PAPERS IN PHYSICAL OCEANOGRAPHY AND METEOROLOGY

PUBLISHED BY

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

AND

WOODS HOLE OCEANOGRAPHIC INSTITUTION

(In continuation of Massachusetts Institute of Technology Meteorological Papers)

VOL. III, NO. 4

THE CYCLE OF PHOSPHORUS IN THE WESTERN BASIN OF THE NORTH ATLANTIC

I

Phosphate Phosphorus

BY

H. R. SEIWELL

Contribution No. 64 from the Woods Hole Oceanographic Institution

CAMBRIDGE, MASSACHUSETTS

April, 1935

CONTENTS

INTRODUCTION

The importance of phosphorus for organic production in the sea appears to have been recognized first by Brandt (1899) and the earlier determinations of this element in the coastal seas of northern Europe (Brandt, 1920; Raben, 1920; Mathews, 1917) suggested a correlation between seasonal variation of phosphate and growth of phytoplankton. These earlier determinations were later shown to be too high (Atkins, 1926, a) and did not indicate the complete exhaustion of phosphate from the water, so it was not until several years later that Atkins (1923), employing the rapid and more accurate colorimetric ceruleo-molybdate method of Denigès, illustrated the complete dependence of algal growth on phosphate (in the English Channel) and thus established the foundation for modern studies of marine chemical fertility.[1]

The beginning of our knowledge of phosphate content of the open ocean may, as far as is known to me, also be attributed to Atkins (1926, a) and even though these early results were frequently somewhat vitiated by storing of the samples before analyses, they represented the order of magnitude of phosphate concentration in the sea. Within recent years phosphate determination has become a component part of the program of most deep sea investigations and much general information on its distribution and variation in the open ocean has been brought to light.

From a geographical standpoint the most widespread investigation of phosphate in the oceans (Atlantic, Pacific, and Indian) was made on the recent cruise of the "Dana" (Thomsen, 1931); and this together with the researches from the various "Discovery" cruises, principally in the South Atlantic (Deacon, 1933); by Ruud (1930) on the whale factory s/s "Vikingen" in the Weddell Sea; by the "Meteor" both in the South Atlantic (Wattenberg, 1933) and northern North Atlantic (Böhnecke, et al, 1932); by the "Carnegie" in the North Atlantic and Pacific (Moberg, et al, 1930; Seiwell, 1931); by the "Nautilus" in the high latitudes of the North Atlantic (Sverdrup, 1933); and by the "Atlantis" in the western North Atlantic have all contributed a wealth of material to our knowledge of phosphate distribution in the ocean basins.[2,3]

The material for this report has been obtained principally from "Atlantis" cruises in the western North Atlantic and it is planned to follow the present account with a second part treating other phases involved in the phosphorus cycle of this region.

Professor Henry B. Bigelow has guided the preparation of this report and Professor C.-G. Rossby has been consulted on the theoretical discussion.

[1] See Atkins (1926, a) for references to earlier work.

[2] References to these cruises are not complete and merely serve as a guide to more detailed information.

[3] A number of important studies of the phosphate content of coastal waters of northern Europe and North America have been made during the past decade. For bibliography and references see especially: Gran and Thompson (1930); Gran (1932); Braarud and Klem (1931); and Buch (1932).

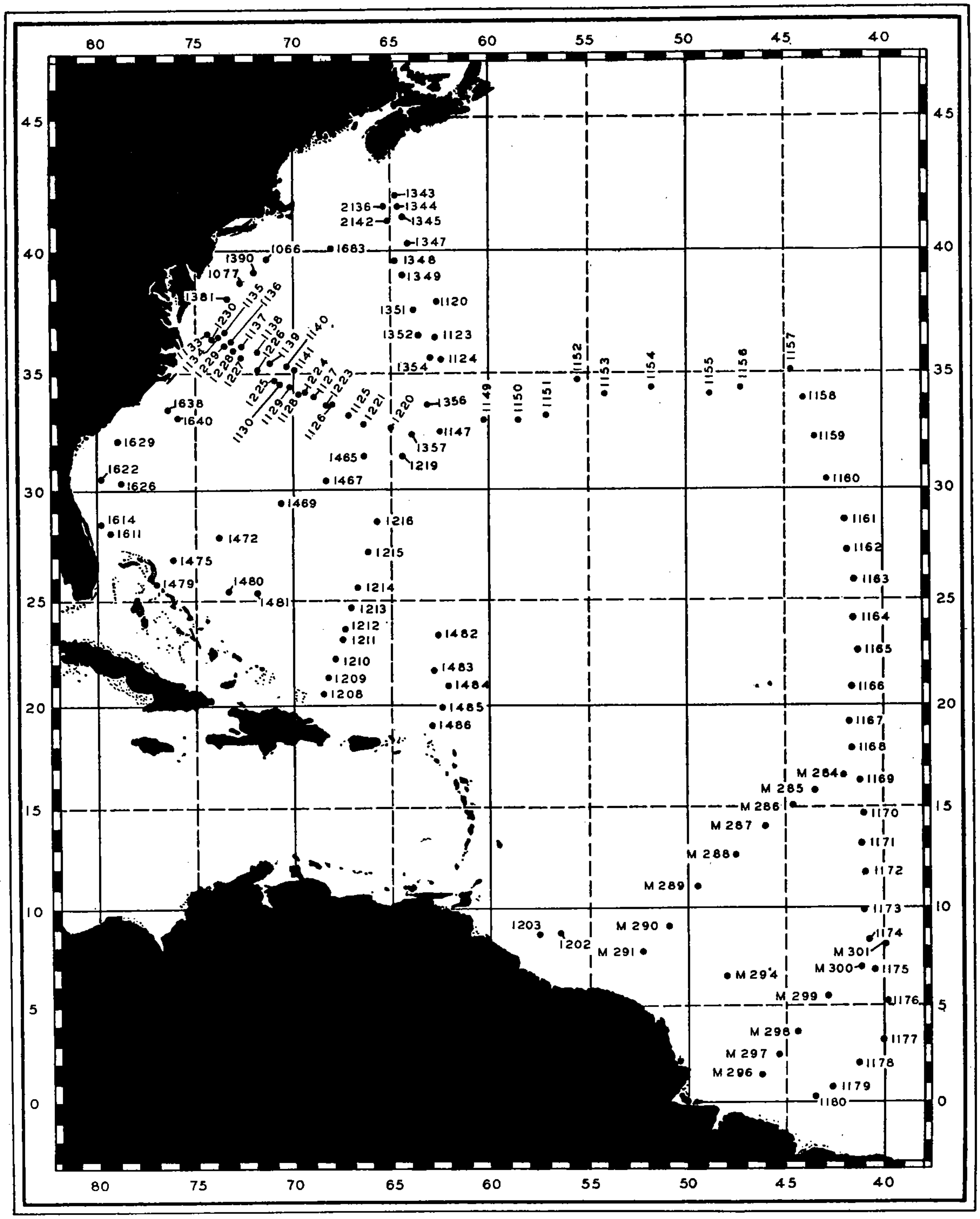

FIG. 1. Chart of area of investigation in western North Atlantic. All stations were made by "Atlantis" except M stations by "Meteor" (Wattenberg, 1933).

REGION OF INVESTIGATION

This discussion is confined to the western basin of the North Atlantic (fig. 1) and is based principally on observations obtained during the following cruises of "Atlantis":

Bermuda eastward to 35th meridian: stations 1147–1157, February 24 to March 4, 1932.

Latitude 35°N to equator, along 40th meridian: stations 1157–1179, March 4–21, 1932.

Haiti to Bermuda: stations 1208–1219, April 7–13, 1932.

Bermuda to Chesapeake Bay: stations 1134–1142, February 12–15, 1932; and stations 1220–1231, April 17–23, 1932.

Nova Scotia to Bermuda: stations 1343–1357, August 14–21, 1932.

