

Observations on the Phosphate-Content and Hydrogen-Ion Concentration of the North Sea, the Southern Entrance to the Norwegian Sea, and the Water South of Iceland.

By

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1. Introduction.

The phosphate and hydrogen-ion analyses on which the principal part of this paper is based were made by the author on board the yacht *Carnegie* while en route from Hamburg, Germany, to Reykjavik, Iceland, July 1928.

The material has been placed at the disposal of the author by Mr. JOHN A. FLEMING, Acting Director, Department of Terrestrial Magnetism, Carnegie Institution of Washington.

Appreciation is expressed to Captain J. P. AULT, Commander of the *Carnegie*, and his navigating assistants for determining the positions of the observing stations, as well as to other members of the scientific staff of the *Carnegie* who gave assistance to the author in various ways.

2. Positions of Observing Stations.

(Plate I.)

The North Sea stations (July 8th to 11th, 1928) extended in an almost straight line from near the mouth of the Elbe River, station 1, to the vicinity of the Shetland Islands, station 15.

Stations 16 to 22 (July 11th and 12th) were on an almost direct line stretching between the northeast extremities of the Shetland and Faero Islands, thus crossing the eastern part of the Faero—Shetland Channel. Of this latter group of stations No. 17 was over the steep southeast bank of the Channel; Nos. 18 and 19 were over the deepest part of the Channel; and No. 20 was over the steep northeast bank.

Stations 24 to 29 (July 13th and 14th) were located over the Faero—Iceland Ridge. At station 26 observations extended from surface to bottom.

Stations 30 to 37 (July 15th to 19th) were located at distances varying from fifteen to seventy-five miles off the south coast of Iceland, the average was about forty miles. The depth of water ranged from 150 meters close inshore to 2,000 meters farthest from the coast. At station 31 a vertical series of observations was obtained from surface to bottom.

The bathymetric positions of the stations have been determined both from HELLAND-HANSEN and NANSEN's bathymetric chart of the Norwegian Sea (1, plate I), and from soundings taken by the Carnegie (2).

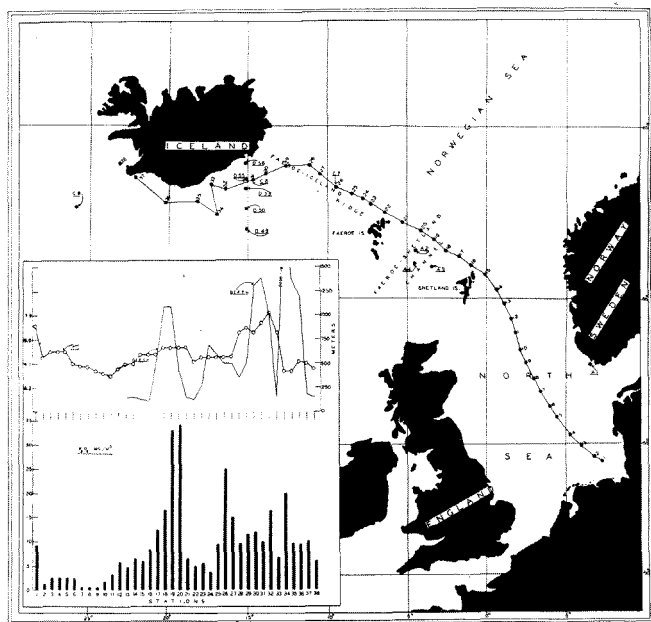


Plate I — Observing stations of the Carnegie between Hamburg, Germany and Reykjavik, Iceland, and other stations mentioned in this paper.

Inset — Surface phosphate-content, pH, and depth at «Carnegie» stations.

3. Phosphate in the Surface-Water of the North Sea, July 8th to 11th, 1928.

All phosphate estimations were made by means of the coeruleo-molybdate colorimetric method of DENIGÈS (3), using Nessler color comparison tubes more than 100 centimeters long, the bottoms of which had been replaced by colorless polished glass discs.

Stations 1 to 11, inclusive, have been considered as being in the main part of the North Sea. Reference to plate I will indicate that the surface-waters of this area were almost exhausted of phosphate, and with the exception of station 1, which may have a higher surface-content because of proximity to the mouth of the Elbe River, the P_2O_5 content ranged from 0.6 to 3.1 milligrams per cubic meter. Near the north center of the North Sea (stations 7, 8, and 9) the surface-water had practically reached a state of complete phosphate exhaustion.

This low phosphate-content of the surface-water is in accordance with the results obtained two to three weeks earlier in the season by the author while working in the southern part of the North Sea. The average P_2O_5 content of the surface-water for a mean latitude of $52^{\circ}34'$ North was then found to be 3.44 milligrams per cubic meter (4).

ATKINS, from the results of investigations in the North Sea has concluded that the seasonal changes in the phosphate of the water were very similar to those taking place in the English Channel, the minimum values occurring in July and early August. The almost complete utilization of phosphate from surface to bottom is indicated by analyses on July 8th, 1922, near the center of the North Sea, when ATKINS recorded 3 milligrams per cubic meter of P_2O_5 for the surface water and 5 milligrams per cubic meter for the bottom water at a depth of fifty meters (3).

