

The Hydrogen Ion Concentration of Sea Water in its Relation to Photosynthetic Changes.

Part II.

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With Figures 1-12 in the Text.

CONTENTS.

	PAGE
INTRODUCTION	93
THE COLORIMETRIC METHOD OF DETERMINING HYDROGEN ION CONCENTRATIONS	94
THE RELATION OF THE WATER OF PLYMOUTH SOUND TO THAT OF THE OPEN SEA THROUGHOUT THE YEAR	96
THE SEASONAL CHANGES IN THE HYDROGEN ION CONCENTRATION OF THE OPEN SEA AT VARIOUS STATIONS AND DEPTHS	101
VARIATION IN HYDROGEN ION CONCENTRATION IN RELATION TO THE MOVEMENT OF FISHES	112
SOME FACTORS AFFECTING THE PHOTOSYNTHETIC ACTION OF THE ALGAL PLANKTON	113
SUMMARY	116

INTRODUCTION.

IN the first publication under the above general title* the seasonal changes in sea water were studied, but as explained previously it was not possible to regard all the data as of an equal degree of accuracy. For this and other reasons the seasonal changes were further traced in the hydrographical cruises up to October, 1922, when the approach of the winter equilibrium made it profitless for some months to continue. Since, however, at times from April to September the changes are relatively rapid it may be advisable to follow up the matter during the period mentioned at shorter intervals.

* Journ. Mar. Biol. Assoc., Vol. XII, No. 4, p. 717, 1922.

The precise positions of the stations are recorded, and shown on a map, in the first paper (1922), but it may be said that L 1 is in Plymouth Sound, below the Laboratory, L 2 at the Breakwater, L 3 at Rame Head on the line to the Eddystone, which is L 5, L 4 being intermediate. From that onwards L 6, E 1 and E 2 are on the course to Ushant, which is near E 3. The stations N 1, N 2, N 4 and N 5 lie between Ushant and Cork Harbour, N 3 lies between the Scillies and Cornwall, and E 6 is further north in the Bristol Channel. E 7, a station which is now usually omitted, lies S.E. from the Wolf Light off the Lizard. Stations N 4 and N 5 were worked by the Irish boat.

THE COLORIMETRIC METHOD OF DETERMINING HYDROGEN ION CONCENTRATIONS.

The determinations were made in hard glass test tubes of 12 mm. internal diameter. The tubes were graded so that their external diameters did not vary by more than ± 0.5 mm. The water was examined immediately after it was drawn, and 10.0 c.c. measured from a pipette was added in each case to 0.50 c.c. of indicator. The tops of the tubes were closed by rubber caps. Before comparison it is necessary to allow the freshly drawn water to reach the same temperature as the standard tubes in the cabin. If this is not done the colder sea water in winter appears more alkaline than in reality it is. It must be emphasized that sufficient accuracy is not obtained by adding drops of indicator from a pipette or dropping bottle. The motion of the ship usually makes it impossible to keep the tube vertical, accordingly measurements were invariably made with a pipette of the first quality divided into 0.01 c.c. These pipettes are 145–187 mm. in length for 1.00 c.c., so with the tip against the side of the test tube it is thought that 0.50 c.c. can be measured to ± 0.005 c.c., namely, that the meniscus is within approximately one millimetre of the 0.50 position.

The indicator used was mainly cresol red, 0.02 per cent. In the presence of a little toluene as preservative the standard tubes with this indicator have undergone no perceptible change since mixed on November 8th, 1921, a period of twenty months. It may be added that portions of the standard buffer at pH 8.14 to which cresol red was added on November 8th, 1921, and February 28th, 1922, were indistinguishable when first compared and are still so. When not in use the tubes are kept in the dark as a precaution. It was intended to use this set throughout the year, but as the bottle of indicator was spilled during a storm the supply failed. A fresh dilution of cresol red was made on March 28th, and standard tubes with it were in use up to the end of the work in October. The

measuring out of the buffer solution anew is necessary for each fresh dilution of indicator, so it is advisable to make up a supply sufficient to last through the work contemplated.

The standards were the borax, boric acid, sodium chloride mixtures of McClendon (1917), corrected for the chloride normality of the sea water off Plymouth. The standards were at pH7.99, 8.04, 8.09, 8.14, 8.16, 8.19, 8.24, 8.29. For estuarine water a small correction was applied as previously mentioned. In addition to these standards the tubes in a depth series and from station to station were compared with each other, a further aid to uniformity being thus obtained.

For the more alkaline samples, pH8.24 and upwards, thymol blue was used as well as cresol red, since the latter is nearing the end of its range, taking into account that pH0.18 has to be taken off for salt error. Thymol blue is a serviceable indicator, and sealed tubes containing it were used for work in the Pacific by Mayor (1922) for two years without appreciable change. When the solution is sterile and access of carbon dioxide is prevented tubes with thymol blue have been found by the writer to be quite satisfactory, but in the alkaline range where this indicator is serviceable traces of carbonic acid, whether of endogenous or exogenous origin, have a marked effect.

Xylenol blue (*p*-xylenol sulphonephthalein) introduced by A. Cohen (1922) has also been tried. Its acid range is given as pH1.2-2.8, the same as that of thymol blue, and its alkaline range as pH8.0 (yellow) to 9.6 (blue) as against pH8.2-9.8 for thymol blue. When compared for two months with thymol blue no change could be noticed in solutions at pH8.24 and 8.29; moreover, the distinction between pairs of tubes at pH0.05 interval was appreciably greater with xylenol blue in 0.02 per cent concentration than with an equal volume of 0.04 per cent thymol blue. In Clark and Lubs' buffer solutions xylenol blue gives a grey blue at pH8.6 and a good blue at pH9.0, whereas thymol blue is yellowish blue at pH8.6 and light slaty blue at pH9.0. There are thus, with xylenol blue, very easily observed changes in a region of importance in the study of photosynthesis, and the overlap with cresol red is rather better than is the case of thymol blue. For the region over pH9 the latter is the more satisfactory.

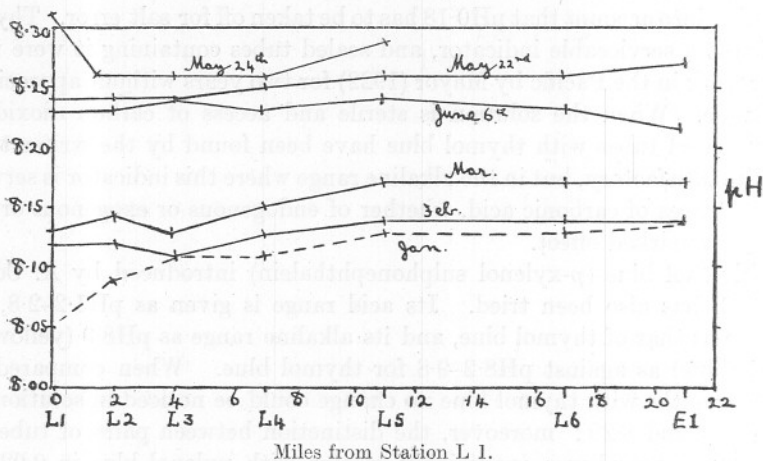
The indicators used by Palitzsch and again recommended by him (1922), namely, *a*-naphtholphthalein and phenolphthalein, were tried and rejected on account of their lack of permanence of colour, which necessitates the mixing of fresh standards each day. Neutral red is also recommended by Palitzsch for use between pH6.5-7.8. It has the disadvantage that it precipitates slowly in the more alkaline region, for which reason phenol red is to be preferred. Thymolphthalein, tetra-brom phenolphthalein, *a*-naphthol sulphonephthalein and cresolphthalein

were also tried and found to be less satisfactory than the sulphone-phthaleins previously mentioned, though cresol phthalein gives a more stable solution than the other phthaleins tested.