Miscellaneous "Atlantis" stations: 1465–1486 and 1611–1640 made during the late winter and spring of 1933.

The "Atlantis" observations are published in the Bulletin Hydrographique (1933) without correction for salt or temperature error and the corrected data on which this report is based (page 8) is graphically presented herein and can be scaled with a fair degree of accuracy.

METHODS

With slight variations adapted to fit the particular conditions,[4,5] the "Atlantis" phosphate determinations for 1931 and 1932 were made by the colorimetric method of Denigès as modified by Atkins (1924).

Reagents

1. Ammonium molybdate-sulphuric acid mixture. A 10 per cent solution of ammonium molybdate is diluted with three times its volume of 50 per cent (by volume) sulphuric acid and kept in dark glass bottles; 2 cc are required for 100 cc of sample.

2. Stannous chloride solution. This solution is prepared fresh for each set of analyses by dissolving about 0.1 gram of tin foil in 2 cc of concentrated hydrochloric acid with one drop of 3 to 4 per cent copper sulphate solution and then diluting to 10 cc. Depending on the phosphate concentration of the sample, 1 to 3 drops are required per 100 cc of sample.

3. Standard phosphate solutions. A series of standard phosphate solutions with concentrations ranging from 6.2 to 62.0 milligrams of P per cubic meter, in 6.2 milligram intervals, were prepared for each series of analyses by diluting appropriate amounts of M/50,000 KH_2PO_4 with distilled water to 100 cc; the standards and samples are treated simultaneously with reagents.

[4] The 1933 "Atlantis" phosphate observations in the western basin of the North Atlantic (comprising a very small part of the total number) were made by investigators who used procedures differing from that described here (see Bulletin Hydrographique pour L'Annee, 1933).

[5] Also see Harvey (1928 and 1929) for discussion of method of phosphate estimation in sea water.

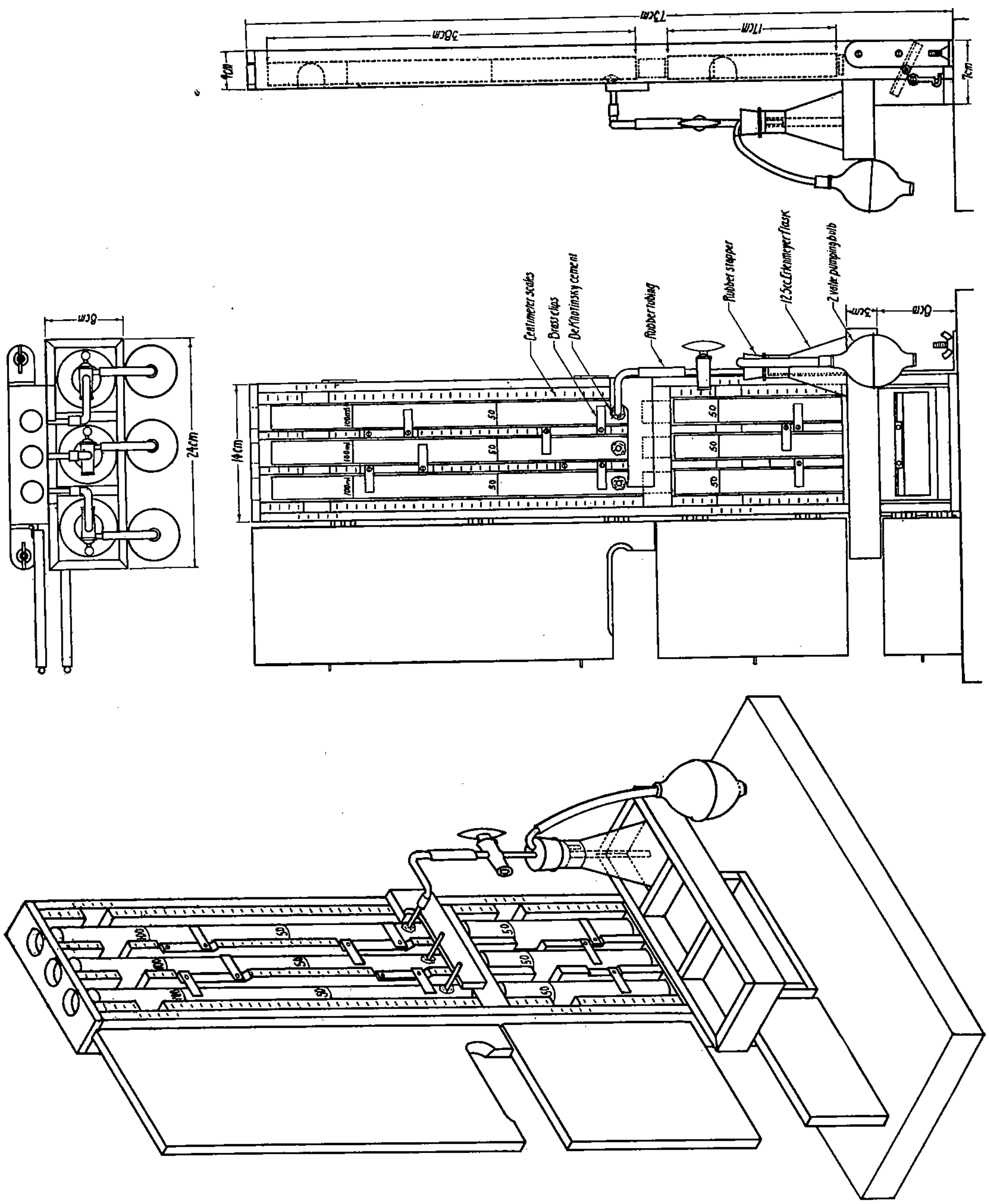

FIG. 2. Design of apparatus for colorimetric estimation of phosphate. See text, page 7.

Colorimeter

Figure 2 shows the design and construction of the colorimeter used on "Atlantis" from October 1932 to September 1933. The instrument and a colorimeter lamp were bolted to a firm table in a semidarkened corner of the laboratory. Color comparisons are made in the upper set of three uniform color comparison tubes (sample in center with consecutive standards on either side); this arrangement allows several readings to be made rapidly on each sample. The lower tubes are filled with clear distilled water unless the sea water sample (before adding reagents) is turbid or discolored in which case the color balance may be restored by placing a sea water sample without reagents in each tube below those containing the standard phosphate solutions.

Procedure

Phosphate analyses were completed within a few hours after collecting the samples and frequently it was necessary (because of other duties) to make determinations before the sea water samples had warmed up to laboratory temperature. During 1931 and 1932 temperatures of both standards and samples at time of comparison were recorded so that whenever necessary the results have been corrected according to the following equation:

$$P = P' + k_t(t_s - t_w)P'$$

where P is corrected phosphate value; P', the estimated phosphate value according to Beer's law; t_s, temperature of phosphate standard; t_w, temperature of sample at time of comparison; k_t, a coefficient for temperature influence on intensity of the phosphomolybdate blue (0.012 to 0.016 for conditions of this investigation, Brujewicz and Krasnova, 1933). By applying this temperature correction the original phosphate result may be increased 10 to 20 per cent and in a few extreme cases even higher; in general, greater corrections are applied to results from the great depths.

The data have not been corrected for salt error except as noted for certain purposes of calculation. The effect of sea salt on the colorimetric estimation of phosphate in sea water has been studied by Kalle (1934), Ibañez (1933), and Brujewicz and Krasnova (1933); whenever required the adjustment factor (1.34 to 1.36 for salinities between 32 o/oo and 38 o/oo) proposed by Brujewicz and Krasnova has been used.

