involved. The chlorinity stratification perhaps returns first whereas there is a noticeable lag in the establishment of phosphate and oxygen levels of varying concentrations.

The horizontal changes in the Bay are considerable, as shown by the surface records in Table II (Figure 28). Horizontal variations accompanying decrease in chlorinity in an up-river direction are pronounced (Figure 27). In general, the phosphorus concentration increases at all depths accompanying an increase of river water. It has been suggested that the type of relationship represented in Figure 27 implies a lack of contribution of phosphorus to the Bay by the river waters and might be accounted for on a basis of utilization by river plankton according to the theory of Harvey (1928). Riley (1938) has presented very convincing evidence that the Mississippi makes substantial contributions to the waters of the Gulf of Mexico. In interpreting the condition shown to exist in the Patuxent River (Table I), further knowledge of the water movements and the results of the daily mixing processes and the subsequent dilution effects is highly desirable.

In general, the summer concentrations of phosphorus in the Patuxent River are above 1.0 mg. atoms per m.<sup>3</sup> The effect of rainfall in increasing the river concentrations is immediate and quite significant.

#### SUMMARY

1. Experimental evidence is presented to show the need for immediate analysis of phosphate samples in order to assure best results for Chesapeake waters during summer.

2. Previous preliminary observations on the occurrence of pronounced diurnal variations in the concentration of phosphorus have been confirmed.

3. The daily variations in phosphorus content during the summer of 1939 were found to vary from mere traces to about 1.5 mg. atoms per m.<sup>3</sup> Concentrations above 0.3 mg. atoms per m.<sup>3</sup> frequently occurred. The peak seemed to have been reached in August and was followed by an abrupt decline in early September accompanying a marked reduction in turbidity of the local waters. This latter condition has continued during the fall period.

4. The waters of the Solomons Island region show a lack of homogeneity noticeably reflected in the horizontal variations in phosphorus content at the different levels. Highest concentrations occur in the bottom waters which frequently contain between 0.6 and 1.1 mg. atoms of  $P/m.^3$ 

5. A pronounced increase in the concentration of phosphorus accompanies the decrease in chlorinity toward the headwaters of the Patuxent River. The river waters usually range between 0.9 and 1.8 mg. atoms per m.<sup>3</sup> in summer.

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#### EDITORIAL NOTE

## ON THE PREPARATION OF FIGURES FOR PUBLICATION

Experience in the publication of the first two volumes of this Journal indicates a considerable amount of uncertainty among authors and illustrators in the choice of lettering-sizes suitable for a clearly readable reproduction. The accompanying diagram (Figure 29) has therefore been prepared as a guide for determining height of letters and size of symbols to be used on original drawings.

The three curves indicate the height in millimeters (scale at right) of Large, Medium and Smallest permissible letters suitable for use on original drawings according to the amount of reduction (scale below) for which they are intended or which they require for publication. Rates of reduction between 1:3 and 1:6 are given on a smaller scale than that used for those between 1:1 and 1:3. The words (LARGE, MEDIUM, SMALLEST) used at the left to identify each of the 3 curves also illustrate the appearance after reduction of original lettering selected by the use of this diagram.

Authors wishing to use special dimensions for final reproduction should compute the rate of reduction involved and use the scale at the bottom. Those who merely wish to use the maximum size available on the pages of this Journal may take advantage of either of the scales given at the top, by which the usable heights of lettering may be determined directly from the overall width of the original, measured either in centimeters or in inches. The printed page of this Journal measures 61/2 by 41/4 inches, or 16.5 by 10.8 centimeters. For figures intended to be viewed with the page held in normal reading position the maximum width is thus 41/4 inches and the maximum depth 6 inches or 15.2 cm. (to allow for legend) and the lower scale given above the diagram in Figure 29 should be used. Illustrations demanding a greater width may be arranged to be viewed with the page held at right angle to normal reading position, as done with Figures 16 and 17 on pp. 66 and 68 preceding. In these cases the upper scale above the diagram should be used for determining letter size, and the maximum permissible height of the illustration after reduction is 4 inches or 10.2 cm.

Attempts to reproduce an illustration without reduction normally results in a coarsening of details. A minimum reduction at the rate of 1 : 1.2 is desirable for clearness, and this is the least reduction which will be applied to any drawing submitted for use in this Journal.

It is desirable to limit all lettering to capital letters only. Lower case letters of corresponding size are less readable after reduction. If mixed capital and lower case characters are used, the letter-height suggested in Figure 29 as "Medium" (for capital letters alone) should be regarded as minimum size in the mixed composition,



Figure 29. Curves for the determination of capital letter heights for use in original drawings. See text.

# LARGE SIZE - HEAVY, MEDIUM, LIGHT MEDIUM SIZE - HEAVY, MEDIUM, LIGHT

SMALLEST SIZE- HEAVY, MEDIUM, LIGHT

Figure 30. Appearance of lettering from figure 29 before reduction at the rate of 1:1.6

1940]

It should be noted that slanting letters appear larger than straight letters of equal size. The captions for the two scales above the diagram in Figure 29, starting with the words "WIDTH OF," are lettered with characters of the same height and weight of line to illustrate this point.

Samples of heavy, medium, and light lettering in Large, Medium and Smallest permissible size are included in the diagram. This sample legend is also reproduced separate in Figure 30 as it would appear in an original intended for reduction at the rate of 1 : 1.6.

The curves for suitable letter-heights also give the usable transverse dimensions of identifying marks such as circles and dots as shown by the examples entered in the figure. The following reservations apply to the use of the curves to determine the required size of identifying marks in the original. 1) A diameter corresponding to the smallest permissible height of capital letters can only be used when not more than 2 kinds of identifying marks (circles and dots) are needed for differentiation. If it is necessary to differentiate between 3 or more identifying marks the smallest usable diameter should correspond to the medium height of capital letters. 2) Polygonal forms should be avoided so far as possible. If absolutely required to obtain sufficient variety of identifications, one polygonal form (triangles) may be used when dimensions not smaller than the medium height of capital letters are employed. For 2 polygonal forms (triangles and squares) a size of identifying marks not smaller than the height of "LARGE" capital letters is desirable. More than two types of polygonal forms\* (in addition to circular marks) should not be used under any circumstance. Crosses, or crosses enclosed in circles are less desirable than the types of circular marks suggested in Figure 29, and require a larger minimum size. Whether or not they are preferable to polygonal forms when additional differentiating marks are absolutely required is a matter of taste.

The use of cross-section paper ruled or printed with *blue* lines can not be too strongly recommended. These lines disappear in the process of reproduction without any necessity of retracing the drawing or using colorfilter methods, at the same time as all the advantages of the cross-rulings are preserved for the checking of figures with tables, etc., in the writing and editing of manuscripts. Figure 29 has been drawn on blue cross-section paper of which only the lines emphasized in black India ink remain in the reproduction.

#### A. E. PARR

#### D. T. PITCHER

\* Each of which may be used in both black and white (outline) form on the same graph.