In the deep water off Norway, however, ATKINS has pointed out that an analysis of the water on August 30th, 1924, latitude $57^{\circ}51'$ North longitude $6^{\circ}39'$ East (station A1 on chart, plate I) indicates that the deeper layers have not been denuded of phosphate as those of the same depth have at station E1 in the English Channel. This he assumes to be due to the fact that there is less mixing of the epithalassa with the hypothalassa (3).

In summarizing the temperature-observations of the North Sea, KNUDSEN and GEHRKE (5) have shown that in summer the region north of Dogger Bank (about latitude 54° North), depth considerably less than one hundred meters, there is an average temperature-difference surface to bottom of 7° to 8° . To the south of Dogger Bank the water column has at all times of the year nearly the same temperature surface to bottom.

As most of our observations were north of Dogger Bank, the surface values obtained do not necessarily give any indication of the amount of phosphate present in the deeper layers for photosynthetic activity, as surface observations would in the water to the south of Dogger Bank. However, as the depth of water in the North Sea is generally less than one hundred meters, we should expect in summer to find the phosphate to be more or less utilized throughout the whole column. In the deeper water of Norway, where the depth may extend below the limits of plant activity, and where the surface-layers are warmer than they are in the center of the sea, there is considerably more resistance to vertical mixing and phosphate may then accumulate in the deeper layers.

The phosphate-content of the surface-water lying between stations 11 and 15, near the Shetland Islands, increased to 5—6 milligrams P_2O_5 per cubic meter. This enrichment may be the result of an influx of richer Atlantic water flowing to the south of the Shetlands.

4. Phosphate in the Surface-Water lying between the Faero and Shetland Islands, July 11th and 12th, 1928.

Perhaps the most striking thing about the surface phosphate-values (plate I) obtained for this series of stations is the enormous quantities recorded at stations 19 and 20 (32.8 and 33.8 mg/m³ P_2O_5). The surface phosphate-content increased continuously from station 15 (5.8 mg/m³) south of the Shetland Islands, to reach its maximum at station 20, and then to drop sharply again at stations 21 (6.5 mg/m³) and 22 (4.9 mg/m³) on the Faero Bank.

Thus, the phosphate-content of the surface-water between the Shetland and Faero Islands was greatest at the east central and northeast part of the Faero-Shetland Channel.

The hydrographical observations of HELLAND-HANSEN and NANSEN (1) in this region have shown that the main part of the Norwegian Atlantic Current enters the southern part of the Faero-Shetland Channel, and running toward the northeast or to some extent east, it generally keeps close to the Shetland Bank. A smaller volume of water enters the northern part of the Channel and running towards the south or southeast it joins the main body of the current.

Between the Shetland and Faero Islands it has been shown (6) that the surface-water is largely Atlantic water while the bottom-water is Norwegian Sea water. Between the Atlantic water and bottom-water there exists an intermediate layer formed by the mixing of Atlantic water with bottom-water and water introduced from the East Icelandic

Arctic Current. The characteristic mixings of the layers are met with especially in the shallower parts of the area in question, out to a depth of 200 meters, but also out in the middle of the channel there is a zone where mixing is very pronounced owing to eddy formation in connection with the strong currents.

HELLAND-HANSEN and NANSEN (1) have pointed out that the Arctic water is brought by the East Iceland Arctic Current along the northern slope of the Faero-Iceland Ridge into contact with the Atlantic Current already in the northern mouth of the Faero-Shetland Channel. By numerous great and small horizontal vortices (with vertical axes) formed during the northward course of the Atlantic Current, its waters are continually more and more intermixed with those of the Arctic Current. A study of temperature- and salinity-sections across the Channel shows the occurrence of numerous vertical vortex movements (with horizontal axes) which cause a considerable intermixture with underlying bottom-water, and a similar intermixture with underlying bottom-water is also produced by horizontal vortex movements.

It thus appears as if the very high phosphate-content of the surface-water in the Faero-Shetland Channel might be due principally to the mixing of surface with deeper rich phosphate water resulting from the vertical and horizontal vortex movements of the water. For purposes of illustration HELLAND-HANSEN and NANSEN's chart of circulation of the Norwegian Sea (1, fig. 2, page 9) is helpful.

In this same season, July 6th, 1925, ATKINS (7) recorded values of 30 and 23 milligrams P_2O_5 per cubic meter for the surface-water at two stations in the Faero-Shetland Channel (stations A2 and A3, plate I). Also on August 5th, 1924, this same author (3) recorded a value of 74 milligrams P_2O_5 per cubic meter for the surface-water to the north of Scotland (station A4, plate I). The accuracy of these analyses of ATKINS may be somewhat impaired due to storage of the samples for several weeks before analyses, but the magnitude of the results lend evidence that high surface phosphate-content as well as perhaps other nutrient materials may prevail in the surface-waters of the Faero-Shetland Channel throughout the summer months.

5. Phosphate in the Surface-Water over the Faero-Iceland Ridge, July 13th and 14th, 1928.

Stations 24 to 29 were over the Faero-Iceland Ridge stretching between the Faero Islands and Iceland, and forming a fairly level plateau at depths ranging between 400 and 500 meters. Some parts of the ridge

rise above 400 meters and near the Faero Islands the depths are frequently greater than 500 meters.

The opening between the Faero Islands and Iceland, like the Faero-Shetland Channel, forms one of the gateways through which the Atlantic Current streams into the Norwegian Sea. The conditions existing on each side of the ridge are sharply contrasted, to the south the salinities and temperatures being very high as compared with conditions north of the ridge. A sharp boundary between warm salt Atlantic water and colder more diluted waters moving southwards along the eastern coast of Iceland is always found near Vestre Horn.