THE RELATION OF THE WATER OF PLYMOUTH SOUND TO THAT OF THE OPEN SEA THROUGHOUT THE YEAR.

The observations of hydrogen ion concentration, temperature and salinity recorded in Part I were continued up to October, 1922, and the results for the L series of stations are given in the following tables, the pH values being corrected for salt error. Figure 1 shows the pH values

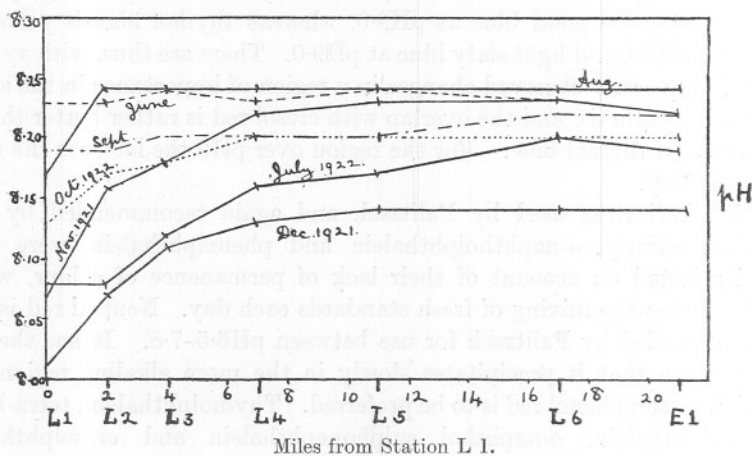
SEASONAL CHANGES IN pH, SURFACE.



Miles from Station L 1.

FIG. 1.

SEASONAL CHANGES IN pH, SURFACE.



Miles from Station L 1.

FIG. 2.

from L 1 to E 1. It may be seen that from January onwards to May the water is increasing in alkalinity, and whereas the surface water of the open sea is more alkaline than that of the Sound in winter, in May there is little difference, or a slight advantage in favour of the Sound. For June the values are somewhat lower than in the end of May. A comparison of the values for May 22nd, 24th, and June 6th leads one to the conclusion that the calmness of the sea and consequent undisturbed state of the surface layers is an important factor, since the more alkaline water produced by the intense photosynthesis in the surface layers is not mixed up with the deeper water. Figure 2 shows the June values again, by comparison with which a great fall is noticeable early in July. August shows high values, thereafter a slow fall takes place to the winter conditions of December and January. The value for November, 1921, seems abnormally high, consequent upon the exceptionally hot and sunny weather experienced that autumn.

Station.	May 22nd, 1922.			June 6th.		
	t °C.	pH.	s ‰	t °C.	pH.	s ‰
L 1	14.4	8.24	31.62*	13.8	8.23	34.09*
L 2	13.0	8.24	33.27	13.3	8.23	34.59
L 3	12.9	8.24	34.34	12.6	8.24	35.16
L 4	12.9	8.25	34.62	12.8	8.23	35.24
L 5	12.3	8.26	35.15	12.8	8.24	35.26
L 6	12.6	8.26	35.14*	12.8	8.23	35.29*

Station.	July 11th.			August 3rd.		
	t °C.	pH.	s ‰	t °C.	pH.	s ‰
L 1	13.8	8.08	33.49	14.6	8.18	34.37
L 2	13.9	8.08	33.80	13.8	8.24	35.22
L 3	14.1	8.12	34.89	14.3	8.24	35.24
L 4	15.3	8.16	35.26	14.2	8.24	35.29
L 5	14.0	8.17	35.37	14.3	8.24	35.30
L 6	14.1	8.20	35.33	14.5	8.24	35.29

Station.	September 22nd.			October 12th.		
	t °C.	pH.	s ‰	t °C.	pH.	s ‰
L 1	14.6	8.19	34.79	13.8	8.13	33.03*
L 2	14.5	8.19	35.23	14.1	8.17	34.63
L 3	14.6	8.20	35.23	14.1	8.18	34.83*
L 4	14.4	8.20	35.31	14.2	8.20	35.22
L 5	14.4	8.20	35.32	14.3	8.20	35.33
L 6	14.6	8.22	35.31	14.2	8.20	35.24

* Denotes mean of duplicate titrations.

The seasonal changes at the surface in pH value and in temperature are shown in Fig. 3 for L 1 and L 3, taken as a coastal station, since it lies off Rame Head, and the water bottle may be lowered safely to 45 metres. Thus while not removed from coastal influences the water is fairly deep. The fall in pH value at L 1 in December and July, with the rise in May and September, are clearly brought out. The L 3 values are steadier in December, but the July fall is noticeable, also rises in May and August. It may be observed that while there is a general similarity between the curves for pH and temperature it is obvious that the variations in pH are not purely temperature changes. Under the section dealing with E 1 will be found a figure (Fig. 7) showing the pH values corrected to 12° C., as explained there. The corrected values for L 1 and L 3 are given in the following table :—

	L 1			L 3		
	t °C.	pH.	pH corr. to 12 °C.	t °C.	pH.	pH corr. to 12 °C.
Nov. 9th . .	11.6	8.07	8.07	14.0	8.18	8.16
Dec. 12th . .	10.6	8.01	8.02	11.8	8.11	8.11
Jan. 11th . .	10.0	8.05	8.07	10.3	8.11	8.13
Feb. 6th . .	8.2	8.12	8.16	8.9	8.11	8.13
March 15th . .	8.5	8.12	8.16	8.9	8.13	8.15
March 29th . .	8.0	8.12	8.16	8.6	8.14	8.16
May 22nd . .	14.4	8.24	8.22	12.9	8.24	8.23
May 24th . .	13.7	8.31	8.29	14.1	8.26	8.24
June 6th . .	13.8	8.23	8.21	12.6	8.24	8.24
July 11th . .	13.8	8.08	8.06	14.1	8.12	8.10
Aug. 3rd . .	14.6	8.18	8.15	14.3	8.24	8.22
Sept. 22nd . .	14.6	8.19	8.16	14.6	8.20	8.17
Oct. 12th . .	13.8	8.13	8.11	14.1	8.18	8.16

A few exceptionally high pH values for May 24th, recorded in a later section, include observations on the L series as well as the remainder of a long coastal run. The results are plotted in Figure 1.

The changes in salinity for stations L 1 to L 5 are shown in Figure 4, from August, 1921, to October, 1922. The values for L 6 and E 1 were similar to those for L 5, so are omitted for clearness. The minima in January and in May are noticeable. For the inner stations more frequent readings would be necessary correctly to show the changes. It suffices here to establish the fact that even at L 3, and out to L 4, the disturbing effect of the river water is noticeable.

In viewing any station from a biological standpoint it is of importance to consider the uniformity or otherwise of the conditions from surface to

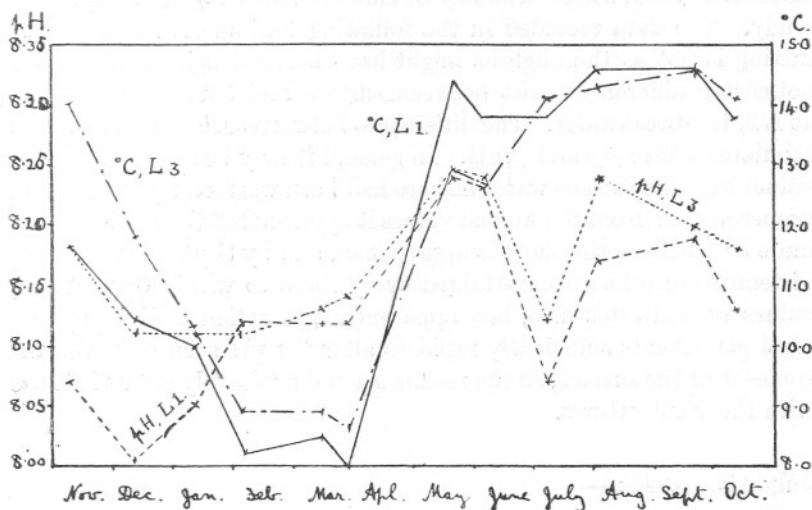
SEASONAL CHANGES IN TEMPERATURE AND pH AT STATIONS
L 1 AND L 3, SURFACE.