Accuracy of Results

Because of the variable factors which may cause errors in phosphate analyses at sea it is not possible to assign definite limits of accuracy to the results on which this discussion is based. However, it is reasonable to assume (since most of the observations contained herein were made by a single investigator using the same apparatus and the same method) that the results, in general, have a fair relative correctness. And as they are in agreement with the few observations made by other observers in the area of investigation (page 33) it seems that the order of magnitude of correctness is about the same as that for customary analyses of this kind when made at sea. The question of variability of the results is discussed later (pages 21 and 27).

The ability of the individual observer to obtain reasonably consistent results from colorimetric analyses at sea (assuming that the procedure and apparatus is correct) depends largely on the variable sensitiveness of vision to different concentrations of color and on the amount of error which may arise from fatigue and eyestrain. Eyestrain in particular may become quite prominent as frequently the investigator must work long continuous periods to complete the analyses and the desire to obtain a large number of observations may sometimes unknowingly result in a sacrifice of accuracy. On the other hand, among different observers working under dissimilar conditions divergence of analytical results are liable to result both from the above factors as well as from the use of different technic and equipment, and from the varying degrees of correctness by which different individuals judge colors.[6] However, by the use of carefully worked out analytical procedures, and by the calibration of colorimeters, with mechanical and optical defects kept at a minimum, much can be done to eliminate errors.

[6] For discussion of fallacies in colorimetry see Dehn (1917).

VERTICAL DISTRIBUTION OF PHOSPHATE PHOSPHORUS

In vertical section the phosphate content of the western basin of the North Atlantic is lowest (usually 0–4 mg P per m^3) in the more or less homogeneous water overlying the thermocline[7] (<400 to >40 meters thick) below which it increases to a maximum value (<30 to >60 mg P m^3) at intermediate depths of usually 800 to 1000 meters. In still deeper water phosphate content either decreases or remains relatively constant so that at 2000 meters the usual horizontal range is 25 to 35 mg P per m^3. Significant phosphate gradients below depths of maximum concentration occur only when the maximum is high, e.g., in the southern half of the area. Within the area of investigation variations in the vertical phosphate gradient are principally due to: (1) variation in thickness of the phosphate poor surface layer; and (2) variation in value and depth of the maximum phosphate concentration. In order to bring out regional differences in the vertical distribution of phosphate, conditions as existing along the several "Atlantis" sections at the times of observation are considered separately.[8]

Northeastern Sargasso Sea Between Bermuda and 35th Meridian[9]

The distribution of phosphate along this section (fig. 3) is typical of the region which it crosses (fig. 1). During February 24 to March 4, 1932 the essential features to be stressed were as follows. The surface phosphate content was 1 to 3 mg P per cubic meter (table 1) and the phosphate poor layer, containing less than 5 mg P per cubic meter, extended to depths of 350 to 550 meters, below which phosphate increased to its maximum value (about 30 mg P per m^3; table 1) at intermediate depths of 800 to 1000 meters. In the still deeper water phosphate content declined but little with increasing depth (at 2000 meters values were usually between 25 and 27 mg P per m^3) so that the maximum values at intermediate depths are not well defined, but merely mark out the lower limit of the increasing phosphate gradient in the upper part of the water column (fig. 4).

At the time of observation the surface temperature along this section was probably near its annual minimum (17.69°–19.32°; table 1) and the water overlying the principle thermocline was nearly homogeneous (fig. 5). The depths at which the thermocline began are somewhat difficult to determine as there is no sharp distinction between it and the overlying water strata, but the first significant change of curvature on the temperature-depth graphs (fig. 5) usually began between 300 and 400 meters depth. As the thick overlying homogeneous layer of water in this region is probably an accumulation

[7] In this paper the depths designated as the beginning of the thermocline are those at which permanent significant decreases of temperature appear to begin, which are assumed to represent the maximum depths reached by homogeneous water.

[8] Phosphate values in this discussion are not corrected for salt error unless specifically indicated (page 7).

[9] Observed salinity range for this section is 34.91 o/oo to 36.69 o/oo; factor for correcting phosphate values for salt error is 1.35, according to Brujewicz and Krasnova (1933).

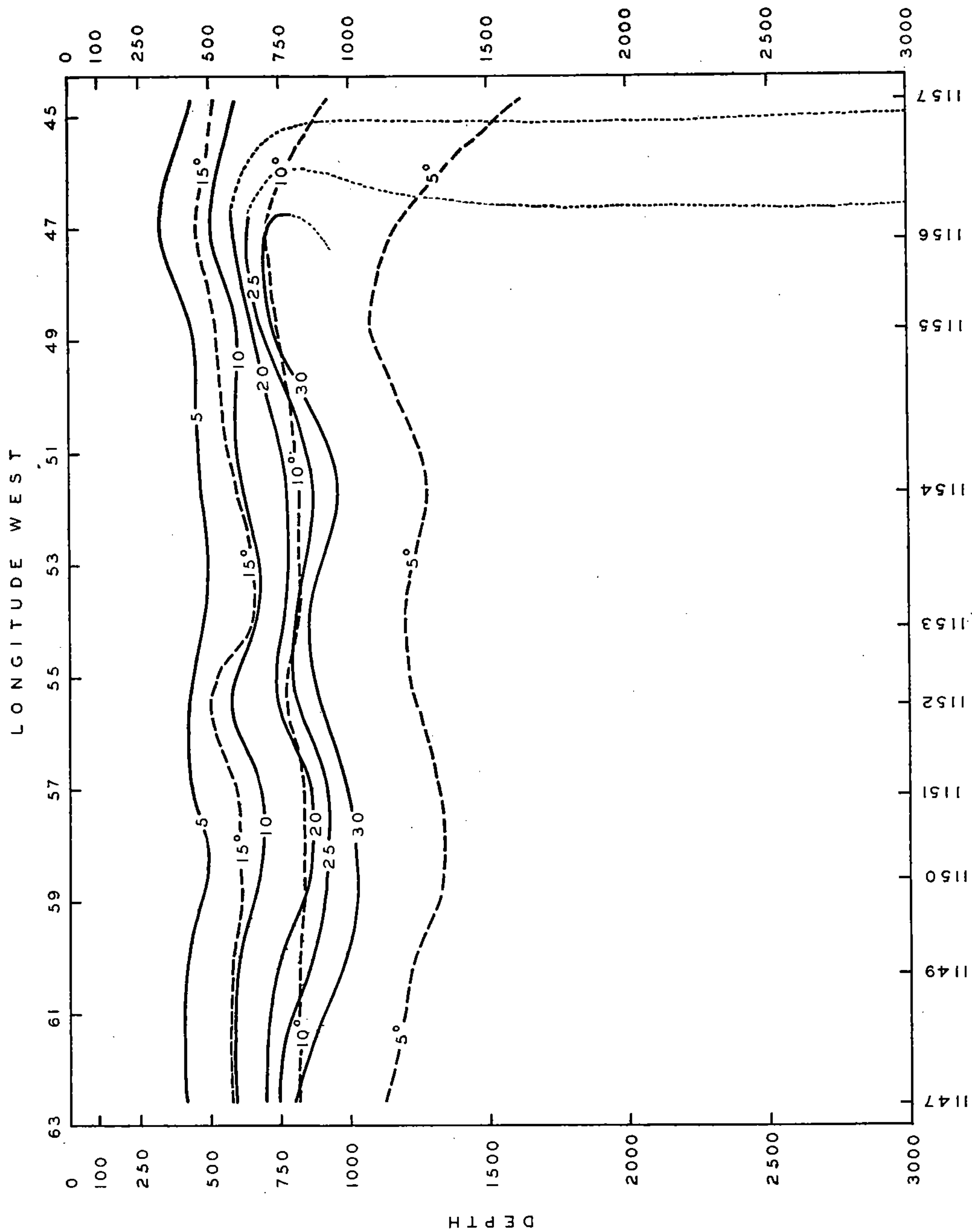

FIG. 3. Distribution of phosphate, milligrams of P per cubic meter, "Atlantis" stations 1147–1157, longitude 62°35′W to 44°40′W between latitude 32°37′N and 35°10′N; February–March 1932.