Vertical mixing, no doubt, occurs on the ridge owing to eddy formation resulting from the currents and enriches the surface-layers with nutrient materials brought up from the deeper water. The phosphate-content of the water over the ridge (stations 24 to 29) ranged from 3.8 to 25 milligrams per cubic meter, higher values were recorded over the central

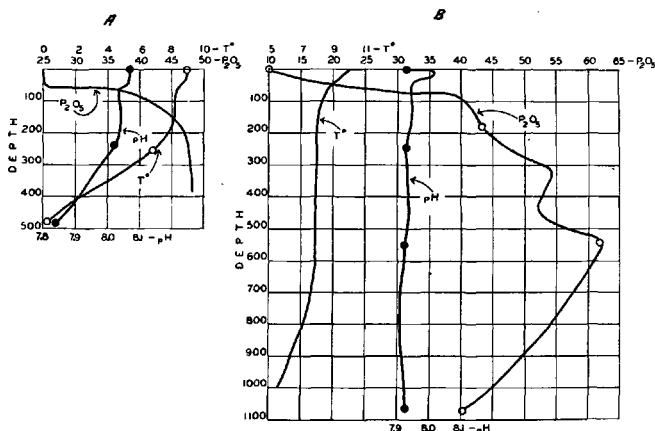


Plate II — A, vertical distribution of phosphate, pH, and temperature at station 26 (Carnegie station 7); and B, vertical distribution of phosphate, pH, and temperature at station 31 (Carnegie station 8).

and northern part of the ridge. The average phosphate-content of the surface-water over the ridge ($12.3 \text{ mg/m}^3 \text{ P}_2\text{O}_5$) was about one half of that recorded for the surface-water of the Faero-Shetland Channel.

The vertical distribution of the temperature¹⁾ and phosphate at station 26 (Carnegie station 7) near the centre of the ridge is illustrated in plate II. The temperature of the upper two hundred meters was almost uniform, range 8°.92 to 7°.81, below the two hundred meter level the gradient increased, the temperature decreasing to 0°.31 at 483 meters. The phosphate in the water mass varied from 25 mg/m³ at the surface to 48 mg/m³ at 400 meters. In the lower portion of the water column, between 200 and 400 meters, the phosphate-content was practically uniform.

At the time of the year our observations were taken, photosynthetic activity in this locality should be close to its maximum and consequently the phosphate-content of the layers available for plant activity should be at a minimum, unless phosphate as well as other manurial substances, are continually being brought up from the deeper water through circulation of the water mass. The relatively large amount of phosphate present in the upper 200 meters at station 26 would seem to indicate that vertical circulation plays an important part in keeping the upper layers supplied with phosphate.

As an index of the resistance of the water mass to vertical mixing near the central part of the Faero-Iceland Ridge, we have from the specific volume calculations of AULT²⁾ computed the state of the vertical stability. The stability of the water mass has been computed after the method suggested by SANDSTRÖM (8) by determining the number of isosteric surfaces per ten meters depth, and is graphically illustrated by a vertical line the thickness of which has been drawn proportionate to the stability. The state of the vertical at station 26 (Carnegie station 7) is represented in plate III. The water mass tends toward a more or less uniform stability and nowhere in the vertical column is there a stable layer developed which would offer a great resistance to vertical stirring.

6. Phosphate in the Surface-Water South of Iceland, July 15th to 19th, 1928.

The phosphate-content of the surface-water fifteen to seventy five miles off the south coast of Iceland (stations 30 to 37) ranged 6 to 20 milligrams P₂O₅ per cubic meter; in general the phosphate-content of the surface-water was highest where the water is deep and farthest from shore.

¹⁾ Temperature observations and calculations by J. P. AULT, Commander of yacht Carnegie.

²⁾ Specific volume calculations at Carnegie stations 7, 8, and 9 by J. P. AULT.

The vertical distribution of phosphate and temperature at station 31 (Carnegie station 8) is graphically represented in plate II. Similar to station 26 the phosphate-gradient is greatest in the upper 100-meter layer, the values recorded for the 100-meter level were the same at both stations. Below 100 meters the phosphate increased to more than 60 milligrams per cubic meter at 550 meters depth and then decreased to 40 milligrams per cubic meter at 1066 meters depth. An apparent dif-

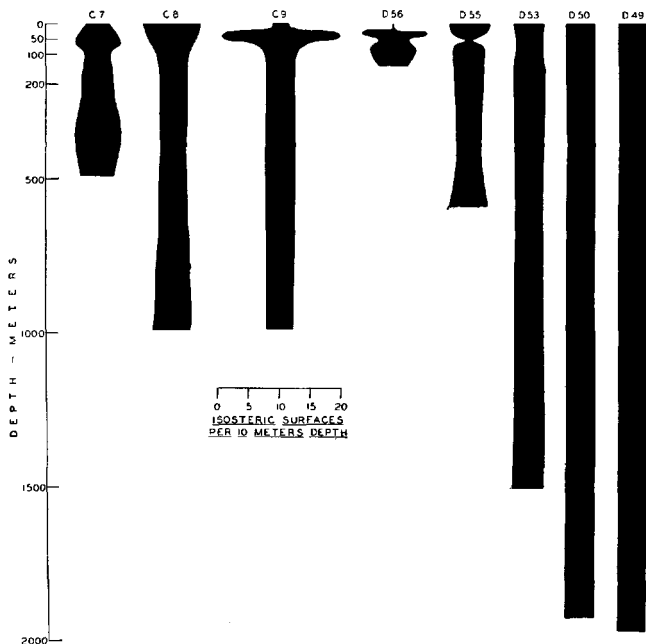


Plate III — Stability of water around Iceland. For positions of indicated stations see plate I.

ference exists between stations 26 and 31 in the phosphate-content below 200 meters. In the former case we have seen it was practically uniform and in the latter it increased with depth showing the deeper water to be richer in phosphate.

