THE CYCLE OF ORGANIC PHOSPHORUS IN THE GULF OF MAINE

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It is generally recognized that the fertility of the sea depends upon a cycle in which carbon, nitrogen, phosphorus and other substances are assimilated under the influence of photosynthetic processes in surface waters and are set free again by processes of digestion or decay. The total organic productivity of a region is limited to the rate at which this cycle is completed. While it is apparent that in many localities the principal limiting factor is the rate of restoration of the inorganic products of decay (NO_3, PO_4) to the surface or photosynthetic zone, little is known concerning the exact locus within the sea at which decomposition actually sets these substances free, or of the rate at which the cycle as a whole or in part is completed.

The concentration of the ultimate products of decomposition, such as NO_3 and PO_4, tell us little about these points since they are stable substances capable of accumulating over a long period of time to high concentrations, and of being transported far from their place of origin. The actual site of decomposition is better indicated by the presence of intermediate products of decay such as ammonia, nitrite, and organic compounds of nitrogen and phosphorus.

The present paper is an account of the distribution of phosphorus throughout the year at a standard station in the Gulf of Maine. At all depths the amount of phosphorus present has been measured in three forms: (1) inorganic phosphate (PO_4), (2) dissolved organic phosphorus, and (3) particulate organic phosphorus. The analysis of these data gives some indication of the magnitude of the synthetic and disintegrative processes undergone by phosphorus compounds in different parts of the water column at different times of year, and of the extent to which phosphorus is transported from one depth to another.

The station chosen for study was located in the deeper portion of the western basin of the Gulf of Maine, 30 miles northeast of Highland Light. The surface water in this region is apparently relatively free from strong non-tidal currents, being sufficiently far offshore to avoid the coastal drift which accompanies the freshening of the water along

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the margin of the Gulf. In this part of the Gulf, as the result of freedom from strong currents, there develops each summer maximal surface temperatures and maximal stability of the water column. In this location one also finds relatively deep water (230–270 meters) free from strong non-tidal currents. Preliminary measurements made by Dr. E. E. Watson with current-meter indicate maximal tidal velocities of 11 cm. per second at 40 cm. above the bottom, and 14 cm. per second at 177 cm. above the bottom. The oxygen content in the deep water below 200 meters is low, varying from 4 to 4.5 cc. per liter. The point chosen for study thus presents conditions in which there exists above the bottom a considerable column of water too poorly illuminated to permit of photosynthesis, which terminates at a depth of 40 to 50 meters (Clarke and Oster, 1934) and in which decomposition occurs in sufficient magnitude to maintain a low oxygen concentration, and one as well chosen as may be to avoid disturbances due to the non-tidal drift of the water.

TABLE I

Station positions and dates.

Atlantis Station Number	Date	Location	Depth of water
			meters
2440	May 18, 1935	42° 22′ N. 69° 35′ W	249
2468	August 20, 1935	42° 20′ N. 69° 32′ W	232
2493	November 8–9, 1935	42° 21.5′ N. 69° 32′ W	256
2495	February 26, 1936	42° 22′ N. 69° 33′ W	270
2558	May 14, 1936	42° 27′ N. 69° 31.5′ W	254

Stations were made on five occasions separated by intervals of three months, thus completing one yearly cycle. Their positions and dates are given in Table I. The approximate position is indicated by a circle in Fig. 1.

ANALYTICAL PROCEDURE

Inorganic Phosphate

Phosphate samples were collected in black bottles and analyzed for inorganic phosphate at room temperature on shipboard by the Deniges-Atkins method, except that the solution of stannous chloride used contained 0.1 gram $SnCl_2.2H_2O$ in 10 ml. of 1 to 10 hydrochloric acid. Salt effect correction factor as measured was 1.35. Corrections for salt error and reagent blank were both applied.

Particulate Organic Phosphorus

Samples of water of about 300 ml. volume were filtered on shipboard as soon after collection as possible.

The procedure by which particulate organic phosphorus was determined is as follows. The particulate matter is filtered out by suction on a precipitate of barium sulfate on a 3G4 Jena sintered glass funnel with polished surface. The barium sulfate precipitate is prepared by stirring 0.6 ml. of normal barium chloride into about 10 ml. of hot water containing excess sulfuric acid. It is poured over the funnel, the liquid sucked through, and filter and flask washed thoroughly with distilled water. The sea water sample is run through the

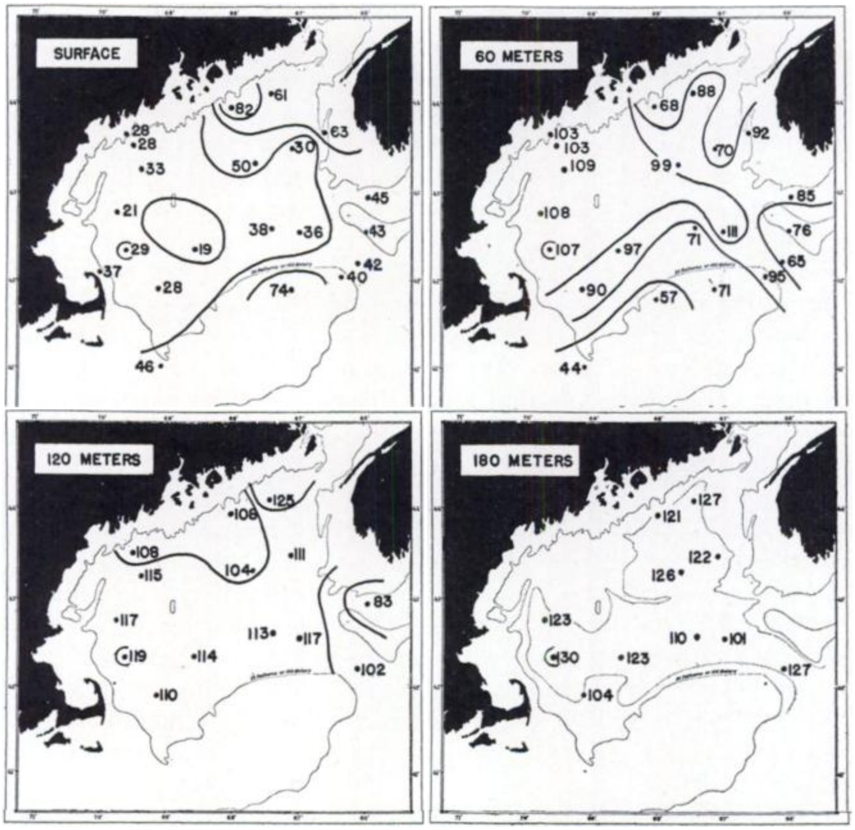

FIG. 1. The distribution of inorganic phosphate, PO_4, throughout the Gulf of Maine in May, 1934, at the surface and at the depths of 60, 120, 180 meters. The circle indicates the position of the stations at which the present investigations were made.