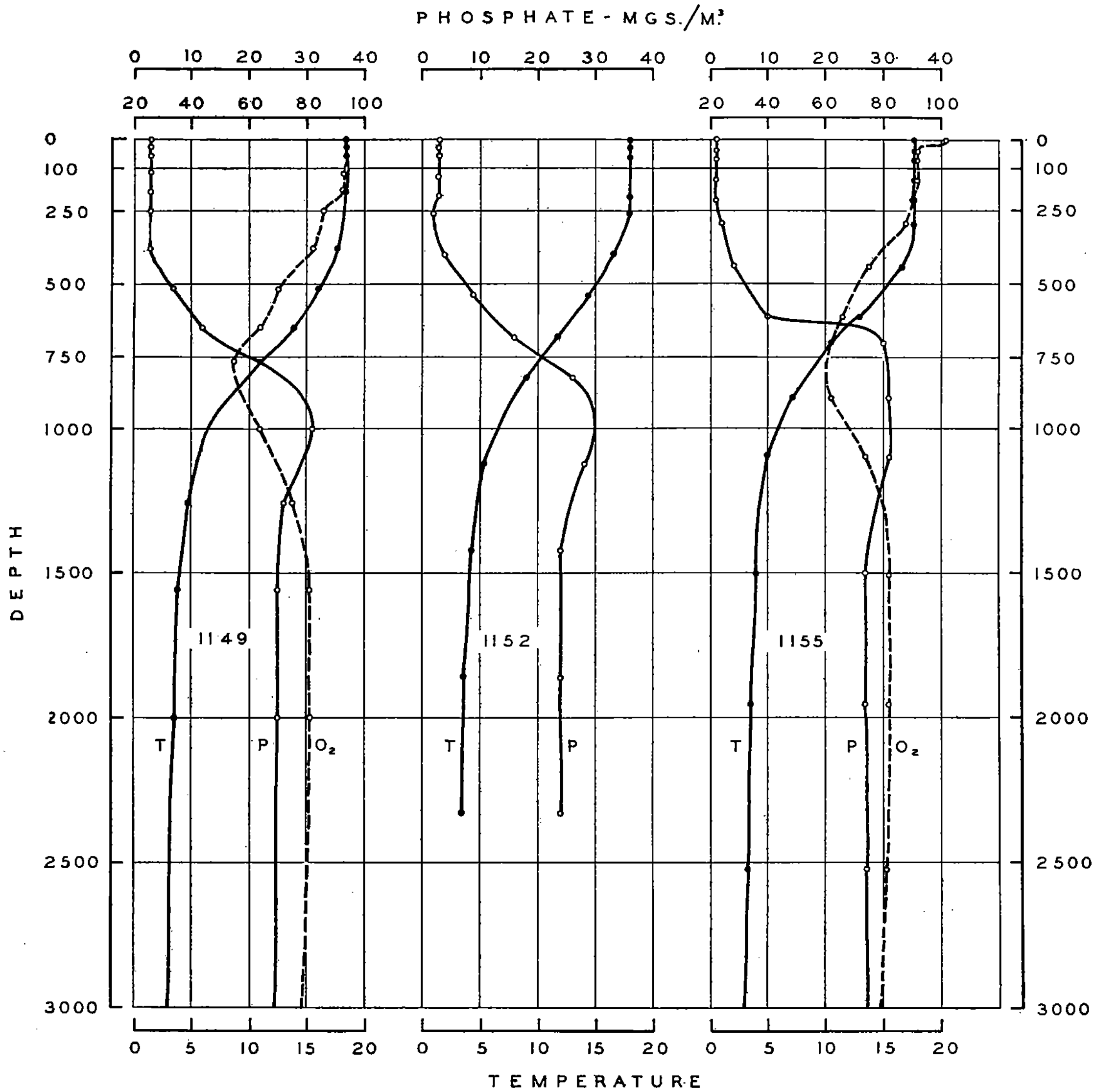

FIG. 4. Vertical distribution of phosphate (mg P per m³), oxygen (per cent of saturation), and temperature in northern Sargasso Sea; February–March 1932. For station positions see table 7.

of surface water it is understandable that its phosphate content should be very low (1–4 mg P per m^3) and its oxygen content very high (figs. 4, 5). The small but distinct oxygen and phosphate gradients sometimes occurring in the lower part of the homogeneous layer (see stations 1149, 1150, and 1151; fig. 5) are presumably due to a concentration of products resulting from decomposition of organic materials below the depth of plant activity which have not yet been redistributed throughout the entire layer. That complete stirring of the homogeneous layer occurs in winter appears to be indicated by the uniform vertical gradients of phosphate, oxygen and temperature as at stations 1152, 1153, and 1154 (fig. 5). Mixing of the homogeneous layer does not appear to extend into the phosphate rich layers of the thermocline (fig. 4) but will bring within range of plant organisms nutrient substances which may by various means tend to accumulate above the thermocline. Resistance of the water overlying the main thermocline to vertical mixing is greatly increased during summer by the development of an upper temporary thermocline about 100 to 150 meters thick due to warming of the surface layers, illustrated by station 1041 (36°55′N, 52° 41′W; August 15, 1931; fig. 5).[10]

Throughout this section significant increases of phosphate and decreases of oxygen content begin at about the same depths as the thermocline; phosphate remains relatively constant below the depth of its maximum concentration whereas oxygen content, after reaching its minimum, reverses its gradient and increases in the still deeper water so that the water below 2000 meters contains large amounts both of phosphate and of oxygen (table 1; fig. 4).

[10] In August (1931) at station 1041 (36°55′N, 52°41′W) the average vertical variation of σ_t in the 0–100 meter layer was 2.1×10^{-2} units per meter; whereas during the following February (1932) at station 1154 (34°20′N, 51°45′W) the σ_t variation in this layer was zero.

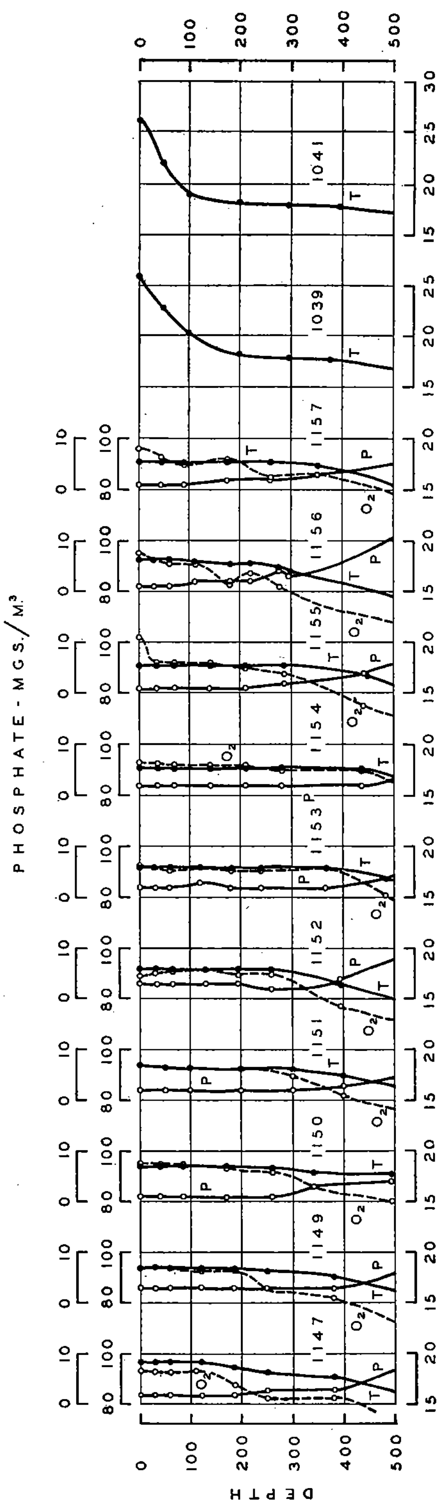

FIG. 5. Vertical distribution of phosphate (mg P per m^3), oxygen (per cent of saturation), and temperature in the upper 500 meters in northern Sargasso Sea; February–March 1932. For station positions see table 7.