FIG. 3.

SEASONAL CHANGES IN SALINITY, STATIONS L 1 TO L 5, SURFACE.

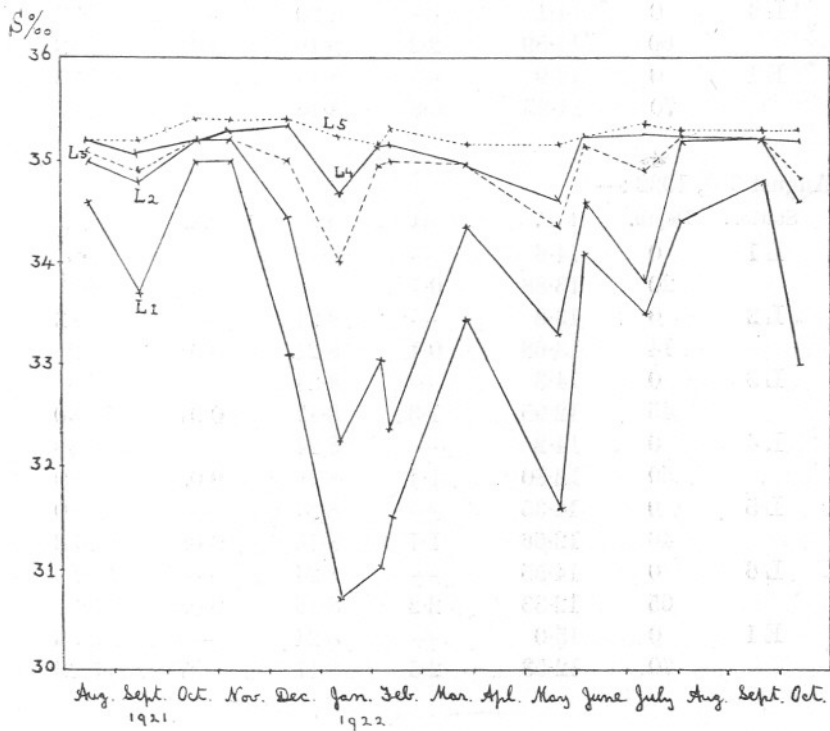


FIG. 4.

bottom. This has been done in detail for the international stations, but in consequence of the shallower water and more thorough mixing at the stations of the L series, economy of effort precluded a similar systematic study. The data recorded in the following tables show, however, that mixing is not as thorough as might have been thought, and that quite noticeable differences exist between surface and bottom water, except at L 2, the Breakwater. The differences between surface and bottom are tabulated under Δt and ΔpH . In general it may be seen from the July values that the surface water inshore had been warmed up more than the deeper water; from the August values it appears that the mixing becomes more complete as the shore is approached, and by September uniformity of temperature has been attained everywhere to within 0.4° . The pH values indicate this also, but apparently the action of light upon the algal plankton is sufficiently rapid to alter the pH soon after the water comes near the surface, so the results are not as sharply cut as is the case with the temperatures.

July 11th, 1922 :—

Station.	Depth.	t °C.	Δt	pH	ΔpH	s ‰
L 5	0	14.0	—	8.17	—	35.37
	50	12.08	1.9	8.16	0.01	35.35
L 6	0	14.1	—	8.20	—	35.33
	60	11.89	2.2	8.16	0.04	35.42
E 1	0	12.9	—	8.19	—	35.38
	70	11.95	0.8	8.16	0.03	35.37

August 3rd, 1922 :—

Station.	Depth.	t °C.	Δt	pH	ΔpH	s ‰
L 1	0	14.6	—	8.18	—	34.37
	20	13.88	0.7	—	—	35.17
L 2	0	13.8	—	8.24	—	35.22
	14	13.68	0.1	8.21	0.03	35.28
L 3	0	14.3	—	8.24	—	35.24
	45	12.95	1.3	8.17	0.07	35.30
L 4	0	14.2	—	8.24	—	35.29
	50	12.80	1.4	8.16	0.08	35.30
L 5	0	14.35	—	8.24	—	35.30
	46	12.66	1.7	8.16	0.08	35.32
L 6	0	14.55	—	8.24	—	35.29
	65	12.33	2.2	8.16	0.08	35.34
E 1	0	15.0	—	8.24	—	35.32
	70	12.53	2.5	8.17	0.07	35.32

September 22nd, 1922 :—

Station.	Depth.	t °C.	Δt	pH	ΔpH	s ‰
L 1	0	14.6	—	8.19	—	34.79
	20	—	—	—	—	—
L 2	0	14.5	—	8.19	—	35.23
	14	14.4	0.1	8.19	0.00	35.21
L 3	0	14.6	—	8.20	—	35.23
	45	—	—	—	—	—
L 4	0	14.4	—	8.20	—	35.31
	50	—	—	—	—	—
L 5	0	14.4	—	8.20	—	35.32
	46	14.33	0.1	8.20	0.00	35.28
L 6	0	14.6	—	8.22	—	35.31
	65	14.24	0.4	8.18	0.04	35.28
E 1	0	14.4	—	8.22	—	35.30
	70	14.17	0.2	8.18	0.04	35.29

THE SEASONAL CHANGES IN THE HYDROGEN ION CONCENTRATION OF THE OPEN SEA AT VARIOUS STATIONS AND DEPTHS.

The observations were made at E 1 monthly, and at the other stations, weather permitting, during the five annual cruises, February, end of

SEASONAL CHANGES, STATION E 1, SURFACE AND BOTTOM.

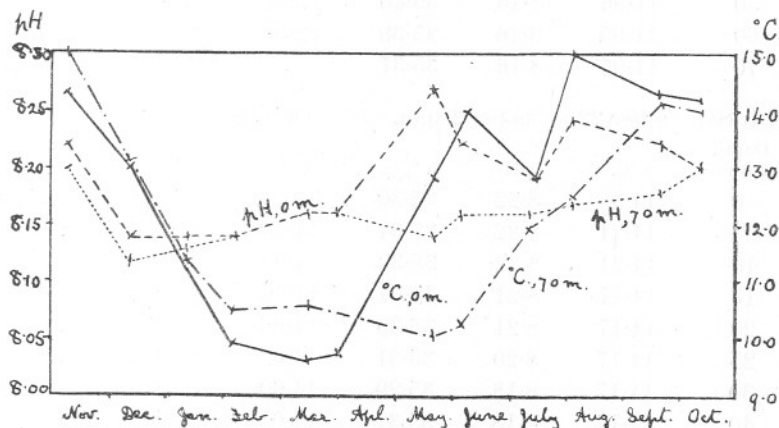


FIG. 5.

March, May, July and November. The continuation of the results for E 1 is shown in the following tables, and these and the former values are plotted in Figures 5, 6, 7 and 8.

E 1, May 22nd, 1922, 1-3 p.m.

June 6th, noon-2 p.m.

Depth in metres.	t °C.	pH	s ‰	t °C.	pH	s ‰
0	12.8	8.27	35.24	13.95	8.22	35.30*
5	12.70	8.27	35.23	13.89	8.22	35.23*
10	12.05	8.27	35.26	13.58	8.21	35.28
15	12.00	8.25	35.26	12.12	8.20	35.28
20	11.28	8.25	35.27*	10.60	8.17	35.25
25	10.50	8.24	35.33	10.41	8.17	35.26*
30	10.25	8.21	35.34	10.41	8.17	35.21
40	10.10	8.16	35.40	10.37	8.17	35.22
50	10.08	—	35.39	10.27	—	35.22
60	10.08	8.14	35.35	10.27	—	35.22
70	10.05	8.14	35.38*	10.27	8.16	35.22

E 1, July 11th, 4-6 p.m.