filter, and the volume of the filtrate measured. Plankton and barium sulfate are washed off the filter into a 125-ml. Erlenmeyer flask with a stream of distilled water. The sides and bottom of the filter are cleaned with a rubber policeman and all the precipitate transferred to the flask to insure removal of the plankton. The funnel is cleaned by reverse suction, treatment with sulfuric and chromic acids and thorough washing.

After the addition of 2 ml. of 38 per cent (by volume) sulfuric acid to the plankton, the flask is evaporated on the steam-bath to charring of the organic matter. The flask is ignited to fumes of sulfuric anhydride, and a drop of phosphate-free hydrogen peroxide (Cooper, 1934) (prepared by vacuum distillation of concentrated hydrogen peroxide) is added. A few seconds heating without loss of sulfuric anhydride fumes suffices to destroy the organic matter. The excess hydrogen peroxide is decomposed by heating the sample at 120° C. for one hour on an oil-bath. The cooled samples are diluted with ca. 50 ml. of distilled water and warmed on a steam-bath before filtering through a sintered glass funnel to remove the barium sulfate. The filtrate is diluted to 100 ml. in a glass-stoppered bottle. After the addition of 2 ml. of 2½ per cent ammonium molybdate each sample is shaken. Standards of similar phosphate content as potassium dihydrogen phosphate are made up with 2 ml. of 38 per cent sulfuric acid, 2 ml. ammonium molybdate and distilled water to 102 ml. and shaken. Two drops of stannous chloride solution containing 2.5 grams $SnCl_2.2H_2O$ in 100 ml. of 1 to 10 hydrochloric acid are added to each sample and standard with immediate shaking. After five minutes the samples are compared with the standards in a colorimeter with about 30 cm. depth of solution. Phosphate in the reagents for the development of the color (designated as Blank A) is determined by intercomparison of dilute standards. Phosphate introduced in the treatment of the unknowns (designated as Blank B) is determined by carrying through the procedure on a barium sulfate precipitate not treated with sea water. Blank A is added to the standards to give their true phosphate content. Both Blanks A and B are subtracted from the phosphate found in the unknowns. The net phosphorus in grams $\times 10^{-6}$ found in the unknowns multiplied by $\frac{1{,}000}{\text{ml. sample}}$ gives the plankton phosphorus in grams $\times 10^{-6}$ per liter. Errors in the analysis due to loss of phosphorus by volatilization or change in acidity by loss of sulfuric anhydride are shown to be negligible by carrying through blank analyses with known amounts of added phosphorus.

A procedure employing nitric acid as the oxidizing agent (Robinson and Kemmerer, 1930), in which the nitric acid was evaporated off and the last traces removed by an evaporation with hydrochloric acid gave check results with the hydrogen peroxide procedure but a poor color match with the distilled water standards. It might be possible to use a procedure similar to that of von Brand (1935) for separation of the diatoms from sea water. No effort was made to differentiate between phosphorus and arsenic in the plankton phosphorus determinations. It was found, however, that the procedure of Zinzidze (1935) using bisulfate and sulfuric acid will bring about the complete reduction of at least 9×10^{-6} grams of arsenic to the limit detectable by the cerulio-molybdate method (2×10^{-7} grams) and make possible a distinction between phosphate and arsenic in plankton analyses.

Dissolved Organic Phosphorus

The phosphorus in solution in organic combination was obtained by subtracting the inorganic phosphorus from the total phosphorus in the filtrate from which the particulate matter had been separated. The following procedure for the determination of total phosphorus in a sea water sample was devised with a view to avoiding the interference of pentavalent arsenic with the ceruleo-molybdate phosphorus determination and to insure the complete destruction of organic matter. In the more rapid methods of analysis which have been used, in which sea water is treated directly with oxidizing agents, arsenic in the sample is oxidized and not subsequently reduced, while organic matter is not completely destroyed in solutions containing large amounts of chloride.

Fifty-milliliter samples of sea water are treated with 3 ml. of concentrated sulfuric acid (arsenic-free) in a 125-ml. Erlenmeyer flask. After evaporation on a steam-bath under a hood to carbonization of the organic matter, each sample is evaporated to the formation of fumes of sulfuric anhydride with swirling to avoid bumping. A drop of phosphorus-free 5 per cent hydrogen peroxide (prepared by vacuum distillation of 30 per cent hydrogen peroxide) is added. The flask is heated in the same manner without loss of sulfuric anhydride for half a minute more to make the solution colorless. If necessary, more hydrogen peroxide may be added. About 60 ml. of distilled water is added to the cooled sample, which is set on the steam-bath for complete solution of the precipitated salts. After transfer to a 500-ml. Erlenmeyer and addition of 8.5 ml. of concentrated ammonia water, the excess of ammonia is boiled off and the volume of solution reduced to about 30 ml. The sample is transferred to a small ground-glass-stoppered bottle and warmed on the steam-bath, open, with 2.47 ml. of 38 per cent (by volume) sulfuric acid. Four milliliters of 10 per cent sodium sulfite (anhydrous, or hydrated salt in double the concentration) is added, and the stopper held in with a clip to prevent the escape of sulfur dioxide. Excess hydrogen peroxide is immediately destroyed, but eight hours heating on the steam-bath is necessary to reduce pentavalent arsenic to the trivalent form. The sample is transferred to a 500-ml. Erlenmeyer, boiled for five minutes to remove sulfur dioxide, cooled, and diluted to 100 ml. in a ground-glass-stoppered bottle. The residual acid in the sample is 2 ml. of 38 per cent sulfuric. After the addition of 2 ml. of 2.5 per cent ammonium molybdate the sample is shaken. Standards which will develop about the same color intensity as the unknowns are made up from a potassium dihydrogen phosphate solution with the addition of 2 ml. 38 per cent sulfuric acid, 2 ml. of 2.5 per cent ammonium molybdate solution, and distilled water to 102 ml. These are shaken. Each standard and sample is again immediately shaken after the addition of two drops of a solution containing 2.5 grams of $SnCl_2$ $0.2H_2O$ in 100 ml. of 1 to 10 hydrochloric acid. After four or five minutes for the development of the color the samples are compared with the standards in a colorimeter with about 30 cm. depth of solution.