TABLE 1

Station	Surface		Thermocline Beginning			P Gradient End		2000 Meter
	T°	P Mg/M³	Depth	T°	P Mg/M³	Depth	P Mg/M³	P Mg/M³
1147	19.32	2	382	17.76	3	808	33	27
1149	18.42	3	384	17.63	3	1002	31	25
1150	18.49	1	496	17.82	4	937	27	(25)
1151	18.48	2	400	17.50	3	1000	31	(27)
1152	17.89	3	262	17.88	2	821	28	24
1153	17.94	2	363	17.90	2	836	30	25
1154	17.76	2	435	17.65	2	934	27	(26)
1155	17.69	1	285	17.71	2	892	31	27
1156	18.15	1	296	16.94	3	758	30	(27)
1157	17.80	1	351	17.38	3	1003	18	18

"Atlantis" stations between Bermuda and 45th meridian, February–March 1932. Thermocline beginning estimated from observed data (see page 9); 2000 meter values scaled from station curves; bracketed values estimated. End of phosphate gradient means depth at which rapid increases of phosphate content with increasing depth cease as determined by direct observation. This is also depth and value of phosphate maxima, except at station 1151 where a concentration of 32 mg P per cubic meter was observed at 1200 meters depth. For station positions see table 7.

Mid Atlantic along 40th Meridian between Latitude 35°N and Equator[11]

The distribution of phosphate along this section changes from north to south (fig. 6); at the time of observation (March 4–21, 1932) the essential features were as follows. The surface concentration ranged from 0 to 4 mg P per cubic meter; and the phosphate poor layer, containing 5 mg P or less per meter, extended to about 400 meters depth north of latitude 26°N, to the south of which it gradually diminished in thickness to 25 meters near latitude 8°N; increasing again to about 100 meters near the equator. In deeper water phosphate content increased rapidly with increasing depth to a maximum value at intermediate depths; north of 27°N this maximum was 30 mg P or less per cubic meter at about 900–1000 meters; south of 27°N it increased up to 60 mg P per cubic meter and, in general, the rapidly increasing phosphate gradient ended 100 to 300 meters closer to the surface than it did north of 27°N. In the still deeper water phosphate tends to approach a uniformity. At 2000 meters depth it was usually in the neighborhood of 30 mg P per cubic meter; so that with increased concentration at intermediate depths the phosphate maximum is better defined in the south (table 2; figs. 6, 7).

Table 2, figures 6 and 7 illustrate that in the northern part of the section (stations 1157, 35°10′N, to 1160, 30°26′N) the phosphate content below the phosphate poor layer is much lower than the average for the remainder of the area of investigation. At this time it is not possible to judge if the difference is real or represents an observational error. But it is noteworthy that the phenomenon occurs in that part of the area where Iselin[12] found a well defined salinity anomaly (presumably indicating considerable admixture of Mediterranean water); and since Thomsen (1931) has shown that Mediterranean water is very poor in phosphate, ranging from 2 to 15 mg P per cubic meter (5 to 35 mg P_2O_5 per cubic meter) between 1000 and 4000 meters depth an explanation of the phenomenon may be inferred.

At the time of observation surface temperature of this section was, no doubt, close

[11] Salinity range observed in this section is 34.51 o/oo to 37.34 o/oo; factor for correcting phosphate values for salt error is 1.35–1.36 (Brujewicz and Krasnova, 1933).

[12] Personal communication.

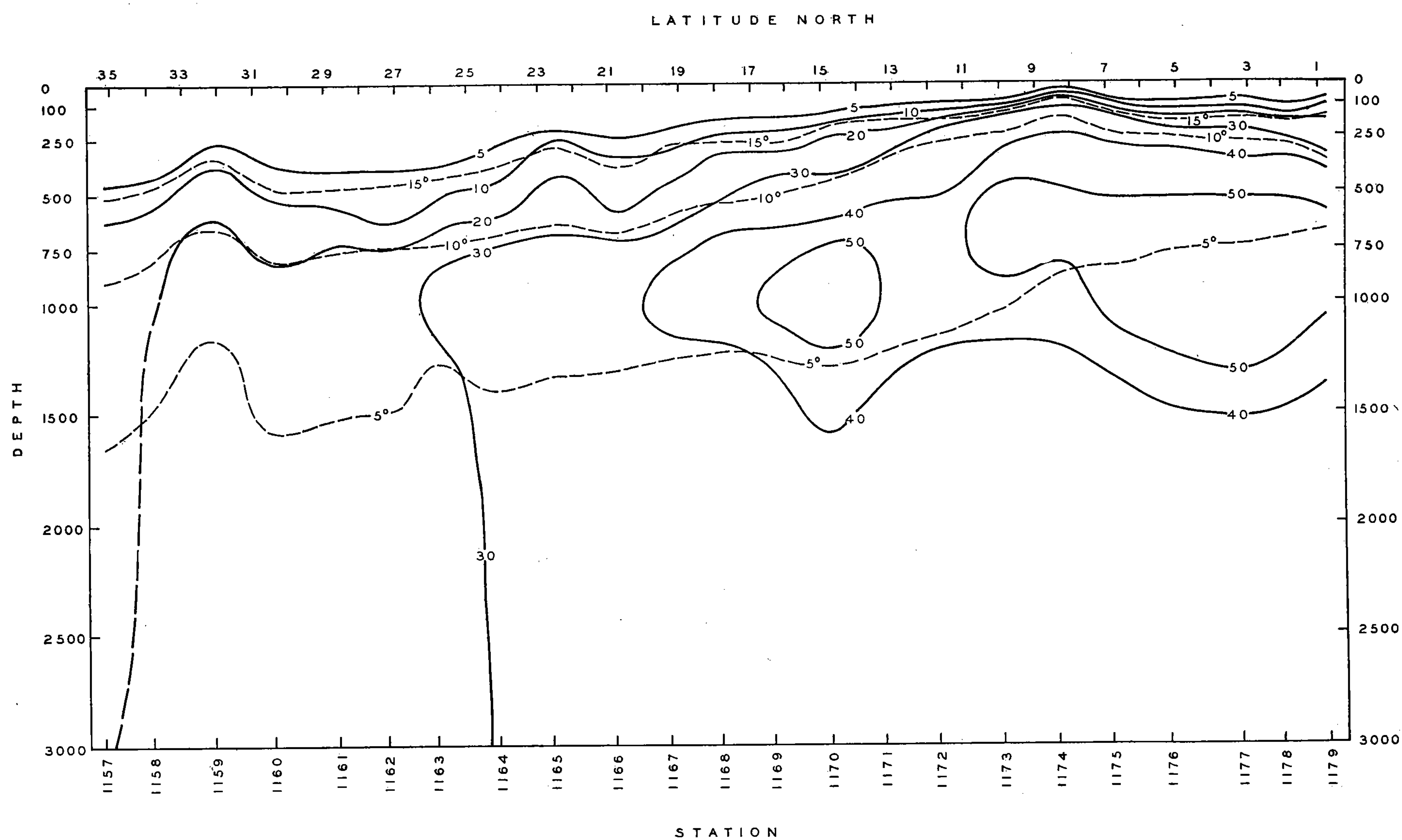

FIG. 6. Distribution of phosphate (mg P per m³) in mid Atlantic along 40th meridian between latitude 35°N and equator; March 1932. For station positions see table 7.