August 3rd, noon-2 p.m.

Depth in metres.	t °C.	pH	s ‰	t °C.	pH	s ‰
0	12.8	8.19	35.38	15.00	8.24	35.32
5	12.34	8.19	35.35	14.58	8.24	35.32
10	12.08	8.19	35.36	14.58	8.24	35.29
15	12.07	8.19	35.35	14.41	8.23	35.32
20	12.03	8.18	35.35	12.81	8.17	35.29
25	12.00	8.18	35.36	12.45	8.17	35.36
30	12.00	8.17	35.37	12.40	8.17	35.33
40	11.97	8.16	35.38	12.38	8.17	35.35
50	11.96	8.16	35.40	12.38	8.17	35.34
60	11.95	8.16	35.39	12.38	8.17	35.34
70	11.95	8.16	35.37	—	8.17	35.32

E 1, September 22nd, noon-2 p.m.

October 12th, noon-2 p.m.

Depth in metres.	t °C.	pH	s ‰	t °C.	pH	s ‰
0	14.3	8.22	35.30	14.2	8.20	35.31
5	14.21	8.22	35.31	14.10	8.20	35.25
10	14.21	8.22	35.30	14.08	8.20	35.26*
15	14.17	8.21	35.31	14.06	8.20	35.28
20	14.17	8.21	35.30	14.06	8.20	35.28
25	14.17	8.20	35.31	14.02	8.20	35.27
30	14.17	8.18	35.29	14.00	8.20	35.26
40	14.17	8.18	35.31	14.01	8.20	35.25
50	14.17	8.18	35.29	14.00	8.20	35.27*
60	14.17	8.18	35.30	14.02	8.20	35.26
70	14.17	8.18	35.29	14.02	8.20	35.29

* Denotes mean of duplicate titrations

The variations of temperature and pH value from November, 1921, to October, 1922, at both surface and bottom, are displayed in Figure 5. The values all fall in early winter, the temperatures for the bottom being slightly higher than those for the surface from November to March. The surface minimum temperature was noted in the middle of March, the bottom in May, though possibly it may have occurred in April or even late March, since observations are wanting then. The sunny weather of late May led to a rapid warming up of the surface water, which the winds of June mixed with the deeper layers as shown by the approximation of the two temperature curves. The maximum surface temperature was noted in August, and the bottom maximum in September. Then and in October the two were close together.

At no time of the year are the surface pH values below those for the bottom, though during the winter, up to March, the two are almost or absolutely identical. The noticeable feature in the curve is the rapid rise to the maximum late in May, followed by the secondary minimum in July. That this is not due merely to mixing appears to be shown by Figure 8, and the data upon which it is based, as will be explained later. Figure 5, too, shows no marked rise in the pH curve for the bottom during June and July to account for the fall in the surface values. The rise occasioned by photosynthetic removal of carbon dioxide by the algal plankton, which has become abundant by May, is thus seen to be followed by a fall in pH value. For this several factors may in part be responsible, namely: (1) Mixing with deeper water consequent upon rough weather in June; (2) the absorption of atmospheric carbon dioxide tending to restore the equilibrium value; (3) respiration carried on by the algal plankton transported into deeper water with insufficient illumination, and by the plankton fauna increasing both in numbers and size as a result of the abundant algal food supply.

By October the mixing at E 1 has become complete, and the value pH8.20 is back to the figure of the previous November at 70 metres depth. Stormy weather, through addition of carbon dioxide and also apparently a heavy death rate in the plankton, tend to lower the pH value to the winter equilibrium.

In the foregoing discussion the physical effect of alteration in temperature has been temporarily left unconsidered. Pure water changes its hydrogen ion concentration from pH7.00 to pH7.10, as the temperature falls from 22° C. to 16° C., and the change proceeds uniformly for many degrees above and presumably below this range. Such changes are, however, automatically corrected in the colorimetric method by the changes in the standard tubes, provided sufficient time elapses for the samples to reach the temperature of the standards as already mentioned. There is, however, another temperature effect, namely, upon the solu-

bility of carbon dioxide in water and upon the equilibrium between calcium carbonate, bicarbonate and carbonic acid. By boiling, the removal of carbon dioxide results in a continual dissociation of bicarbonate till only carbonate is left, pH 10-10.2 resulting for sea water. Conversely on cooling more carbon dioxide goes into solution, and the pH value falls. McClendon (1917) gives the temperature coefficient as pH 0.01 added for each rise of 1° C. That the temperature effect is not the only one operative in the case of sea water is evident from Figure 6, in which the pH values and temperatures at 10 metres are plotted. Thus pH 8.20 may be found with temperatures from about 10.5-14.5° C., and a temperature of 12° C. may be accompanied by pH 8.14-8.25. The 10-metre values were plotted because conditions at that depth are less subject to fluctuations than at the surface, especially fluctuations of temperature.

In the table which follows are given the surface and bottom values at E 1 for temperature and pH, also the latter corrected to 12° C. by

	t °C.	pH	pH corr. to 12 °C.	t °C.	pH	pH corr. to 12 °C.
Nov. 9th .	14.96	8.23	8.20	14.98	8.20	8.17
Dec. 12th .	12.95	8.14	8.13	13.11	8.14	8.13
Jan. 11th .	11.24	8.14	8.15	11.35	8.13	8.14
Feb. 6th .	9.9	8.14	8.16	10.50	8.14	8.15
March 15th	9.6	8.17	8.19	9.62	8.17	8.19
March 29th	9.7	8.16	8.18	—	—	—
May 22nd .	12.8	8.27	8.26	10.05	8.14	8.16
June 6th .	13.95	8.22	8.20	10.27	8.16	8.18
July 11th .	12.8	8.19	8.18	11.95	8.16	8.16
Aug. 3rd .	15.00	8.24	8.21	12.53	8.17	8.17
Sept. 22nd	14.3	8.22	8.20	14.17	8.18	8.16
Oct. 12th .	14.2	8.20	8.18	14.02	8.20	8.18

McClendon's coefficient. This temperature was chosen as entailing, on an average, the minimum amount of correction, the May maximum remaining unaffected, and the December and January values being reduced and increased by pH 0.01 respectively. The corrected values are shown graphically in Figure 7, which may be compared with Figures 3 and 5, showing the uncorrected values.

The December minimum is well marked at all three stations, as are also the May and August maxima and the depression in July. The meeting of the surface and 70 metres pH curves in October is noteworthy.

The pH values at various depths at E 1 have been given in Part I and in the tables in this section. The results are shown graphically in Figure 8. The marked fall in pH for the whole column of water from November to

SEASONAL CHANGES, STATION E 1, 10 METRES.

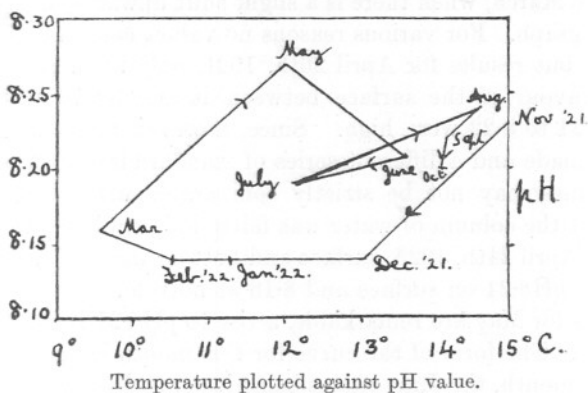


FIG. 6.

SEASONAL CHANGES IN pH, CORRECTED TO 12 °C.