The vertical temperature-gradient at station 31 is more uniform

than at station 26; there is no influx of cold water above 500 meters as in the latter case where the temperature at 483 meters was almost 0° .

The vertical state of stability at station 31 has been determined by the same method used for station 26, and is graphically illustrated in plate III. The most stable part of the vertical occurs in the upper 100-meter layer, in lower levels the stability decreased in linear proportion to depth. The upper 100-meter layer of station 31 was somewhat more stable than that layer at station 26, and this difference in stability may partially account for the difference in the phosphate-content of the surface-water between station 26 (25 mg/m³) and station 31 (10 mg/m³). The phosphate-content at 100 meters is almost the same at both stations (40 mg/m³).

As a provisional test of the stability of the water mass to the south of Iceland, in relation to distance from shore, we have calculated the specific volume and hence the stability from the temperature- and salinity-data obtained by the Danish investigators in this region in May 1896 (9). The Danish stations selected for stability computation lay on a straight line about 100 miles east of stations 32 and 34, extending from 15 to 110 miles off shore (D stations, plate I). The results are graphically illustrated in plate III, and indicate that the most stable verticals at this season of the year exist in the shallower water close to the coast (station D 56). In the deeper off-shore water (stations D 49, D 50 and D 53) the water mass was of constant stability.

7. General Conclusions of the Distribution of Phosphate in the Area Investigated.

It would appear from plate II, as well as the foregoing discussion, that observations on the phosphate-content of the surface-water do not always give a true indication of the amount of this material available for photosynthetic processes. We have seen that at stations 26 and 31, where the surface phosphate-content was 25 and 10 milligrams per cubic meter, respectively, that at one hundred meters approximately 40 milligrams per cubic meter was recorded for each station. This was also the case at Carnegie station 9 in the open Atlantic (plate I, station C9) where 15 milligrams per cubic meter P_2O_5 were recorded for the surface-water and 41 milligrams per cubic meter for the 100-meter level (10). Similar results have been obtained by the author in tropical waters of the North Atlantic, where surface-waters were almost exhausted of phosphate (3.5 to 5 mg/m³ P_2O_5), yet at one hundred meters there were quantities ranging from 41 to 90 milligrams P_2O_5 per cubic meter (10).

Quite obviously, inorganic phosphate, as well as other nutrient materials, in the off-shore surface-layers depend to a great extent on the amount of mixing with the rich subjacent layers and the intensity of this vertical mixing is indicated by the stability of the water. In the area investigated the factors affecting vertical stability are principally changes in the density of the water column resulting from temperature and salinity alterations (principally the former) and eddy formation resulting from strong currents. Evidence seems to point to vertical mixing in the Faero-Shetland Channel and on the Faero-Iceland Ridge as principally the result of smaller vortex movements of the water, while that in the sea south of Iceland may be principally the result of convection currents resulting from changes in the density of the water.

In the sea south of Iceland it has been shown by NANSEN (11) that between Rockall Bank and Iceland the density increases in a northerly direction due to slowly decreased temperature of the surface-water in the same direction. Cooling of the ocean's surface results in producing convection currents in the sea south of Iceland which may extend to a depth of nearly 800 meters, there being a great uniformity of temperature and salinity in this region between 100 and 800 meters resulting from this circulation. The effect of vertical circulation in the upper one hundred meters is less marked in July on account of solar warming.

Solar warming of a surface-layer of variable thickness increases resistance to vertical circulation and may produce a marked effect on the phosphate-content of the surface-water. In regions where there is a sufficiently strong cyclonic vortex motion, the deeper water may be brought close to the surface and the warm layer may be quite thin, but in the absence of this vortex motion, the warm stable layer may extend to various depths, and in the shallow water over the banks the warm layer may reach from surface to bottom.

The uniform condition of the column of water over the northeast part of the Faero Bank and the northern part of the Shetland bank as compared with the deeper water farther off-shore has been illustrated by NANSEN (11, *tafel XVI*). The water over these banks is of almost uniform salinity and temperature, while farther off-shore cyclonic vortex movements bring up colder deeper water closer to the surface. As the bank-water is shallower than the surrounding water, during summer it is heated to a higher temperature and becomes lighter than surrounding water at the same levels. Thus, an interchange of water between it and the deeper layers is inhibited. As the phosphate is utilized in the water over the banks in summer and additional material is not forthcoming from the richer deeper waters to replenish the supply, we should expect

that it would eventually become greatly reduced or even exhausted (stations 15, 21, 22, etc.).

On the other hand in the surface-layers of the deeper water, eddy movements resulting from the velocity of currents produce a mixing of the surface and subjacent layers which will tend to enrich the surface-layers with phosphate and other nutrient materials (stations 18, 19, 20, etc.).