Intercomparison of dilute standards in distilled water is made to estimate the phosphate in the reagents for producing the color (designated Blank A). A blank determination carried through with reagents alone gives the phosphate introduced by reagents in the treatment of the sample (designated Blank B). Blank A is added to the standards to give their true strength in calculating the phosphate in the unknowns. Both Blanks A and B are subtracted from the phosphate found in the unknown. The salt effect correction has been determined as 0.885 for unknowns by analysis of the same sea water with varying amounts of phosphate added. The slope of the graph of phosphate added against phosphate recovered is the salt effect correction. No variation in salt effect correction was found with salinity from 31.5 to 38.5. A similar procedure gave a salt effect correction of 0.81 in determining Blank B. Change of salt effect correction with temperature was not studied but extremes of temperature were avoided in making the analyses.

Since several samples of sea water gave identical analyses with or without the addition of as much as 165 mg. per cubic meter of arsenic (about eight times the amount found in sea water), arsenic was assumed to be reduced completely by the procedure used. Reduction of arsenic in solutions for determining Blank B was found to be much slower than in sea water samples and quantitative only for amounts of added arsenic equivalent to 50 mg. per cubic meter or less. The difficulty was avoided by the use of reagents containing negligible amounts of arsenic. Schering-Kahlbaum "pro analysi" sulfuric acid was found suitable. The method can easily be adapted to use with a photometer although this was not attempted.

Table II, containing representative data from the analysis of samples of sea water, illustrates the procedure used in computing the dissolved organic phosphate, and gives some indication of the dependability of the methods. The total phosphorus in the samples obtained by combining the phosphorus in the filtrate with the particulate phosphorus retained by the filter (column IV) is compared with the total phosphorus in the water obtained by direct analysis without filtration (column V). It is evident that some small losses result from filtration, but these do not greatly exceed the normal variation of the Deniges-Atkins method. The values for the particulate phosphorus are small, but are consistent within themselves. The smaller values do not greatly exceed that of the blanks employed and in one set of data (for Station 2468, August 20, 1935) the values for the particulate phosphorus are in doubt owing to uncertainty in the value of the blank. The values for dissolved organic phosphorus in these samples are consistently positive and larger than the apparent errors of the method. During a large part of the year, as will be shown, much less soluble organic phosphorus is present in the water. Since this fraction is obtained by taking the difference of two large measures, each subject to considerable errors, it sometimes eventuated at such times that negative values were obtained for this fraction. The methods employed evidently do not give an exact measure of the distribution of the phosphorus fractions, but they do serve to indicate the general magnitudes of the quantities in which each occurs.

The meaning of the particulate and dissolved fractions of organic phosphorus depends upon the properties of the barium sulfate filter. When a suspension of diatoms, *Nitzschia closterium*, containing a known amount of phosphorus is filtered, the phosphorus may be recovered quantitatively from the filter. The refiltration of a filtrate leaves no detectable amount of phosphorus upon the filter. Evidently diatoms and microorganisms of similar size are completely retained in the particulate fraction. Dr. Charles E. Renn has kindly tested the filter for the retention of bacteria. After filtering sea water containing some 400 bacteria per milliliter the filtrate contained about one-sixth that amount. The particulate organic phosphorus fraction probably contains the phosphorus of all the larger phytoplankton and smaller zoöplankton and the greater portion of the bacteria and detritus as well. The dissolved organic phosphorus fraction may include a small

TABLE II

Specimen of data on phosphorus fractions in samples of sea water. Concentrations expressed as milligrams PO_4 per cubic meter.

Depth in meters	I Inorganic phosphorus	II Particulate phosphorus	III Phosphorus in filtrate	IV Total phosphorus II + III	V Total phosphorus. Direct analysis	VI Difference	VII Organic phosphorus III − I
1	45	10	64	74	62		
			70	80	86		
			68	78			
			67	77	71	+ 6	22
10	27	13	64	77	68		
			60	73	86		
			64	77			
			63	76	77	− 1	36
20	39	14	66	80	86		
			70	84	86		
			45	59			
			60	74	86	−12	21
60	110	6	116		130		
					116	− 1	6
				122	123		
100	110	4	126		142		
					142		
				130	142	−12	16
125	115	5	132		138		
					146		
				137	142	− 5	17
					160		
					156		
150	111	5	142	147	158	−11	31
200	123	5	152		154		
					162		
				157	158	− 1	29
225	108	8	148		162		
					158		
				156	160	− 4	40

portion of the bacterial flora, perhaps some minute nannoplankton, and detritus which has been reduced to the smallest dimensions in addition to organic compounds of phosphorus in colloidal form or in true solution. Renn (1937) has estimated that a bacterial population of 100,000 cells per milliliter would represent only 2.9 mg. PO_4 per cubic meter. It is evident that the much larger values of dissolved organic phosphorus obtained in our analyses can be due in only negligible part to the presence of bacteria. We believe, consequently, that our measurements represent chiefly the presence of phosphorus compounds in solution.

TABLE III

Inorganic phosphorus. Concentrations expressed in milligrams PO_4 per cubic meter. Depths not corrected for wire angle, which in no case would reduce by more than 4 per cent.