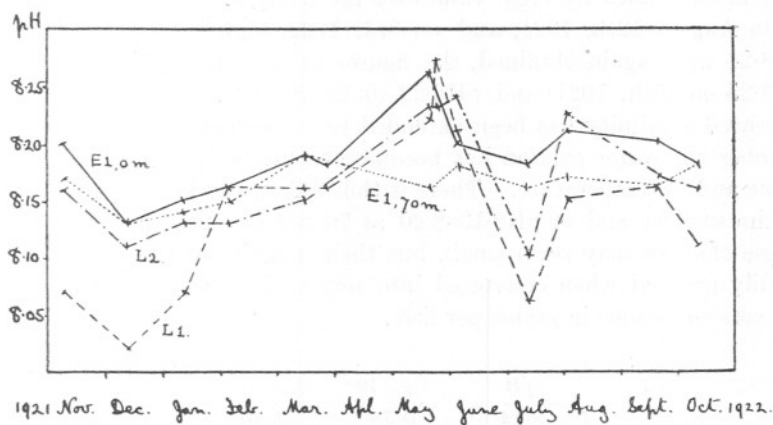


FIG. 7.

SEASONAL CHANGES, STATION E 1, pH VALUES AT VARIOUS DEPTHS.

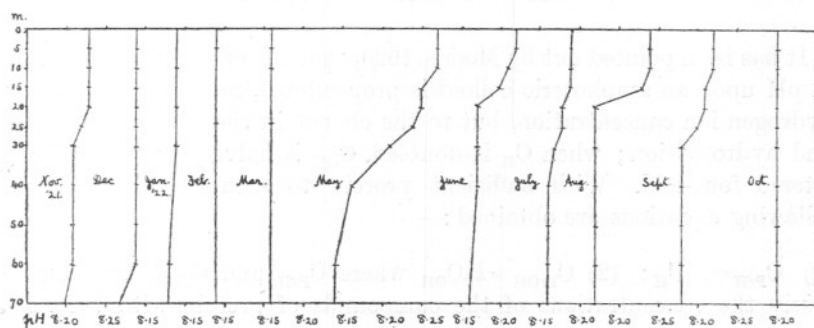


FIG. 8.

December, 1921, is at once evident, as is also the uniformity of the column up to March, when there is a slight shift upwards, namely, to the right in the graph. For various reasons no values could be obtained for April, 1922, but results for April 26th, 1921, only show a difference of pH 0.02 in favour of the surface between it and 30-70 metres. The values pH 8.24 to 8.22 were high. Since, however, these were the first estimations made and a different series of standard buffers was used, the absolute values may not be strictly comparable with those for 1922. The fact that the column of water was fairly uniform is, however, established. On April 24th, 1923, surface and bottom were at pH 8.18 at E 1, E 2 being at pH 8.24 on surface and 8.18 at bottom.

The values for May are remarkable, a rise to pH 8.21 being found even at 30 metres. The form of the curve for this month is quite unlike that of any other month, the June values being lower and tending towards the summer minimum early in July. As mentioned in detail further on, both in 1921 and 1922, low values for the eastern stations at this time were accompanied by high values for the western.

On August 12th, 1921, and on 3rd, 1922, high values, pH 8.27 and pH 8.24 were again obtained, the figures remaining high in September, pH 8.25 on 15th, 1921, and pH 8.22 on 22nd, 1922. By September the increased alkalinity has been extended to a considerable depth, and by October the water column has become absolutely uniform, both in pH value and in temperature. There is thus a range at E 1 of pH 8.14-8.27 at the surface, and of pH 8.13-8.20 at 70 metres, close to the bottom. These changes may seem small, but their magnitude may be the more readily grasped when converted into terms of hydrogen and hydroxyl ion concentrations in grams per litre.

E 1	pH	$C_H \times 10^{-8}$	$C_{OH} \times 10^{-6}$	Percentage fall in C_H .
Surface {	8.14	0.72	1.40	—
	8.27	0.54	1.88	25
Bottom {	8.13	0.74	1.37	—
	8.20	0.63	1.60	15

It has been pointed out by Moore (1920) that the effect of an alteration in pH upon an amphoteric colloid is proportional, not to the change in hydrogen ion concentration, but to the change in the ratio of hydrogen and hydroxyl ion; when C_H is doubled, C_{OH} is halved and the ratio is altered four-fold. With sufficient protein to saturate all ions the following equations are obtained:—

(1) $C_{PrH} = k_1 C_H$; (2) $C_{PrOH} = k_2 C_{OH}$ where C_{PrH} and C_{PrOH} are respectively the concentrations of the compounds of protein with the ions.

By division (3) $\frac{C_{PrH}}{C_{PrOH}} = K_1 \frac{C_H}{C_{OH}}$. But for water $C_H \cdot C_{OH} = k_3$, or $C_{OH} = \frac{k_3}{C_H}$, so by substitution in (3) $\frac{C_{PrH}}{C_{PrOH}} = \frac{K_1}{k_3} [C_H]^2 = K_2 [C_H]^2$.

Taking the values for the sea at E 1 surface, summer and winter extremes, the $\frac{C_{PrH}}{C_{PrOH}}$ ratio is altered as $\frac{100^2}{75^2}$, namely, in ratio 1.00 : 0.56, and for the bottom 1.00 : 0.72.

The results obtained at the other international stations from July, 1921, to July, 1922, inclusive, are given in Part I and in the tables which follow here.

E 2, May 22nd, 8-10 p.m.

July 11th, 10 p.m.-midnight.

Depth in metres.	t °C.	pH	s ‰.	t °C.	pH	s ‰.
0	12.5	8.24	35.36	13.9	8.17	35.37
5	12.30	8.24	35.34	12.85	8.17	35.36
10	11.80	8.19	35.29*	12.72	8.17	35.35
15	11.00	8.19	35.32	12.72	8.17	35.35
20	10.92	8.16	35.31	12.70	8.17	35.35
25	10.73	8.16	35.31	12.70	8.17	35.35
30	10.68	8.15	35.34	12.70	8.17	35.35
40	10.62	8.15	35.31	—	—	—
50	10.60	—	35.34*	12.67	8.17	35.37
60	10.60	—	35.33	—	—	—
70	10.62	—	35.35	12.70	—	35.37
85	10.60	8.15	35.36	12.67	8.17	35.34

E 3, May 23rd, 1922, 4-6 a.m.

July 12th, 1922, 6-8 a.m.

Depth in metres.	t °C.	pH	s ‰.	t °C.	pH	s ‰.
0	11.9	8.18	35.28*	11.9	8.16	35.31
5	11.40	—	35.29	11.81	8.16	35.31
10	11.20	8.18	35.29	11.81	8.16	35.31
15	—	—	—	11.80	8.16	35.29
20	—	—	—	11.81	8.16	35.34
25	11.02	8.17	35.29	11.81	8.16	35.31
30	—	—	—	11.81	8.16	35.33
50	—	—	—	11.70	8.15	35.32
60	—	—	—	11.65	—	35.33
75	—	—	—	11.65	8.15	35.29
100	11.05	8.16	35.31	11.60	8.15	35.32

* Denotes mean of duplicate titrations.

N 1, May 23rd, noon to 2 p.m.

July 12th, 1-3 p.m.

Depth in metres.	t °C.	pH	s ‰.	t °C.	pH	s ‰.
0	12.9	8.18	35.29	13.7	8.22	35.26
5	12.46	—	35.29	13.19	8.21	35.26
10	11.58	8.18	35.26	11.83	8.21	35.28
25	11.00	8.17	35.28	11.38	8.17	35.28
75	10.51	—	35.34	10.74	8.14	35.31
100	10.50	8.16	35.33*	10.72	8.14	35.28

N 2, May 23rd, 7-9 p.m.

July 12th, 6-8 p.m.

Depth in metres.	t °C.	pH	s ‰.	t °C.	pH	s ‰.
0	12.0	8.17	35.15	13.6	8.21	35.26
10	11.30	—	35.18	12.70	8.20	35.25
25	10.4	8.16	35.17	12.48	8.17	35.26
75	10.28	8.15	35.20	—	—	—
85	—	—	—	11.98	8.16	35.26

N 3, May 23rd, midnight.