In contrast to the summer conditions of water over the banks, it has been shown by NANSEN (11) that since the layer of bank-water is thinner than in the deep sea, cooling during the winter must make the water colder and consequently heavier than in the surrounding deeper regions. This bank-water, now instead of being warmer than the surrounding water is colder and heavier and it will sink down along the sides of the bank to a position of equilibrium and be gradually replaced by water from the sides. The importance of this winter circulation in restoring the bank-water with phosphate and other nutrient materials from the deeper layers is evident.

The greater part of the North Sea covered by our investigations was in practically all cases sufficiently shallow (100 meters or less) so that photosynthetic activity could extend throughout the whole column of water. As a result of this it is quite probable that over the greater part of the shallow North Sea, phosphate is more or less utilized from surface to bottom during the summer months in spite of the existence of an appreciable thermocline during this season. This condition is corroborated by results of ATKINS in the North Sea; exceptions as in the deeper water off the coast of Norway have been noted.

8. The Method Employed in the Estimation of the Hydrogen-Ion Concentration.

The hydrogen-ion concentration, reported in terms of the Sørensen unit, pH, was determined colorimetrically by means of a double wedge comparator such as described by BARNETT and BARNETT (12) and MØBERG (13). The apparatus used in this investigation was carefully checked at a temperature of 26° against La Motte standardized buffer mixtures at the beginning of the investigation in Hamburg, Germany, and at the end in Reykjavik, Iceland. The indicator used was cresol red, and the results have been corrected for salt-error after RAMAGE and MILLER (14), these authors give a correction of -0.27 unit of pH to be applied for salinities lying between 32 and 35 ‰.

The pH determinations on surface-samples were always made im-

mediately after collection of the sample, the temperature of the indicator-solutions in the wedge being the same temperature as the sample at the time of collection. For the measurement of pH on samples obtained in a depth series, as at stations 26 and 31, the temperature of the indicator-solutions in the wedge as well as that of the samples were all adjusted to the temperature of the surface-water. The pH-values used in the discussion have only been corrected for salt-error, other possible corrections are discussed elsewhere.

9. Hydrogen-Ion Concentration of the Region Investigated.

The hydrogen-ion concentration, corrected for salt-error, increased from pH 7.94 at station 1 in the southern part of the North Sea, near the mouth of the Elbe River, to pH 8.15 at station 11 in the north central part of the North Sea. In the vicinity of the Shetland Islands (stations 15, 16 and 17), the pH dropped to 8.06, while in the Faero-Shetland Channel, the pH was still lower, 8.03, rising to 8.09 in the shallow water over the Faero bank (station 22).

Over the southern half of the Faero-Iceland Ridge the pH was consistently 8.07, but considerably lower values were encountered over the northern part of the ridge and in the water to the south east of Iceland (pH 7.89 to 7.97). The pH of the water to the southwest of Iceland ranged 8.09 to 8.13.

In a general way the variation of the surface hydrogen-ion concentration is coincident with the differences in circulation existing in the region. The most alkaline water was found in the northern parts of the North Sea, while the most acid was over the northern part of the Faero-Iceland Ridge and the adjoining water southeast of Iceland. In this latter area the low pH may be partially due to the mixing of the colder water brought down by the East Icelandic Arctic current with the warmer water of the Atlantic. Similarly, the pH was lower in the surface of the strongly mixed Faero-Shetland Channel than in the surrounding surface bankwater.

Photosynthesis at this time of the year, no doubt, tends to increase the pH, but in areas of strong vertical circulation where the surface-layers are mixed with the water from the lower levels as in the Faero-Shetland Channel or on the Faero Iceland Ridge this effect would tend to be offset by the replacement of surface-water by the more acid water from the lower levels.

The vertical distribution of hydrogen-ion concentration, corrected for salt-error, at station 26 (Carnegie station 7) is illustrated in plate II.

The maximum variation from surface to bottom at 483 meters, pH 8.08 to 7.84, is greater than the surface variation on the Faero-Iceland Ridge, pH 7.95 to 8.07.

Similarly we have in plate II the vertical distribution of pH, corrected for salt-error, for station 31 (Carnegie station 8). With the exception of the surface-layers, the gradient is more uniform than at station 26. The measurements recorded for surface and bottom are identical, being almost the minimum value found for the whole vertical column. The maximum variation of pH, corrected for salt-error, (7.91 to 8.02) is less than was recorded for the shallower column of water at station 26 on the Faero-Iceland Ridge and also less than the variation of surface pH south of Iceland (7.89 to 8.13).

Because of different methods and standards used by many investigators for the determination of pH in sea-water, as well as the various salt-error corrections applied to these determinations, it is not always possible to compare results obtained in pH investigations of the sea. It appears, however, from an examination of the results of other investigations that the surface pH of cold northern waters is lower than that of the warmer surface waters of more southern latitudes. Thus, the author on board the Carnegie, using the same method as in the investigation under discussion, found that during the months of July to September the pH of surface-water was generally higher in the southern parts of the North Atlantic than in the more northern parts¹⁾. PALITZSCH (15), during the Thor expedition (1911—1912) made pH determinations on fresh samples of sea-water and found for the surface-waters of the western end of the Baltic, the Skagerak and south of the North Sea the pH was between 8.00 and 8.05, and farther south off the coast of Portugal it had risen to 8.25. This same investigator also found that off the Scotland and Faero Islands the pH varied 8.08 to 8.22, while in the Mediterranean it was usually above 8.22

Measurements given by NANSEN for Spitsbergen waters (15) obtained July and August 1912, during the cruise of the Veslemoy, were mostly low. Using PALITZSCH's mixtures this investigator found that in the cold salt-water, 4°.8 to 0°.55, the values generally lay between pH 7.94 to 8.08, but some remarkably high values, pH 8.19 to 8.25, are also given. With the higher values the gradient of change with depth is steeper than in the warmer seas.