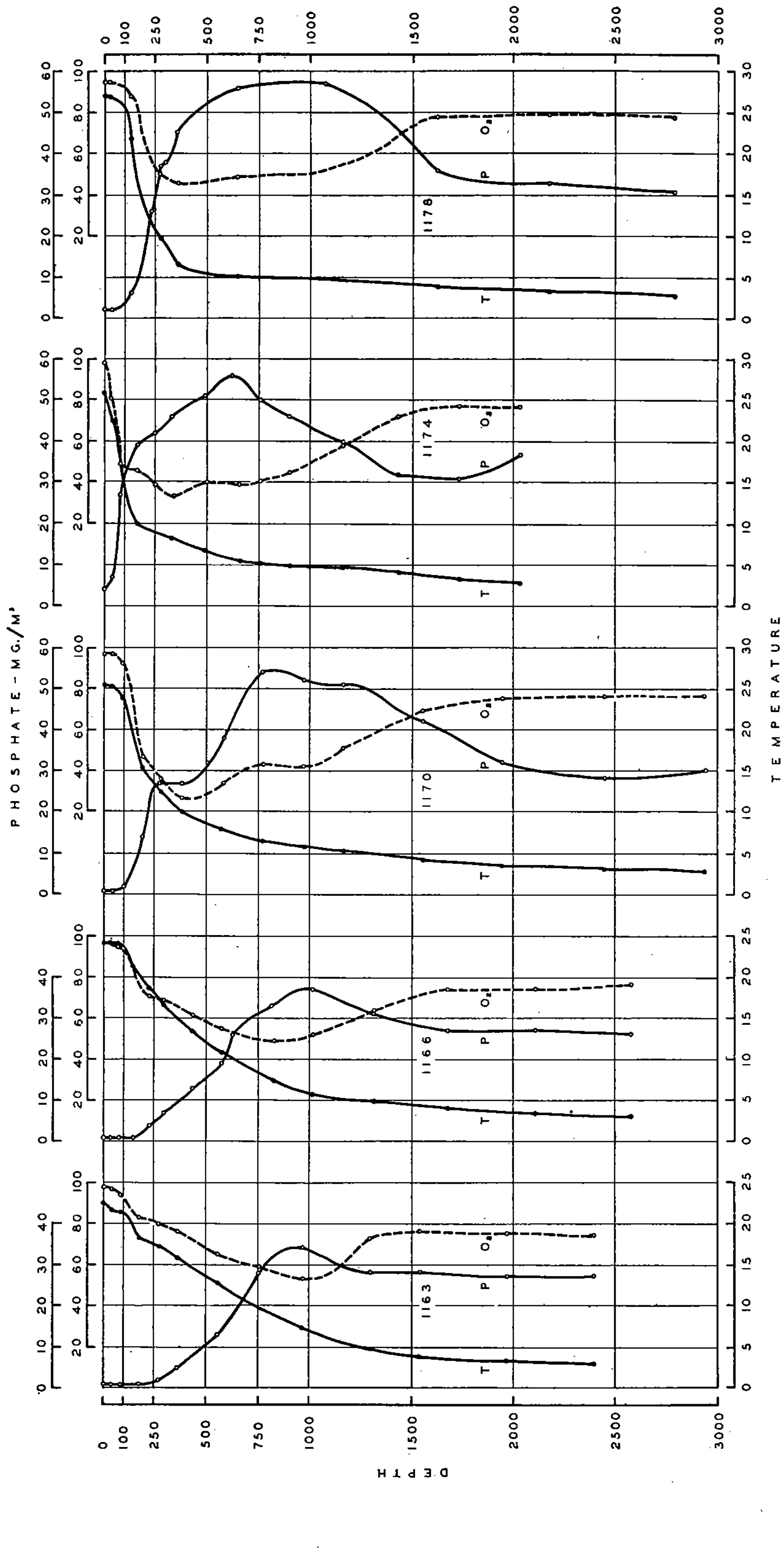

FIG. 7. Vertical distribution of phosphate (mg P per m³), oxygen (per cent of saturation), and temperature in mid Atlantic along 40th meridian; March 1932. For station positions see table 7.

to its annual minimum so that the water overlying the thermocline showed its maximum homegeneity. Fig. 8 illustrates that there is considerable variation of depth at which the thermocline begins along the section: the depths of thermocline given in table 2 are those at which the first significant changes of curvature occurred on the temperature-depth graphs. Thus, north of latitude 32°N (sta. 1159) the thermocline begins more than 200 meters below the surface and is not well marked off from the overlying water, while south of latitude 27°N it is always less than 100 meters from the surface and loosely demarked at first but becoming more distinct toward the south. Comparison of the vertical distribution of oxygen, phosphate, and temperature in the upper part of the water column (fig. 8) shows that north of latitude 32°N (sta. 1159) significant changes in vertical distribution of all three elements begin at about the same depths (below the thick homogeneous layer); further south, in the north central part of the section (stas. 1160 to 1166, latitude 30°26′N to 20°50′N), where the temperature discontinuity layer begins within 100 meters of the surface but is not sharply marked out from the overlying water, the significant increases of phosphate content begin deeper than do decreases of temperature and oxygen; however, still further south (south of station 1166), as the upper boundary of the thermocline becomes more distinct, definite increases in phosphate content parallel decreases in oxygen and temperature.

TABLE 2

Station	Surface		Thermocline Beginning			P Gradient End		2000 Meter
	T°	P Mg/M³	Depth	T°	P Mg/M³	Depth	P Mg/M³	P Mg/M³
1157	17.80	1	351	17.38	3	1003	18	18
1158	17.74	2	281	17.44	2	752	19	21
1159	18.04	2	208	17.06	4	732	26	21
1160	20.38	1	154	19.88	2	954	23	20
1161	20.81	1	74	20.80	2	931	25	25
1162	22.04	2	100	21.80	1	995	27	25
1163	22.47	1	92	21.37	1	967	34	27
1164	22.90	1	95	22.19	1	990	39	31
1165	23.41	2	99	23.00	1	795	33	29
1166	24.26	1	75	24.10	1	1024	37	27
1167	24.50	1	93	24.00	1	882	45	32
1168	24.69	1	94	24.19	1	759	48	29
1169	25.07	2	100	23.09	2	993	54	29
1170	25.45	1	97	23.86	2	784	54	32
1171	25.51	0	80	25.19	0	778	49	30
1172	25.60	0	76	25.55	0	662	48	29
1173	25.64	2	40	25.70	1	629	54	29
1174	25.73	4	<40	>22.62	(5)	634	56	37
1175	27.08	3	84	25.01	2	936	59	29
1176	26.91	3	85	26.90	3	852	59	(33)
1177	27.08	4	53	26.90	2	817	61	(32)
1178	27.05	2	—	—	—	664	56	31
1179	27.50	3	47	27.25	2	890	54	34

"Atlantis" stations along 40th meridian between latitude 35°N and equator. Thermocline beginning estimated from observed values (see page 16); 2000 meter values scaled from station curves; bracketed values estimated. At station 1178 observations in upper part of water column were not sufficiently close to estimate beginning of thermocline. End of phosphate gradient is estimated depth at which rapid increases of phosphate content, with increasing depth, cease as shown by observation. This is also depth and value of phosphate maxima. For station positions see table 7.