Depth in meters	May 18 1935	August 21 1935	November 8–9 1935	February 26 1936	May 14 1936
1	35	5	45	105	14
10	28	21	27	102	10
20	34	53	39	103	15
30	59	96	78	99	82
40	70	92	73	100	95
50	—	—	77	96	97
60	97	93	110	88	116
80	105	110	89	99	117
100	108	109	110	95	120
125	114	107	115	99	129
150	122	122	111	96	147
175	138	132	123	131	152
200	146	137	123	141	146
225	161	136	106	143	157
250	170	139		139	

The distribution of phosphorus in the three forms into which it has been separated is recorded in Tables III, IV, V and VI. Inorganic phosphate represents by far the greater quantity of phosphorus in the water amounting to 72 to 92 per cent of the total at different times. It is rather uniformly distributed at depths greater than 80–100 meters throughout the year, the concentrations increasing somewhat with depth. In the superficial layers, as has been frequently observed elsewhere, the inorganic phosphate becomes greatly reduced in quantity in the spring and is restored to concentrations characteristic of greater depths during the winter.

Particulate organic phosphorus, representing organisms and detritus, is in general the smallest of the three fractions, amounting to about 5 per cent of the total. It occurs in greatest quantity in the upper layers—above 40 meters—corresponding to the observed distribution of phytoplankton (Gran and Braarud, 1935). The quantities in these layers are highest in spring; in midwinter the quantity in surface water is scarcely to be distinguished from that in deep water. The values obtained in August are subject to doubt. Below the photosynthetic zone the distribution of filterable organic phosphorus is on the whole very uniform, amounting to about 5 γ PO_4 per liter. The distribution and magnitude of the concentrations of filterable phosphorus agree well with that of particulate nitrogen observed by von Brand (1937) in these waters in the summer of 1936.

TABLE IV

Particulate organic phosphorus. Concentrations expressed in milligrams PO_4 per cubic meter. Depths not corrected for wire angle, which in no case would reduce by more than 4 per cent.

Depth in meters	May 18 1935	August 21 1935	November 8–9 1935	February 26 1936	May 14 1936
1	20	13	10	6	17
10	18	14	13	5	13
20	15	15	14	5	20
30	20	7	9	4	12
40	12	8	7	4	0
50	—	—	5	4	8
60	5	5	6	6	9
80	8	6	4	4	12
100	5	5	4	4	3
125	4	3	5	3	2
150	3	—	5	3	3
175	5	3	13	3	1
200	4	3	5	3	7
225	4	4	8	4	7
250	6			5	

In May dissolved organic phosphorus occurred in only minimal quantities in the water of all depths except near the surface. During the summer the concentration increases markedly until November, when over 20 per cent of the total phosphorus is in this form. In the early winter there is a rapid disappearance of this form of phosphorus, associated in time with the increase in concentration of inorganic phosphate in the upper waters. The appearance of organic phosphorus commences in May at the surface, and the concentrations appear to grow from the surface downward. Not until November are high concentrations observed near the bottom. These observations suggest that considerable decomposition is taking place throughout the water column and in particular in those depths where phyto- and zoöplankton are known to exist in greatest numbers; and that at this station decomposition at the bottom may be relatively unimportant. The findings concerning organic phosphorus are somewhat similar to those of Kreps and Osadchik (1933), who made studies in Barents Sea. They found organic phosphorus to show a gradual increase from August to January reaching concentrations of some 40 mg. P_2O_5 per cubic meter and actually exceeding the inorganic phosphorus during the latter month. Their observations, which did not cover the earlier part of the year, showed the greatest concentrations in the deeper waters. As will be pointed out in a subsequent publication, the seasonal distribution of soluble organic phosphorus has some resemblance to that of ammonia, which may be considered to be a somewhat analogous stage in the nitrogen cycle.

TABLE V

Dissolved organic phosphorus. Concentrations expressed in milligrams PO_4 per cubic meter. Depths not corrected for wire angle, which in no case would reduce by more than 4 per cent.

Depth in meters	May 18 1935	August 21 1935	November 8–9 1935	February 26 1936	May 14 1936
1	30	49	21	− 2	12
10	15	36	35	0	0
20	−1	50	29	22	35
30	−4	14	7	14	18
40	3	24	36	− 3	3
50	—	—	43	5	3
60	8	36	7	1	26
80	0	24	50	9	55
100	2	30	24	21	22
125	−3	29	20	21	22
150	2	6	38	22	9
175	−6	20	20	4	−11
200	−7	22	30	6	8
225	−2	17	43	− 4	10
250	8			−10	

The data recorded in Tables III, IV and V have been submitted to further analysis with a view to determining in so far as possible, just what alterations take place in the phosphorus cycle at various depths and at different times of year.

The column of water is considered to be virtually a closed system in which every exchange with the surroundings is exactly balanced by an equal and opposite exchange. By dividing the column into a number of segments lying at different depths, in which the quantity of phosphorus in the different forms is recorded from time to time, and by observing certain general biological and hydrographic principles, it becomes possible to estimate to what extent changes in the concentrations of each form of phosphorus may be derived from processes taking place in situ, and to what extent vertical movements of phosphorus from one segment or layer to another must be postulated.

To obtain a workable body of data, Table VI has been drawn up recording the quantity of phosphorus present in each of the three forms for each of four layers each of 60 meters depth at each time of observation. The values are obtained by graphical integration and are expressed as percentages of the total phosphorus in a water column of 240 meters depth at each time of observation. In analyzing these data the following premises are held:

TABLE VI

Summary of distribution of phosphorus fractions.

	Depth in meters	May 18 1935	Aug. 20 1935	Nov. 8 1935	Feb. 26 1936	May 14 1936
Total P as grams PO_4 per sq. m.	0–240	28.7	31.0	32.9	29.9	34.4
Percentage of total phosphorus in each 60-meter layer	0–60	16.4	20.6	18.0	22.0	14.9
	60–120	23.7	23.2	25.0	23.0	28.0
	120–180	27.0	26.3	28.0	25.0	27.9
	180–240	32.9	29.9	29.0	30.0	29.2
	Total	100.0	100.0	100.0	100.0	100.0
Inorganic phosphorus as percentage of total	0–60	11.9	12.6	11.3	19.7	10.6
	60–120	22.1	16.8	18.7	19.4	20.8
	120–180	26.0	22.5	21.6	21.1	25.0
	180–240	32.0	25.6	21.2	28.7	26.5
	Total	92.0	77.5	72.8	88.9	82.9
Dissolved organic phosphorus as percentage of total	0–60	1.5	6.2	5.0	1.4	2.3
	60–120	0.4	5.4	5.4	2.7	6.0
	120–180	0.2	3.2	5.0	3.3	2.5
	180–240	0.0	3.7	6.4	0.6	1.7
	Total	2.1	18.5	21.8	8.0	12.5
Particulate organic phosphorus (organisms and detritus) as percentage of total	0–60	3.0	1.8	1.7	0.9	2.0
	60–120	1.2	1.0	0.9	0.9	1.2
	120–180	0.8	0.6	1.4	0.6	0.4
	180–240	0.9	0.6	1.4	0.7	1.0
	Total	5.9	4.0	5.4	3.1	4.6