July 12th, 10 p.m.

Depth in metres.	t °C.	pH	s ‰.	t °C.	pH	s ‰.
0	12.1	8.19	35.19*	13.0	8.20	35.24
60	10.15	8.16	35.19	—	—	—
70	—	—	—	12.32	8.16	35.21

E 6, May 24th, 3-5 a.m.

July 13th, 1-3 a.m.

Depth in metres.	t °C.	pH	s ‰.	t °C.	pH	s ‰.
0	12.2	8.19	35.00*	13.3	8.20	35.15
5	11.78	—	35.04	13.40	—	35.12
10	11.08	—	35.08	12.64	—	35.15
15	10.94	—	35.07	12.55	—	35.08
20	10.62	—	35.12	12.52	—	35.09
25	10.20	—	35.11	12.48	—	35.08
30	9.90	—	35.20	11.47	—	35.12
40	9.87	—	35.17	—	—	—
50	9.87	—	35.19	11.32	—	35.24
75	9.87	8.16	35.17	11.28	8.16	35.24

Considering in the first place the surface pH values it may be seen that the two years are similar in July. Furthermore, and this is quite remarkable, the more westerly stations are in each case more alkaline than the

* Denotes mean of duplicate titrations.

easterly. These data, from April 1921, onwards, including values for E 1, are tabulated together under the heading "Surface pH values at international stations."

Surface pH values at international stations :—

	E 1.	E 2.	E 3.	N 1.	N 2.	N 3.	E 6.	E 7.
April, 1921	8.24	—	—	—	—	—	—	—
July . . .	8.17	8.17	8.18	8.22	8.22	—	—	8.25
Aug. . . .	8.27	—	—	—	—	—	—	—
Sept. . . .	8.25	—	—	—	—	—	—	—
Nov.	8.23	8.20	8.20	—	8.14	8.14	8.14	8.13
Dec.	8.14	—	—	—	—	—	—	—
Jan., 1922	8.14	—	—	—	—	—	—	—
Feb.	8.14	—	—	—	—	—	—	—
March	8.16	8.17	8.17	8.16	8.15	8.15	8.14	—
May	8.27	8.24	8.18	8.18	8.17	8.19	8.19	8.21
June	8.22	—	—	—	—	—	—	—
July	8.19	8.17	8.16	8.22	8.21	8.20	8.20	8.20
Aug.	8.24	—	—	—	—	—	—	—
Sept.	8.22	—	—	—	—	—	—	—
Oct.	8.20	—	—	—	—	—	—	—

They are shown graphically in Figure 9, on which values for L 1 are also plotted. Though these figures are plotted in a line from L 1 to E 7 it

SEASONAL CHANGES IN pH VALUE, SURFACE.

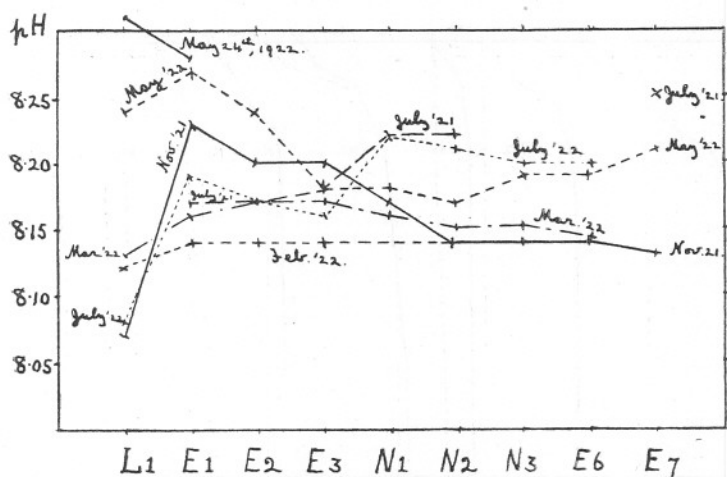


FIG. 9.

CHANGES IN pH WITH DEPTH, MAY, CONTINUOUS LINE AND
JULY, DOTTED LINE.

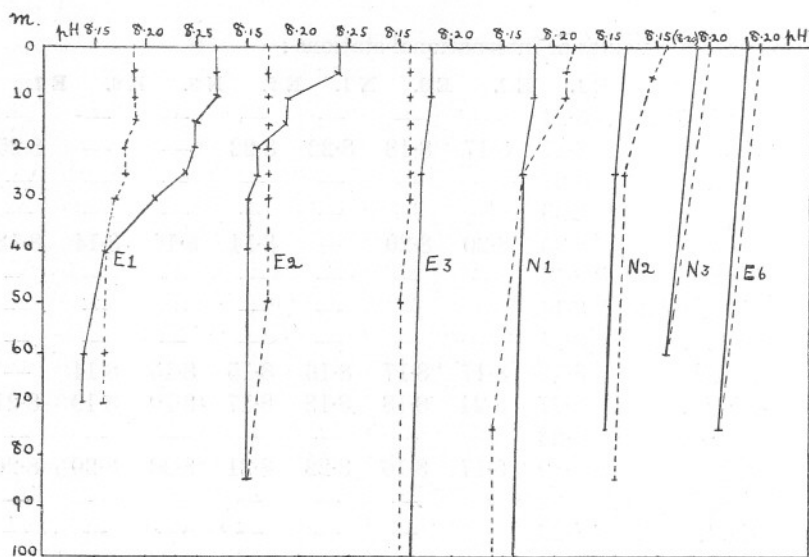


FIG. 10.

CHANGES IN TEMPERATURE WITH DEPTH, MAY, CONTINUOUS
LINE AND JULY, DOTTED LINE.

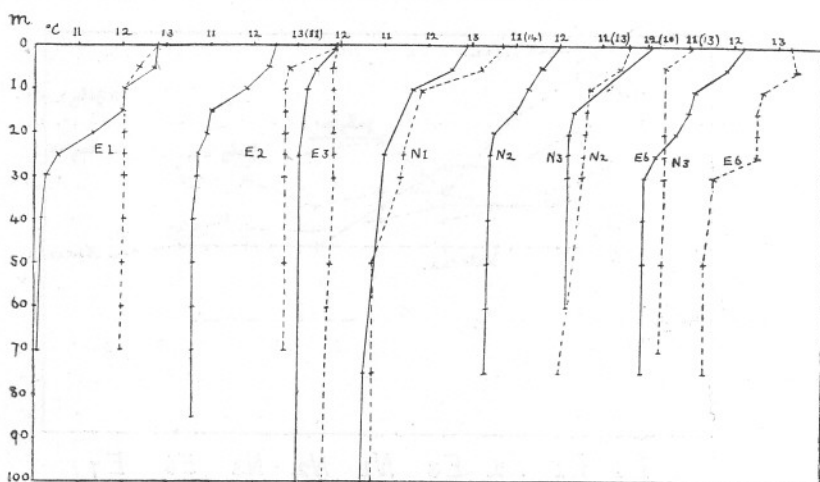


FIG. 11.

must be remembered that the stations form roughly a wide V, with L 1 and E 6 as the N.E. and N.W. apices, with E 3 at the south. E 7 is an extra station off Cornwall. The positions are shown in the map in Part I.

Though the July values are higher at N 1 and N 2 than at E 1 and E 2, yet for the latter the May pH values have the advantage. There is thus some evidence for a lag in the attainment of a high alkalinity as deeper and more open water is reached. The conditions prevailing at the international stations in May and July are rendered clearer by reference to Figures 10 and 11. The former shows the pH values and the latter the temperatures. At E 1 and E 2 the pH values for July are, as previously pointed out, below those for May, whereas the reverse is true in the main for N 1 and N 2. In all cases the temperature is higher in July than in May. The figures obtained for temperature and pH give an indication of the extent to which vertical currents mix the water. The straightening out of the curves for both quantities for E 1 and E 2 point to a better mixing in July than in May. At E 3 mixing is thorough, both then and at other times judging from other temperature records. At N 1, a deep station far from land, mixing is less efficient, whereas it increases at N 2 to N 3, becoming less again at E 6.