The hydrogen-ion results obtained by THOMPSON and his coworkers

¹⁾ Unpublished data on hydrogen-ion concentration of North Atlantic obtained during cruise of Carnegie.

at the Puget Sound Biological Station, and by MOBERG at Scripps Institution of Oceanography are more comparable to those obtained by the author. These investigators have both used the Barnett type of wedge-comparator, and a comparison of their results seems to indicate that the pH was in general lower in the colder water of higher latitudes. JOHNSON and THOMPSON (16) report that during July and August 1928 at the Puget Sound Biological Station, the hydrogen-ion concentration of the surface-water, uncorrected for salt-error, ranged 7.9 to 8.5 units of pH. The average temperature of the surface-water during this period was 10.9°. MOBERG (17) working in the La Jolla region, records an average surface pH, corrected for salt-error (—0.27 unit of pH added to results), for the summer of 1926 of about 8.20 for a station ten miles off shore. The average surface-temperature during this period at the ten-mile station was about 20°.

As the observations under discussion were obtained close to mid-summer, we should expect, because of conditions of phytoplankton production, and temperature of the surface-water, that the pH readings obtained were close to the maximum for the year, although not necessarily the maximum. ATKINS (18) working in the English Channel found that in a general way the pH maximum could be correlated with the diatom maximum in early summer and autumn.

In the Puget Sound region, JOHNSON and THOMPSON (16) found that the pH throughout the year (September 1927 to September 1928) remained practically constant, pH 7.8 to 7.9, uncorrected for salt-error, except during the latter part of July and the month of August when there was considerable fluctuation, pH 7.9 to 8.5. MOBERG (13) also found that in the La Jolla region over a period of four years the pH was higher in summer than in winter. This latter investigator calls attention to the fact that weekly means at the Scripps Institution pier for the period 1922 to 1925, inclusive, indicate that there may be a considerable difference between different years; the pH and temperature maxima and minima not always being synchronous.

10. The Possible Effect of Temperature on Colorimetric Measurements of Hydrogen-Ion Concentration of Sea-Water.

In the discussion of the method of observing pH, we have seen that the double wedge comparator was calibrated at a temperature of 26°, while the temperature at which it was used for pH determinations in the field was, in this investigation, considerably lower — namely, the temperature of the surface-water. In general, the temperature at which

the observations were made ranged from 8°·9 to 14° or 17° to 12° lower than the temperature at which the wedge comparator was colorimetrically calibrated.

K. BUCH (19, 20), from the result of a study of the influence of temperature on the dissociation constants of various indicators when admixed with borax buffer solutions and with sea-water, has concluded that temperature plays a complex role in the accurate colorimetric estimation of pH, and is something which should not be neglected. This investigator, by making spectrophotometric investigations of the absorption of light by various indicators in both buffer solutions and sea water at varying temperatures, experimentally determined two constants, α indicating the amount by which the dissociation exponent of the indicator varies for a temperature change of one degree in the borax buffer solutions, and β , for the color-change of the indicator taking place in sea-water (salinity 34.5 ‰) with changing temperatures.

In the case of cresol red, α , or the alteration of pK per degree in borax buffer mixtures, was calculated by BUCH to have a mean value of 0.0053 (negative as pK declines with rising temperature), and β , or the average amount by which the pH value declines per degree with rising temperature as indicated by the color-change of cresol red, was calculated to have a mean value of 0.006 unit of pH.

On the theoretical assumption that the indicators studied were weak acids which become ionized on the addition of a base, the ion differing in colour from the undissociated acid, BUCH applied the mass action law and deduced a simple formula for the calculation of pH at the time of collection from the colorimetric estimation, provided certain other measurements were taken. The pH and temperature of the water in situ has been designated by pH_{tw} and t_w ; the pH and temperature of the comparison standard as pH_{tb} and t_b . The pH of the water in situ can then be calculated by means of the equation:

$$\text{pH}_{\text{tw}} = \text{pH}_{\text{tb}} + \alpha (t_b - t_w).$$

When the temperature of the sample is several degrees higher at the time of measurement —' (t'_w) than at the time of collection (t_w), the correction $\beta (t'_w - t_w)$ should be added to the above equation.

In accordance with the theory put forward by BUCH (20), and on the basis of the assumption that the pK-value of the cresol-red indicator coloring the solutions in the wedge was altered because of the lower temperature at which the measurements were made in the field, we have in column 9, table 1, tabulated the pH of the surface-water when corrected for this temperature-effect. Similarly in column 6, table 2, are

Table 1.