1. *The horizontal exchange due to the drift of water past the station may be neglected.* This premise is not justified on the ground that the

station is located in a region of minimal drift. There can be little doubt that water is constantly drifting past the station. The observed changes in salinity demonstrate this. The total phosphorus recorded varies ± 7 per cent from the mean value throughout the year. Since this variation shows no seasonal sequence, the total phosphorus being lowest in May, 1935 and maximal in May, 1936, there evidently is some variation in the character of the water occupying the station at different times. These differences are eliminated by expressing the phosphorus fractions as percentages of the total, a procedure which imposes artificially the character of a closed system upon the set of data. The justification of this procedure lies in the relatively small differences in total phosphorus observed from time to time, and in the fact that on the whole the horizontal distribution of phosphorus throughout the Gulf at any time, at least to judge by inorganic PO_4, is much more uniform than is the vertical distribution. The horizontal distribution of PO_4 at various depths throughout the Gulf as observed in May, 1934 are shown in Fig. 4 and illustrate this fact. The general character of the phosphorus cycle may be supposed to be similar in all parts of the basin.

2. *Phosphate present as zoöplankton and nekton and not sampled by the water bottle may be ignored.* A large number of vertical zoöplankton hauls made throughout the years 1933–34 in all parts of the Gulf yielded an average catch of 40 cc. dry plankton per square meter of surface. It may be estimated from analyses made on such material that this would contain about 0.4 per cent of the total phosphorus in the water from which it was strained. Since the particulate organic phosphorus amounts to about ten times this quantity, it may be seen that the neglect of this fraction does not introduce a significant error.

3. *All synthesis of particulate or soluble organic phosphorus compounds from inorganic phosphate takes place in the upper layer.* This is justified by Clarke's measurements on the penetration of light into the Gulf of Maine and on determinations of the compensation point in photosynthesis by diatoms in bottle experiments at different depths (Clarke and Oster, 1934).

4. *All downward movement of phosphorus is due to the sinking of organisms (particulate organic phosphorus).* This is the only fraction affected by gravity. It is also the only fraction displaying a well-marked concentration gradient decreasing downward—a condition essential for downward dispersal by eddy conductivity.

5. *All upward movement of phosphorus is due to the transport of inorganic PO_4 by eddy conductivity.* The gradient of concentration of inorganic PO_4 increases downward and is well marked except in mid-

winter. The soluble organic phosphorus never develops a strong gradient in this direction. Since it is present in much smaller concentrations than is the inorganic phosphate, it may safely be ignored in considering vertical transport by eddy conductivity.

6. *All observed transformations in any layer are attributed to processes occurring in that layer, except so far as vertical transport must be postulated to account for the transformation.* This premise is introduced since without it a unique solution cannot be obtained. It implies that all values arrived at for vertical exchange are minimal.

7. *The portion of the exchange in which the cycle runs to completion is necessarily ignored. All values for the magnitude of the exchange are consequently minimal.*

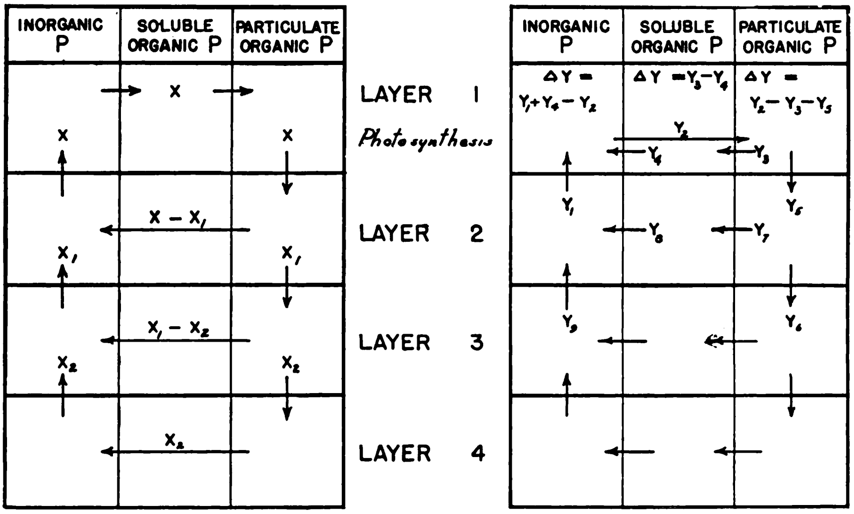

Fig. 2. See text.

A consideration of this limitation may serve to make clear the general basis of the analysis. If we start with the system in a steady state and if, during the period between two sets of observations the cycle has proceeded without change in the relative velocity of the processes in any part, the distribution of the fractions of phosphate in all parts of the system will be the same at the end as it was in the beginning. This does not mean that no exchanges of phosphate between different parts of the system have taken place, rather that all exchanges are exactly compensated. While the system is in a steady state an unobservable quantity of phosphate is undergoing transformation from each stage in the cycle to the next stage. If the system is disturbed, as through seasonal changes in the physical conditions, then transformations of one sort may proceed more rapidly than those of another with the result that differences in the distribution of phosphorus are observed, and from these differences the magnitude and nature of the processes *which have caused* the differences may be deduced. The observations tell us nothing, however, of the basal level of activity on which the differences are superposed.[2]

Figure 2 illustrates the principle of the method. At any time there will be a basal level of activity represented by the transformation of an unobservable quantity of phosphorus, x, through each stage in the cycle. This quantity will have been transported upward from layer 2 into layer 1 to be synthesized into particulate organic form. If the system is to remain unchanged, the equivalent of this material must have sunk back into the deeper layers and been decomposed, passing through the soluble organic form, to exactly replace that which was transported upward. Portions of x, designated as x_1, x_2, etc. may sink to deeper layers before undergoing transformations from organic to inorganic form. The general conditions are that the quantity of x entering and leaving any part of the system shall be equal, that x move upward as inorganic phosphate (Postulate 5), and downward as filterable organic phosphorus (Postulate 4), that it represent synthesis of filterable organic phosphorus only in the upper layer, and that it represent a transformation of organic into inorganic phosphorus in any layer.