In this connection the results obtained by Palitzsch, quoted in Part I should be borne in mind, since they illustrate the penetration of the photosynthetic effect upon pH values to depths at which it seems reasonable to suppose that only mixing with more alkaline water could be the causal agent.

It remains to be considered how far the time of day affects the pH values found and the surface temperatures. There is undoubtedly a warming of the surface in calm sunny weather and an increase in pH value, but as may be seen from the figures in the table on page 112 the pH values do not seem to be appreciably affected, so that the differences from station to station may be considered in the main as real differences.

The figures given on page 112 seem to show that the rise in pH value of the surface water in the course of the day is very small when corrected for temperature by subtracting pH0.01 for each degree rise. The effect of mixing of the water is evident at E 3 as already pointed out, also off the Lizard, where both temperature and pH value are considerably below the values given fairly consistently for the rest of the day. The L 2 values, and the L 3 to some extent on 24th indicate mixing.

Comment may be made on the record for 1.30 a.m., May 24th, in this table. Shortly before this hour the *Salpa* entered a shoal of fish, which darted away from the bows by the hundred, each fish leaving a streak of phosphorescence. There was nothing abnormal in the water sample taken in the shoal. Steaming about nine knots there was no diminution in the numbers of fish by 2 a.m., when plankton tow-nets.

were lowered for twenty minutes. This involved going dead slow, and the nets gave an abundance of copepods, but no fish scales, which strengthens the supposition that the fish were mackerel. On resuming the normal rate of steaming the fish showed no decrease for about a

Locality.	Date.	Hour.	T°C.	pH.	Notes.
L 1	May 22nd	10.45 a.m.	14.4	8.24	One hour flood tide.
L 2	"	11 a.m.	13.0	8.24	
L 3	"	—	12.9	8.24	
L 4	"	—	12.9	8.25	
L 5	"	Noon	12.3	8.26	
L 6	"	1 p.m.	12.6	8.26	
E 1	"	1.30 p.m.	12.8	8.27	Day calm and sunny.
E 2	"	8.15 p.m.	12.5	8.24	
E 3	May 23rd	4 a.m.	11.9	8.18	Mixing of the water.
N 1	"	Noon	12.9	8.18	Day calm and sunny, morning fog.
N 2	"	7.15 p.m.	12.0	8.17	Fish amazingly abundant.
N 3	"	11.30 p.m.	12.1	8.19	
Half-way between N 3 and E 6	May 24th	1.30 a.m.	12.0	8.19	
E 6	"	3.10 a.m.	12.2	8.19	Mixing of the water.
Just off W. point of Lizard	"	10.40 a.m.	11.4	8.21	
Mount's Bay, 4 m. E. of Lizard	"	11.5 a.m.	12.5	8.27	Day calm and sunny.
Off Dodman, 6 miles on E. by N. course, 23 miles from Lizard	"	1.30 p.m.	13.0	8.28	
From Lizard, 34 miles S.W. of Rame Head, 7 m., 1 m. N.W. of L 5	"	2.45 p.m.	14.0	8.28	
L 4	"	3.25 p.m.	14.2	8.29	
L 3	"	3.50 p.m.	14.6	8.26	
L 2	"	4.15 p.m.	14.1	8.25	
L 1	"	4.30 p.m.	13.4	8.25	Mixing of the water. High water.
East slip, below labora- tory	"	4.45 p.m.	13.7	8.29	
	June 10th	3 p.m.	—	8.28	Three hours' flood tide.
East of Breakwater	June 12th	11 a.m.	—	8.22	

quarter of an hour, when they gradually diminished in numbers, so that when E 6 was reached at 3 a.m. a few only were to be seen. The long-continued passage through such numbers of fish was a most remarkable sight.

VARIATION OF HYDROGEN ION CONCENTRATION IN RELATION TO THE MOVEMENT OF FISHES.

As mentioned in Part I the work of Shelford and Powers showed that fishes were able to detect very small changes in hydrogen ion concentration the active migratory fishes being in this respect far more sensitive than those which normally rest on or near the bottom. Powers (1921) also

traced the limits within which various fish were found in Puget Sound and its neighbourhood. Thus herring were only once found in water with a pH above 7.9, and they were never found in water below pH7.71. The greatest number of herring were observed in water at pH7.76-7.73. While such preferences and variations may be observed in estuarine waters, in the sea around this coast, the water is, as demonstrated by the figures already given, very uniform in alkalinity, and during winter not far from pH8.14, yet herring are at times caught in great quantity, as well as other fish. One can only conclude that under such conditions the hydrogen ion concentration of the water can be of no importance in determining the movements of fish. Salinity variations also seem entirely too small to have any significance in this connection. Variation in temperature seems to be the most promising physical factor for correlation with the movements of fish.

SOME FACTORS AFFECTING THE PHOTOSYNTHETIC ACTION OF THE ALGAL PLANKTON.

The balance between photosynthesis and respiration has already been discussed in Part I, and it was pointed out that in the sea light may often be a limiting factor, so that an increase in temperature is unaccompanied by any rise in assimilation. The optimum illumination for one type of alga need not be that for another, and it has been shown by the late Professor B. Moore with Whitley and Webster (1922) that whereas a green alga carried on photosynthesis seven or eight times as actively in sunshine as in a diffuse light, the increase was only five-fold for brown algæ on the average, and for the red the average in the two intensities was the same. Information of this kind, as regards the plankton algæ, is lacking. It has, however, been found by the writer that a pure culture of the diatom *Nitzschia closterium* W. Sm., kindly supplied by Dr. E. J. Allen, may in good north illumination be maintained in a strongly alkaline condition, close to pH9.4. *Ulva latissima* L. in direct sunlight withstood a temperature of 27° C. and brought the reaction of the water to pH9.7. It is not claimed that this denotes a real difference in the power of these algæ to increase the pH value, though it may do so.

The pressure of carbon dioxide must be reduced to a very minute amount at such high pH values. McClendon (1917) has determined the relation of pH and pressure of carbon dioxide, and the following values have been read from his graph. They refer to 20° C., and for lower temperatures pH0.01 should be subtracted for each degree. (See Table, page 114.)

Pressure of carbon dioxide in millimetres of mercury.	pH value at 20° C.	pH at 12° C.
0.10	8.42	8.34
0.14	8.30	8.22
0.16	8.26	8.18
0.19	8.20	8.12
0.21	8.16	8.08
0.25	8.10	8.02

Considering the maximum value for E 1, surface, pH8.27 at 12.8°, this corresponds to 0.13 mm. pressure of carbon dioxide, that for the minimum value, pH8.14 at 9.9° being 0.17 mm. For the bottom the minimum values are practically identical, and when in May the surface water was at pH8.27, the bottom water was at pH8.14 and 10° C., with a pressure of 0.17 mm. Later on in the year, in August, the surface water was at pH8.24 and 15.0°, corresponding to 0.14 mm., here the rise in temperature in part makes up for the lower pH value and helps to keep the pressure low. In October surface and bottom agree in giving pH8.20 at 14°, namely, 0.16 mm.

The extremes for E 1 are therefore seen to be a winter value of 0.17 mm., reduced in spring to 0.13 mm., thereafter increasing to 0.16 in July at at the pH summer minimum and rising later to 0.14 mm. in August and 0.16 in October. Since 0.13 mm. pressure is equivalent to 1.7 parts per ten thousand, and 0.17 mm. to 2.2 of carbon dioxide it is clear that even in winter the sea is capable of absorbing this gas from the air as the normal concentration is slightly over 3.3 parts per ten thousand, corresponding to a pressure of 0.25 millimetres. Direct determinations of the carbon dioxide content of the air over the sea at various seasons would be of interest; for the Pacific, Mayor found a mean value of 3.15 parts.