Station	Latitude North	Longitude	Date 1928	G.M.T. h m	T °C	P ₂ O ₅ mg/m ³	pH*	pH**	Salinity ‰
1	54°21'.9	7°19'.4 E	July 8	16 06	13.6	9.3	7.94	8.00	33.12
2	54 32.6	6 54.6 E	— 8	20 44	14.0	1.1	8.07	8.13	..
3	54 51.1	6 02.0 E	— 9	2 21	..	2.5	8.05	8.12	..
4	55 17.7	5 17.8 E	— 9	8 31	12.2	2.5	8.05	8.12	34.38
5	55 56.7	4 28.0 E	— 9	18 25	12.0	2.5	8.05	8.12	..
6	56 19.5	4 06.2 E	— 9	21 40	12.0	2.5	8.10	8.17	..
7	56 48.5	3 37.7 E	— 10	1 45	..	0.6	8.11	8.18	..
8	57 18.3	3 07.1 E	— 10	5 45	..	0.6	8.11	8.18	34.87
9	57 49.3	2 36.5 E	— 10	10 30	11.8	0.6	8.13	8.20	..
10	58 21.3	2 08.1 E	— 10	14 55	11.6	1.7	8.14	8.21	..
11	58 50.4	1 48.2 E	— 10	19 15	11.0	3.1	8.15	8.23	35.03
12	59 21.3	1 28.1 E	— 11	1 40	11.0	5.7	8.12	8.20	..
13	59 48.1	1 06.9 E	— 11	6 03	..	4.8	8.10	8.18	..
14	60 17.8	0 39.4 E	— 11	10 00	10.8	6.5	8.10	8.18	..
15	60 43.1	0 05.4 W	— 11	14 40	10.9	5.8	8.06	8.14	35.35
16	61 04.6	0 56.5 W	— 11	19 30	10.6	8.2	8.06	8.14	..
17	61 20.3	1 43.0 W	— 11	22 51	10.2	12.3	8.06	8.14	..
18	61 34.9	2 33.3 W	— 12	2 00	..	16.4	8.03	8.11	..
19	61 51.2	3 17.2 W	— 12	6 00	9.5	32.8	8.03	8.11	..
20	62 04.7	4 08.4 W	— 12	9 23	9.6	33.8	8.03	8.11	35.26
21	62 20.3	5 21.0 W	— 12	13 28	9.6	6.5	8.03	8.11	..
22	62 35.8	6 25.3 W	— 12	17 18	9.2	4.9	8.09	8.18	..
23	62 51.7	7 16.5 W	— 12	22 48	9.1	5.4	8.07	8.16	..
24	63 00.0	7 50.2 W	— 13	2 23	..	3.7	8.07	8.16	..
25	63 08.3	8 34.0 W	— 13	7 18	9.5	9.3	8.07	8.16	..
26	63 20.5	9 25.4 W	— 13	14 44	8.9	25.0	8.07	8.16	35.20
27	63 42.7	10 26.4 W	— 13	22 42	9.1	15.1	8.07	8.16	..
28	63 55.6	11 08.9 W	— 14	4 34	..	9.5	7.97	8.06	..
29	63 55.1	12 38.7 W	— 14	6 51	9.6	11.5	7.95	8.03	..
30	63 39.7	13 53.8 W	— 15	3 51	..	11.8	7.97	8.05	..
31	63 30.1	14 40.7 W	— 15	10 06	10.3	10.1	7.93	8.01	35.23
32	63 15.0	16 23.3 W	— 16	2 33	10.4	16.2	7.89	7.97	..
33	63 20.7	17 14.6 W	— 16	13 02	11.8	6.7	7.97	8.04	..
34	62 30.3	16 50.7 W	— 17	1 15	10.6	20.0	8.13	8.21	..
35	62 55.5	18 15.6 W	— 17	12 33	12.0	9.6	8.13	8.20	..
36	62 52.2	20 14.1 W	— 18	6 13	11.7	9.4	8.09	8.16	..
37	63 42.3	22 07.8 W	— 19	14 42	12.3	10.0	8.10	8.17	..
38	63 59.2	23 02.9 W	— 20	1 03	10.9	6.0	8.12	8.20	..
1	2	3	4	5	6	7	8	9	10

*) pH corrected for 'salt-error' (-0.27 unit pH added to observed value), see section VIII.

**) pH corrected for temperature-effect after Buch, and 'salt-errors', see section X.

Table 2.

Station Data	Depth meters	T °C	P ₂ O ₅ mg/m ₃	pH*	pH**
Station 26	0	8.92	25	8.07	8.16
Carnegie St. 7	16	8.92	25	8.07	8.16
	43	8.90	25	8.07	8.16
Lat. 63°20' N	66	8.16	35.7	8.03	8.12
Long. 9°25' W	89	8.12	39.6	8.04	8.13
	111	8.12	42.3	8.04	8.13
July 13, 1928	202	7.79	47	8.04	8.14
	290	5.95	47	7.99	8.11
G.M.T.: 13 : 57	385	2.72	48	7.93	8.09
to 15 : 02	483	0.31	..	7.84	8.02
Station 31	0	10.32	10.1	7.93	8.01
Carnegie St. 8	5	10.22	11.7	8.01	8.09
	27	9.72	15.6	8.02	8.10
Lat. 63°30' N	54	9.08	20.3	7.95	8.04
Long. 14°41' W	80	8.60	37.8	7.95	8.05
	107	8.44	40.7	7.95	8.05
July 15, 1928	214	8.12	44.5	7.94	8.04
	324	8.06	54.3	7.93	8.03
G.M.T.: 9 : 04	432	7.98	52.1	7.94	8.04
to 10 : 11	538	7.95	61.7	7.93	8.03
	749	7.57	55.5	7.91	8.02
	1066	4.24	40.0	7.93	8.07
Column 1	2	3	4	5	6

given the pH-values in situ of the vertical series of samples, computed as before. In this latter case, however, it was necessary in addition to correcting as above, to correct for the alteration of pH-value due to warming of the subsurface samples.