If the system is disturbed between observations, then changes in the quantity of phosphorus, ΔY, in any form and part of the system may be observed. These changes may be accounted for only by additional exchanges between the various parts of the system. The problem is to determine the minimal additional exchanges of this sort, Y_1, Y_2, Y_3 etc., which will account for the change in each part of the system in accordance with the postulates laid down above. The general conditions are that ΔY, the change in any fraction in any layer shall equal the difference in Y_1, Y_2, Y_3 etc., the amounts of phosphorus entering or leaving that fraction and layer during the period between observations. Furthermore, ΔY must be accounted for so far as possible by exchanges taking place within the layer in question (Postulate 6).

An attempted analysis of the changes in phosphorus distribution is presented in Tables VII, VIII and IX.

February to May (Table VII) represents the period in which the

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[2] The method is analogous to the integration of a differential equation, the unobserved basal activity corresponding to the constant of integration. It is only in proportion as the system undergoes great seasonal fluctuation that the partial effects observed approach the total exchanges taking place. The method is applicable consequently particularly to studies made in high latitudes.

great spring flowering of phytoplankton occurs. During this period an amount of phosphorus equivalent to 9.1 per cent of the total disappears from the inorganic phosphate of the upper layer. Of this only 2.0 per cent can be accounted for as an increase in particulate and soluble organic phosphorus remaining in that layer. Seven and one-tenth per cent must have sunk to the deeper layers following its synthesis into organic matter. Only one-eighth of the phosphorus absorbed in photosynthesis has remained as particulate matter in the upper layer. This observation accords with the conclusion of Harvey (1934) that several times more vegetation is produced during the spring flowering of diatoms in the English Channel than is found there at the time of its maximum.

Table VII

Balance sheet of phosphorus exchanges February 26 to May 14, 1936. Numbers represent the change in the phosphorus fractions as percentages of total phosphorus in water column.

Depths		Inorganic phosphorus	Soluble organic phosphorus	Particulate organic phosphorus
0–60 meters	Photosynthesis	−9.1	⟶	+9.1
	Decomposition		+0.9 ⟵	−0.9
		0 ⟵	0	
	Exchange with layer below	0	0	−7.1
	Net change	−9.1	+0.9	+1.1
60–120 meters	Exchange with layer above	0	0	+7.1
	Decomposition		+4.7 ⟵	−4.7
		+1.4 ⟵	−1.4	
	Exchange with layer below	0	0	−2.1
	Net change	+1.4	+3.3	+0.3
120–180 meters	Exchange with layer above	0	0	+2.1
	Decomposition		+0.9 ⟵	−0.9
		+1.7 ⟵	−1.7	
	Exchange with layer below	+2.2	0	−1.4
	Net change	+3.9	−0.8	−0.2
180–240 meters	Exchange with layer above	−2.2	0	+1.4
	Decomposition	0	+1.1 ⟵	−1.1
	Net change	−2.2	+1.1	+0.3

To account for the increasing concentrations of inorganic phosphorus in the deeper layers after allowing for the greatest possible decomposition in situ at least 2.1 per cent must sink past the 120-meter level and 1.4 per cent past the 180-meter level. The phosphorus removed from inorganic form in the upper layer by photosynthesis is redistributed during the spring through considerable depths by the sinking of particulate matter. It is unnecessary to assume that any of the particulate matter sinks beyond the lower level before undergoing decomposition, though it is possible that this may be the case.

May to November (Table VIII) includes the greater part of the growing season. The important feature of this period is the appearance of large quantities of dissolved organic phosphorus at all depths. One-fifth of all the phosphorus in the water is in this form in November. This material can have been produced only by photosynthetic processes taking place in the upper layer. It must have been set free for the most part by decomposition of the particulate fraction in the layer in which it is observed (Postulate 5). In order to account for the

TABLE VIII

Balance sheet of phosphorus exchanges May 18, 1935 to November 8, 1935. Numbers represent the change in the phosphorus fractions as percentages of total phosphorus in water column.

Depths		Inorganic phosphorus	Soluble organic phosphorus	Particulate organic phosphorus
0–60 meters	Photosynthesis	−19.2	→	+19.2
	Decomposition		+3.5 ←	−3.5
		0 ←	0	
	Exchange with layer below	+18.6	0	−17.0
	Net change	−0.6	+3.5	−1.3
60–120 meters	Exchange with layer above	−18.6	0	+17.0
	Decomposition		+5.0 ←	−5.0
		0 ←	0	
	Exchange with layer below	+15.2	0	−12.3
	Net change	−3.4	+5.0	−0.3
120–180 meters	Exchange with layer above	−15.2	0	+12.3
	Decomposition		+4.8 ←	−4.8
		0 ←	0	
	Exchange with layer below	+10.8	0	−6.9
	Net change	−4.4	+4.8	+0.6
180–240 meters	Exchange with layer above	−10.8	0	+6.9
	Decomposition		+6.4 ←	−6.4
		0 ←	0	
	Net change	−10.8	+6.4	+0.5

quantities of dissolved organic phosphorus observed, a large vertical movement of inorganic phosphorus upward through all depths must be postulated as well as an equivalent sinking of organisms to the sites at which the soluble organic phosphate appears. Over 17 per cent of the total phosphorus in the water must pass through the zone of photosynthesis in the course of the six summer months. Since the account is balanced without supposing any phosphorus to pass from the organic back to the inorganic form, a process which must certainly be taking place, this figure may be far below that actually obtaining.

TABLE IX

Balance sheet of phosphorus exchanges November 8, 1935 to February 26, 1936. Numbers represent percentages of total phosphorus in entire water column.