The relationship of phosphate and oxygen content of the water overlying the thermocline to the depth of plant activity is discussed in a later chapter (page 50). The fact that oxygen decreases conformably with temperature seems to indicate that most plant activity occurs above the temperature discontinuity layer, even when the latter begins

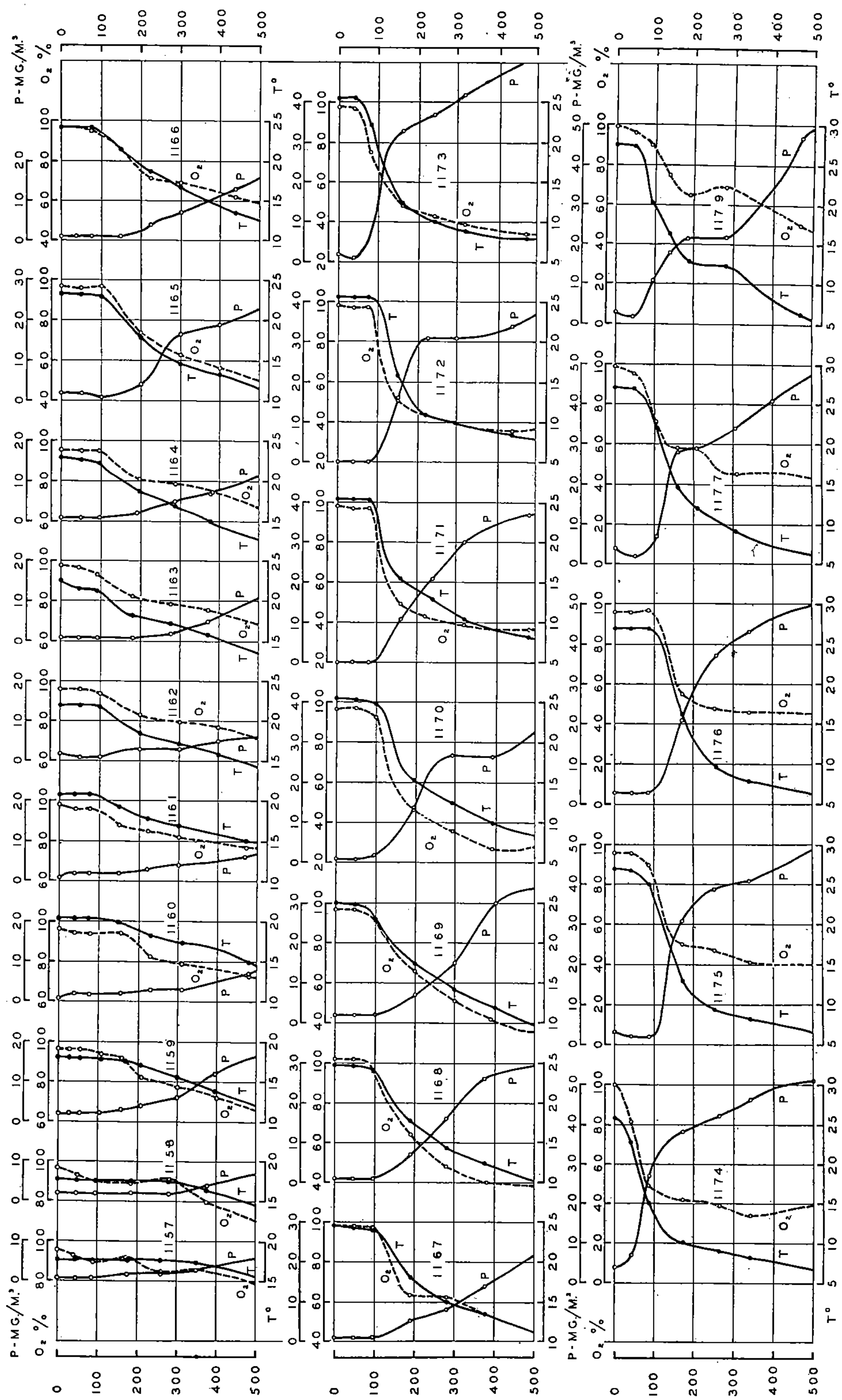

FIG. 8. Vertical distribution of phosphate (mg P per m³), oxygen (per cent of saturation), and temperature in the upper 500 meters of mid Atlantic along 40th meridian between latitude 35°N and equator; March 1932. For station positions see table 7.

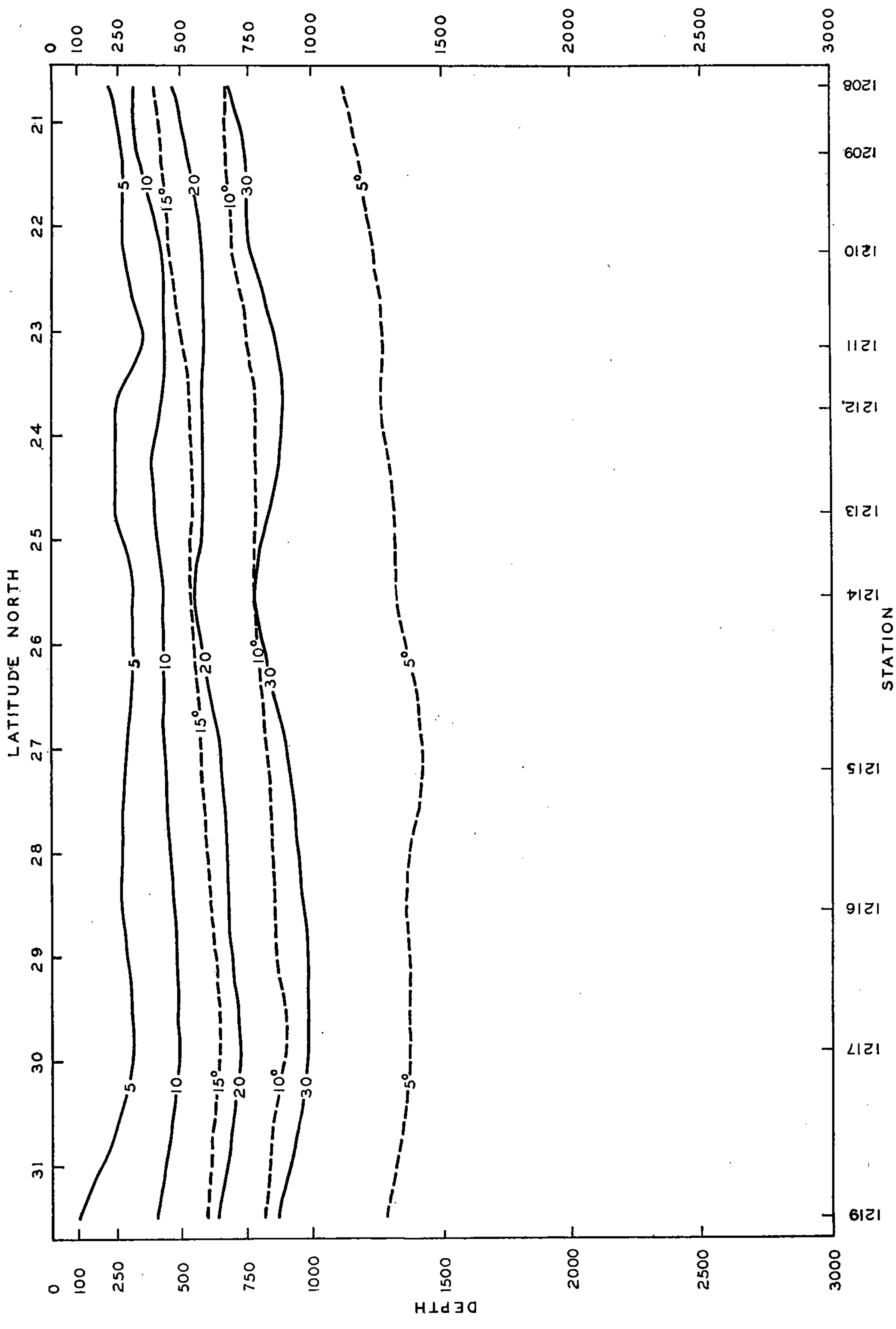

Fig. 9. Distribution of phosphate (mg P per m^3) between Haiti and Bermuda; April 1932. For station positions see table 7.

less than 40 meters from the surface. In the north central part of the section (stas. 1160 to 1166) the extension of the phosphate poor layer into the thermocline does not appear