The effect of this tentative computation of surface pH-values has been to increase the pH 0.06 to 0.09 unit. The effect on the depth series of samples at stations 26 and 31 has been to decrease the vertical pH-gradients, the greatest increases in pH were found for the data from the colder bottom-water which had gone through a greater amount of warming before determination than the less cold samples. This indicates that the bottom-water is more alkaline than supposed.

It should be noted that in this warming of subsurface samples suitable

*) pH corrected for «salt-error», see section VIII.

**) pH corrected for temperature-effect after Buch, see section X, and «salt-error».

precautions were taken to insure no change in the CO_2 equilibrium of the sample. The magnitude of the difference between the two series of results is certainly far greater than the experimental error of the instrument used for determination.

Bibliography.

- (1) HELLAND-HANSEN, B. and NANSEN, F. The Norwegian Sea, Its Physical Oceanography etc. Rept. on Norwegian Fishery and Marine Investigations Vol. II, No. 2. 1909.
- (2) ENNIS, C. C. Note on Preliminary Sonic-Depth Results on Cruise VII of the Carnegie During May 1928 to Sept. 1929. Not yet published. Dept. Terrestrial Magnetism, Carnegie Institution of Washington.
- (3) ATKINS, W. R. G. Seasonal Changes in the Phosphate-Content of Sea-Water in Relation to the Growth of Algal Plankton During 1923 and 1924. Journ. Mar. Biol. Ass. Plymouth. Vol. XIII, No. 3. March 1925.
- (4) SEIWELL, H. R. Phosphate-Content and Hydrogen-Ion Concentration of the Surface-Water of the English Channel and Southern North Sea, June 18—22, 1928. Nature, Dec. 15, 1928.
- (5) KNUDSEN, M. and GEHRKE, J. Hydrographical Section C. Mem. Sur les Travaux, C. P. I. E. Pendant les Années 1902—1912. Copenhagen, 1913.
- (6) JACOBSEN, J. P. and JENSEN, A. J. C. Examination of Hydrographical Measurements from the Research Vessels "Explorer" and "Dana" During the Summer of 1924. Rapp. et Procès-Verbaux. Vol. XXXIX, p. 31. Copenhagen 1926.
- (7) ATKINS, W. R. G. The Phosphate-Content of Sea-Water in Relation to the Growth of the Algal Plankton, part III. Jour. Mar. Biol. Ass. Plymouth. Vol. XIV, No. 2. 1926.
- (8) SANDSTRØM, W. J. The Hydrodynamics of Canadian Atlantic Waters. Canadian Fisheries Expedition, 1914—1915.
- (9) KNUDSEN, M. Hydrography of Danish Ingolf Expedition. Report of Voyage, Vol. I, No. 2. Copenhagen 1899.
- (10) SEIWELL, H. R. The Phosphate-Content of the North Atlantic Ocean. Not yet published. Washington, D. C.
- (11) NANSEN, F. The Waters of the North Eastern North Atlantic. Int. Rev. des ges. Hydrobiologie and Hydrographie. Hydrographisches Supp. zu Band IV.
- (12) BARNETT, G. D. and BARNETT, C. W. Colorimetric Determination of Hydrogen-Ion Concentration by Means of a Double Wedge Comparator. Proc. Soc. Exper. Biol. and Med. 18, pp. 127—131. 1920.
- (13) MØBERG, E. G. The Hydrogen-Ion Concentration of Sea-Water off the Coast of Southern California. Proc. 3rd Pan Pacific Congress, pp. 221—228. Tokyo, 1926.
- (14) RAMAGE, W. D. and MILLER, R. C. The Salt-Error of Cresol Red. Journ. Am. Chem. Soc. Vol. 47, pp. 1230—1235. 1925.
- (15) ATKINS, W. R. G. The Hydrogen-Ion Concentration of Sea-water in its Biological Relations. Journ. Mar. Biol. Ass. Plymouth. Vol. XII, pp. 717—771. 1922.

- (16) JOHNSON, M. W. and THOMPSON, T. G. The Sea-Water at the Puget Sound Biological Station from September 1927 to September 1928. Pub. Puget Sound Biol. St. Vol. VII, pp. 119—128. 1929.
- (17) Moberg, E. G. The Interrelation Between Diatoms, Their Chemical Environment, and Upwelling Water in the Sea off the Coast of Southern California. Proc. Nat. Acad. Sci. Vol. XIV, No. 7. 1928.
- (18) ATKINS, W. R. G. The Hydrogen-Ion Concentration of Sea-Water in its Relation to Photosynthetic Changes, II. Jour. Mar. Biol. Ass. Plymouth. Vol. XIII, pp. 93—118.
- (19) BUCH, K. Über den Einfluss der Temperatur auf die pH-Bestimmung des Meerwassers. Merentutkimuslaitoksen julkaisu, Havsforskningsinstitutets skrift No. 61. Helsingfors, 1929.
- (20) BUCH, K. On the Determination of pH in Sea-water at Different Temperatures. Jour. du Conseil. Vol. IV, No. 3, pp. 267—280. 1929.