Depths		Inorganic phosphorus	Soluble organic phosphorus	Particulate organic phosphorus
0–60 meters	Photosynthesis	0	→	0
	Decomposition		+0.6 ←	−0.6
		+4.2 ←	−4.2	
	Exchange with layer below	+4.2	0	−0.2
	Net change	+8.4	−3.6	−0.8
60–120 meters	Exchange with layer above	−4.2	0	+0.2
	Decomposition		0 ←	0
		+2.7 ←	−2.7	
	Exchange with layer below	+2.2	0	−0.2
	Net change	+0.7	−2.7	0
120–180 meters	Exchange with layer above	−2.2	0	+0.2
	Decomposition		0 ←	0
		+1.7 ←	−1.7	
	Exchange with layer below	0	0	−1.0
	Net change	−0.5	−1.7	−0.8
180–240 meters	Exchange with layer above	0	0	+1.0
	Decomposition		+1.7 ←	−1.7
		+7.5 ←	−7.5	
	Net change	+7.5	−5.8	−0.7

November to February (Table IX) is marked chiefly by the regeneration of inorganic phosphorus, which increases by 16 per cent of the total, and by the equalization of the concentration of this fraction throughout the water column. The table shows that this regeneration is made to a large extent at the expense of the soluble organic phosphorus, that the transformation takes place throughout the entire range of depths, though greatest near the bottom. The decomposition of organic phosphorus compounds in situ and the vertical transport of inorganic phosphate are about equally important in effecting the equalization of the concentration of the latter throughout the water column.

THE MECHANISM OF VERTICAL TRANSPORT

The foregoing analysis indicates that very considerable exchanges of phosphorus take place between various depths of water. At the same time these exchanges appear to diminish in extent as the depth increases. Downward movement has been attributed to the sinking of particulate matter under the influence of gravity. There appears to be no difficulty in considering that in depths of a few hundred meters organized particles of the dimensions of diatoms would sink to the bottom before undergoing decomposition. If such were the case very large quantities of phosphorus would be withdrawn from the water during each growing season. This may be the case in shallow waters, but it does not appear to be happening in the western basin of the Gulf of Maine. If so the total phosphorus in the water should show a marked seasonal change. The situation is probably complicated by biological considerations. Harvey (1934) has presented evidence that the stock of phytoplankton is grazed down by zoöplankton during the summer. This conclusion suggests that the zoöplankton are important active agents in converting particulate organic phosphorus into its decomposition products. Since these animals, and particularly the copepods, make extensive diurnal vertical migrations, and since some time must elapse between the taking of food near the surface and its elimination as waste products, they provide an agency for a limited vertical transport of organic material. From this viewpoint the zoöplankton become an important agency in maintaining the fertility of the water for phytoplankton, since they hasten the conversion of bound nutrients into inorganic form and prevent these nutrients from becoming unavailable by the sinking of particulate matter to great depths or to the bottom.

The vertical transport of inorganic phosphate is simpler since it can be effected only by the mixing of the water. It is pertinent to inquire whether the conditions are such as to permit of the amounts of transport deduced during the various periods of observation. The amount of a constituent, Q, passing through unit horizontal surface in unit time depends upon the gradient of concentration of the constituent

dc/ds and the coefficient of eddy conductivity, A (Austausch coefficient).

$$Q = Adc/ds$$

The coefficient of eddy conductivity, A, represents the volume of water exchanged through each horizontal unit surface in unit time.

The gradient of phosphate concentration observed in February, May and November is shown in Fig. 3. Between May and November, when large vertical movements have been deduced, a well-marked gradient exists particularly in the upper layers, as is required for such movements. In February this gradient has disappeared, and the concentration of phosphate is equal at all depths down to 150 meters. No amount of mixing can effect a change in its vertical distribution. Since this condition must exist during a considerable portion of the winter, it is not surprising that the vertical transports *deduced from our data* between November and May are smaller than those observed in the summer.

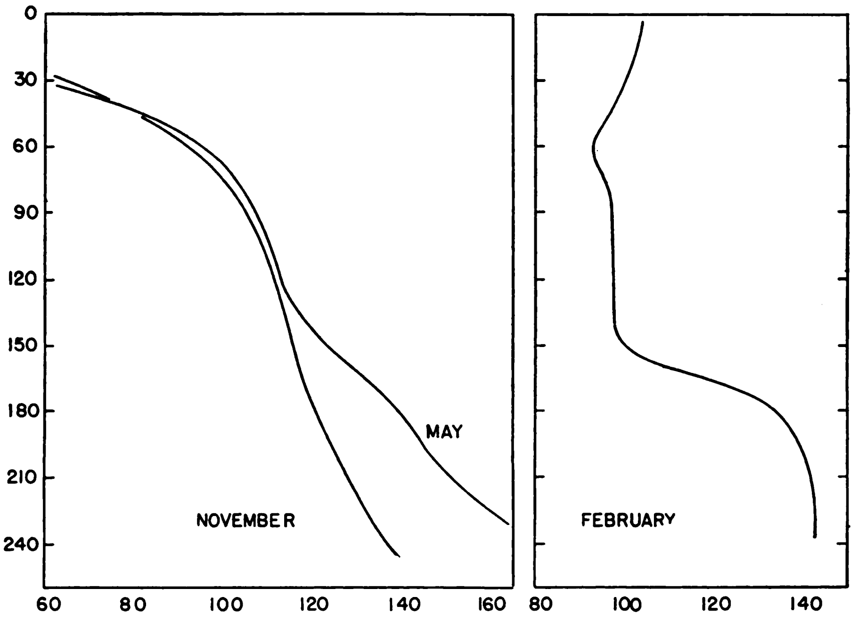

FIG. 3. Distribution of inorganic phosphate concentration with depth in November, 1935 and February and May, 1936 at standard station in the western basin of the Gulf of Maine. Depths in meters measured downward along the ordinate; concentrations in milligrams PO_4 per cubic meter along the abscissa.

A knowledge of the coefficient of eddy conductivity, A, is the key to understanding the nutritive conditions in deep bodies of water.