Since the illumination is the main factor controlling photosynthesis it is of interest to see how the pH value of sea water varies with regard to the sunshine and duration of the day. Accordingly the returns of the Meteorological Office were examined, and the records for the mean number of hours of sunshine per month were found for England, S.W. The results are also expressed as percentages of the total sunshine possible, and from this the average length of the day, from sunrise to sunset, was found for each month. These figures are plotted in Fig. 12, as values for 15th of each month. The pH values, as corrected to 12° C. are also plotted, together with C_{OH} values in order to show the numerical changes in alkalinity corresponding to them. In addition the pressures of carbon dioxide, as found from McClendon's chart for the pH values, are also shown. These are uncorrected for temperature, since an increase in temperature leads to an increase in carbon dioxide concentration which is itself of importance in yielding an ampler supply for photosynthesis.

It is at once evident that there is a close agreement between the maximum of sunshine daily, in May, and the maximum in pH values. The carbon dioxide minimum and the C_{OH} maximum naturally coincide, being derived from the pH values. The duration of the day is, however,

SEASONAL CHANGES AT STATION E 1, SURFACE.

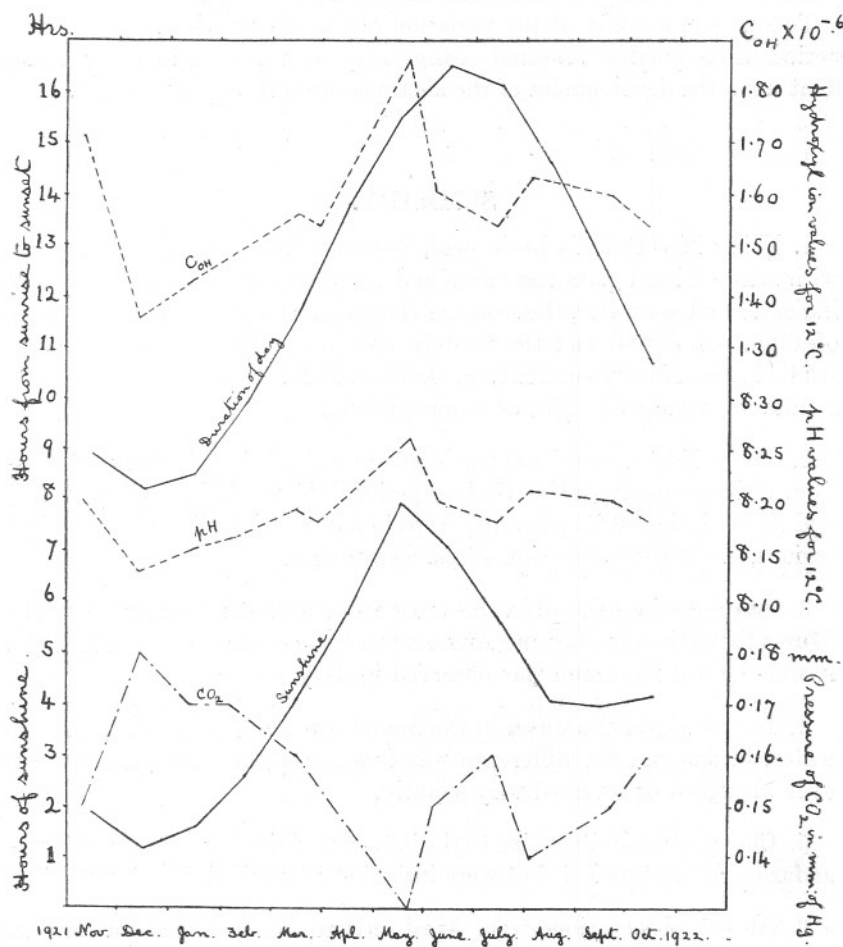


FIG. 12.

greatest in June, and greater in July than in May, yet these months witness the marked drop in alkalinity which appears to be connected with an increase in the marine fauna. In 1922, the highest percentage of sunshine, calculated on the total possible, was in May, and amounted to 51 per cent, or 7.90 hours per day. In 1921, however, the maximum was

56 per cent in April, with 7.72 hours, yet June, with 52 per cent, had 8.59 hours, the greatest amount for the year. It is accordingly clear that sunny weather coming when the days are long has the greatest effect upon the total sunshine, and therefore on the algal plankton. For example, in 1921 the months April to July inclusive averaged 7.99 hours of sunshine a day, whereas in 1922 the number was less, 6.57 hours; the difference, calculated on the latter value, amounts to 22 per cent.

To sum up, a study of the variation of the pH value throughout the period of its greatest seasonal change may be expected to throw some light upon the development of the algal plankton from year to year.

SUMMARY.

1. Using McClendon's boric acid, borax, sodium chloride standards, with selected hard glass test tubes and accurately measured amounts of indicator and sea water, the seasonal changes in the pH value of the water of Plymouth Sound and the western end of the English Channel were studied from November, 1921, to October, 1922. It is thought that the results are accurate to plus or minus pH 0.01.

2. The indicator cresol red was used throughout in 0.02 per cent solution, and is perfectly stable over long periods. Thymol blue (0.04 per cent) and xylenol blue (0.02 per cent) were found useful in the more alkaline regions, the latter possessing slight advantages.

3. At all stations the pH values rose from the December and January figures to maxima in May and August, the former being the more marked. A well-defined minimum was observed in July.

4. In the winter the water in the Sound was less alkaline than the sea water, in summer the difference was diminished, and the gradient was even abolished or reversed very slightly.

5. Changes in salinity owing to the influence of river water were detected as far as the station L 4, but were insignificant at the Eddystone, L 5.

6. At E 1 observations from April onwards showed that the surface was at a higher pH value than the bottom. By July the water column had become more homogeneous, but the rise in pH near the surface during the secondary maximum in August was not finally diffused throughout the column of water till October.

7. In both 1921 and 1922 the May values for the eastern stations, E 1, E 2, E 3 were greater than the July values, whereas at N 1, N 2 and N 3

the July values are the higher. The July temperatures were in every case the greater.

8. Both temperatures and pH values show that vertical mixing of the water is at all times thorough at E 3, off Ushant, whereas at stations well out to sea, such as E 1, E 2 and N 1 the phenomenon is much less marked. This appears to be a factor of considerable biological importance.

9. The pH maximum in May, 1921, corresponds with the maximum average number of hours of sunshine daily, rather than with the length of the day, which reaches a maximum in June. The pH values for E 1, surface, corrected to 12° C., range from 8.14 in December to 8.27 in May, the change amounting to a fall of 25 per cent in the hydrogen ion concentration; for the bottom the range is, pH 8.13 to 8.20, a fall of 15 per cent. These changes affect amphoteric colloids in proportion to the alteration in the ratio of the hydrogen and hydroxyl ions, or in proportion to the ratio of the squares of the hydrogen ion concentrations. For the figures given the effects are in the ratios of 1.00 : 0.56 and 1.00 : 0.72 respectively.

10. The winter pH value and temperature lead to a carbon dioxide pressure of 0.17 mm., which in May is reduced to 0.13 mm. These figures correspond respectively to 2.2 and 1.7 parts of carbon dioxide per ten thousand of air, the normal atmospheric value being 3.3 parts or 0.25 mm., which would be in equilibrium with sea water at pH 8.02 at 12° C. The open sea water is therefore always in a position to absorb carbon dioxide from the air.

11. In a general way the pH maxima may be correlated with the diatom maxima in early summer and in autumn, but no quantitative results have as yet been obtained on this point. The alteration in the reaction of the water may be used to make an approximate estimate of the total crop of algal plankton which has been given in Part I.

12. The variations from place to place in the pH values of the water of the English Channel are so small that they are considered to be altogether unimportant as a factor influencing the migration of fish.

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