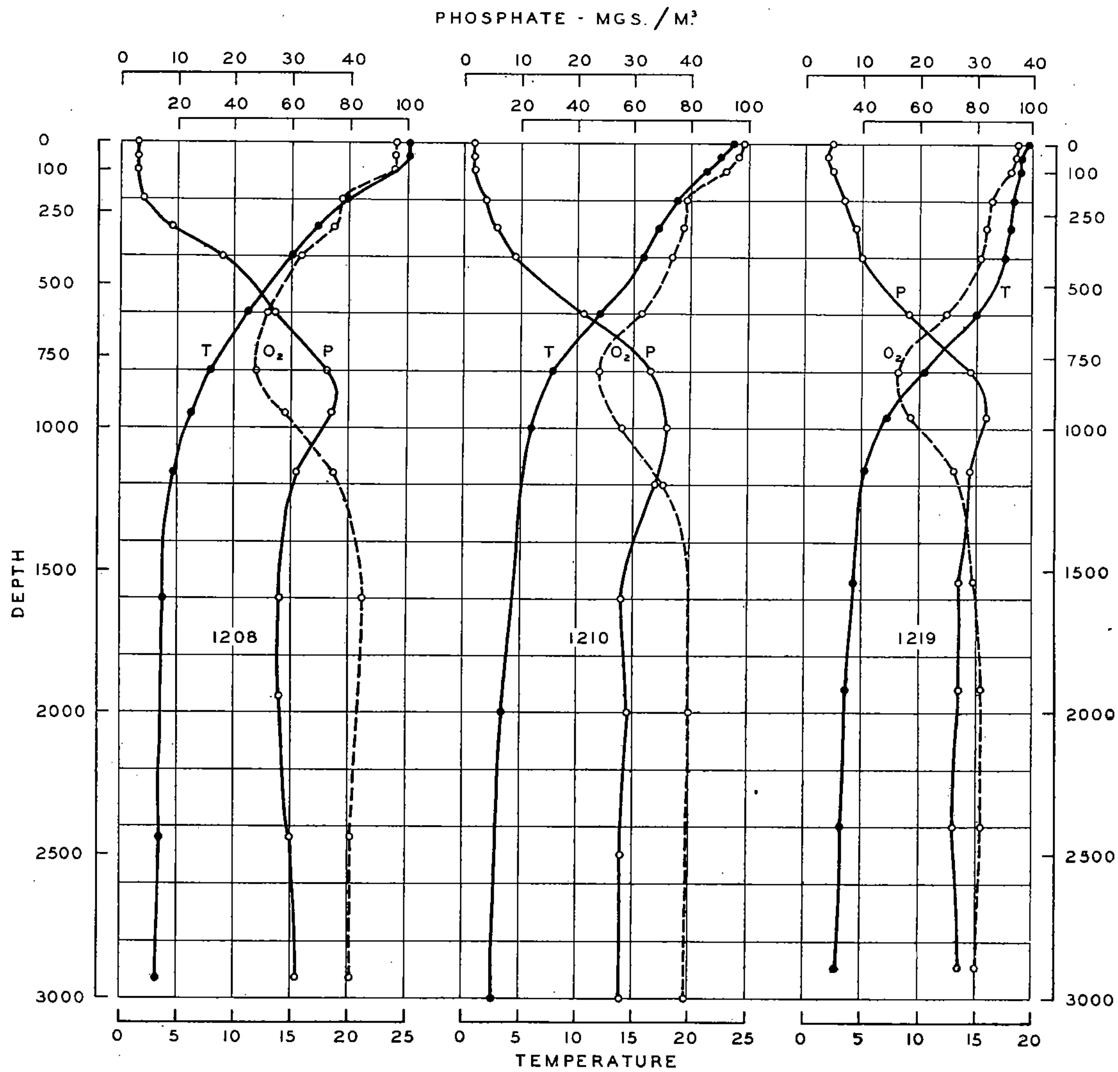

FIG. 10. Vertical distribution of phosphate (mg P per m³), oxygen (per cent of saturation), and temperature between Haiti and Bermuda; April 1932. For station positions see table 7.

to be due to phytoplanktonic activity in situ since the vertical distribution of relative oxygen content, which decreases significantly along with the temperature, suggests otherwise (see sta. 1163; fig. 8).

Between Haiti and Bermuda[13]

The distribution of phosphate along this section as determined in the early spring of 1932 (April 7 to 13) illustrated by figure 9, shows surface phosphate values (usually 1 to 3 mg P per m³) and depth of phosphate poor layer (250–300 meters) to be about the same as described for similar latitudes (32° to 20°N) further east (fig. 6; page 13). The increasing phosphate gradient ended at depths of 800 to 1000 meters, the higher maximum values characterizing the southern part of the section; and in still deeper water phosphate content declined somewhat with increased depth until at 2000 meters it is between 25 and 29 mg P per cubic meter (table 3; figs. 9, 10).

At the time of observation definite warming of the surface layers appears to have set in so that the upper limit of the main thermocline had become indistinct. However, as the high and relatively uniform oxygen and low phosphate contents which characterize the water overlying the main thermocline persisted (fig. 11) we were enabled to estimate the beginning of the main thermocline in doubtful cases, the depths of which are tabulated in table 3. These estimations may be in error 50 meters or more, but conditions in the upper part of the water column (fig. 11) are similar to those at the same latitudes further east (fig. 8) in that the upper limit of the main thermocline is not distinct from the overlying water and in that the phosphate poor water extends well into the thermocline. Depth and concentrations of the maximal phosphate content of the midstrata are also similar.

[13] Observed salinity range in this section is 34.90 o/oo to 36.82 o/oo; factor for correcting phosphate values for salt error is 1.35–1.36 (Brujewicz and Krasnova, 1933).

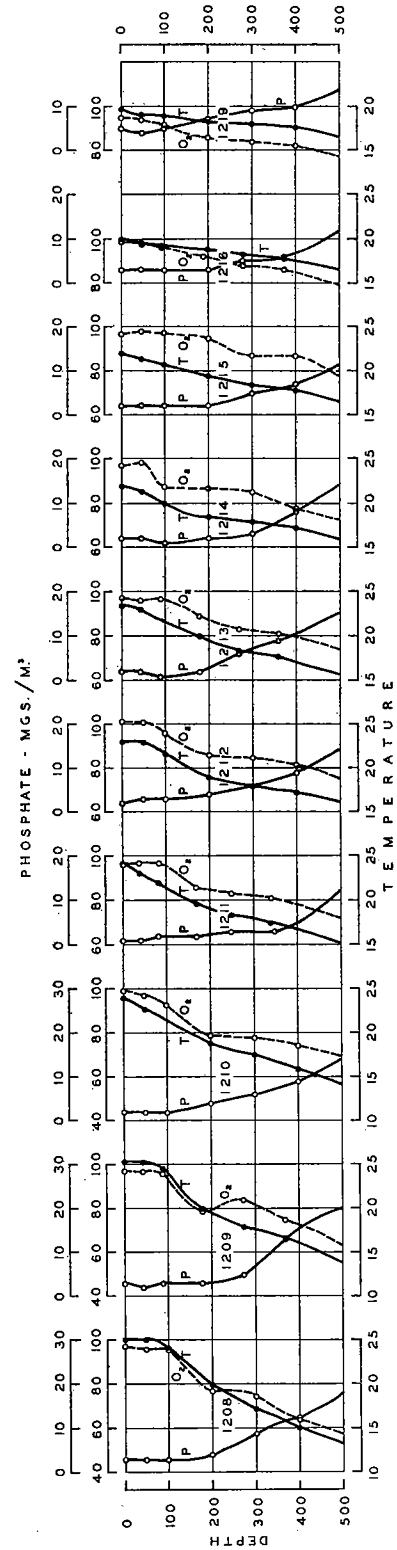

Fig. 11. Vertical distribution of phosphate (mg P per m³), oxygen (per cent of saturation), and temperature in the upper 500 meters between Haiti and Bermuda; April, 1932. For station positions see table 7.