Methods of estimating its value are so indirect that little is known of its magnitude under any circumstances. Although our data are admittedly very unprecise and yield only minimal values for the exchange, it is nevertheless of some interest to use it in estimating the coefficient required to account for the transport of phosphate in the Gulf of Maine. The gradient of phosphate concentration is sufficiently uniform throughout the period May–November to permit a single value to be taken at any level as representative of the entire period. This is not the case during the remainder of the year. We have calculated the value of *A* for the boundary of each of the layers, using the data presented in Table VIII for estimating *Q* and the slopes of the curves in Fig. 3 for *dc*/*ds*. The result is shown in Table X. The values of *A* are minimal and are less reliable at the greater depths. The values obtained are not unreasonable. Seiwell considered *A* to equal 2 C.G.S. units in the thermocline of the tropical Atlantic, whereas values increasing to 50 C.G.S. units have been obtained in various waters (Seiwell, 1935).

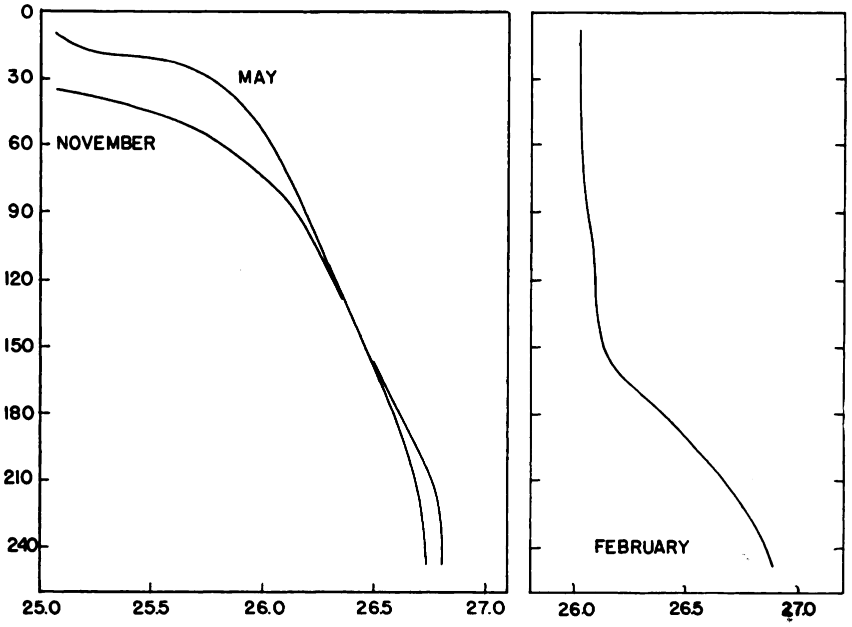

FIG. 4. Distribution of density, σ_t, with depth in November, 1935, and February and May, 1936, at standard station in the western basin of the Gulf of Maine. Depths in meters measured downward along the ordinate; density, σ_t, measured along the abscissa.

The value of the coefficient of eddy conductivity depends upon the forces responsible for mixing and varies inversely with the stability, $\frac{d\sigma_t}{ds}$ of the water. If K represent the mixing forces,

$$K = A \times \frac{d\sigma_t}{ds}$$

Seiwell considers that $K = 4.73 \times 10^{-4}$ in the thermocline of the North Atlantic. Figure 7 shows the distribution of density, σ_t, with depth at the station in the Gulf of Maine in May, 1935 and in November. From these curves the representative values of $\frac{d\sigma_t}{ds}$ entered in Table X are taken. The values of K given by multiplying $\frac{d\sigma_t}{ds}$ by A are of the order obtained by Seiwell. It is concluded that the vertical transport of inorganic phosphate deduced from the seasonal change in the distribution of the various fractions of phosphorus compounds does not require unreasonable assumptions concerning the magnitude of the eddy conductivity.

TABLE X

Estimation of coefficient of eddy conductivity in Gulf of Maine, May to November, 1935.

Depths	Q		dc/ds	A	$d\sigma_t/ds$	$K = A \times \frac{d\sigma_t}{ds}$
meters	*per cent in 3 months*	$\frac{mg.}{cm.^3 \times sec.}$	$\frac{mg.}{ml.\ cm.}$	$\frac{ml.}{cm. \times sec.}$	$\frac{grams}{ml. \times cm.}$	
60	>18	$>3.5 \times 10^{-8}$	6.6×10^{-9}	> 5.2	1.0×10^{-4}	$>5.2 \times 10^{-4}$
120	>15	$>2.4 \times 10^{-8}$	2.0×10^{-9}	>12.0	0.5×10^{-4}	$>6.0 \times 10^{-4}$
180	>10	$>2.0 \times 10^{-8}$	3.0×10^{-9}	> 6.6	0.4×10^{-4}	$>2.6 \times 10^{-4}$

SUMMARY

1. Methods are described for the determination of the phosphorus present in particulate form and of the total phosphorus in a sample of sea water.

2. The distribution of phosphorus present as inorganic phosphate, as dissolved organic compounds, and as particulate matter (detritus and microörganisms) has been determined at all depths throughout the year at a station in the western part of the Gulf of Maine.

3. In late winter over 90 per cent of the phosphorus is in inorganic form and three-quarters of the remainder is present as soluble organic compounds.

4. In the spring—February to May, inorganic phosphorus is converted to organic form by photosynthesis in the upper layer of water. Most of this fraction sinks to considerable depths before undergoing decomposition.

5. During the summer—May to November, large quantities of dissolved organic phosphorus appear at all depths, indicating a very considerable transport of inorganic phosphate from deep water to the surface and the sinking of an equivalent amount of phosphorus in particulate form to the depths in which organic compounds are liberated by decomposition. Decomposition appears to take place throughout the water column.

6. During the winter—November to February, the organic phosphorus compounds are converted to inorganic phosphate. This and vertical mixing of preformed phosphate are about equally important in bringing about the equalization of phosphate concentrations throughout the depth of water.

7. A method is described for analyzing quantitatively the factors producing a seasonal change in the distribution of a compound such as phosphorus. It is shown that the vertical transport of material within the water mass demanded by such an analysis may be accounted for reasonably by the hydrographic conditions obtaining.

8. Values of the coefficient of eddy conductivity at several depths are obtained.

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