

PHOSPHORUS AND SILICON IN SEA WATER OFF PLYMOUTH DURING THE YEARS 1950 TO 1953

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(Text-figs. 1-3)

The analyses reported here refer to water from International Hydrographic Station E1 (lat. $50^{\circ} 02' N.$, long. $4^{\circ} 22' W.$). They extend the sequence begun in 1923 when sufficiently sensitive chemical methods were first applied at this station (Atkins, 1923*a*), and reported thereafter in a series of papers from this Laboratory (Atkins, 1923*a, b*, 1924, 1926*a, b*, 1928, 1930, 1953; Cooper, 1933*a, b*, 1937, 1938; Harvey, 1948, 1950; Armstrong, 1951; Armstrong & Harvey, 1950). This is a factual report and interpretation and comparison with earlier years are deferred.

Since early in 1948 analyses have been made at roughly monthly intervals by the methods listed below, for phosphate and 'total' phosphorus, and, since early in 1950, for silicate also.

I am obliged to Lt.-Cdr. C. A. Hoodless and the crew of R.V. *Sabella*, and to Capt. W. Creese and the crew of M.F.V. *Sula* for assistance at sea. I am also indebted to Dr L. H. N. Cooper for sometimes taking samples at sea, and to him and to Dr H. W. Harvey for their encouraging interest in this work.

METHODS

Samples were taken at approximately monthly intervals, as nearly as the weather allowed. A Nansen-Pettersson insulated water-bottle was used, except occasionally in rough weather, when a wooden bucket was used for taking surface samples. Samples for silicate determinations were kept in polyethylene bottles. Analyses were completed within 48 h of sampling.

Phosphate and 'total phosphorus' were determined by the absorptiometric methods of Harvey (Harvey, 1948; Armstrong, 1949). The results are inherently free of 'salt-error', and are given in microgram-atoms of phosphorus per litre. The factor for conversion to milligrams P per cubic metre is 30.98, and for milligrams P_2O_5 per cubic metre 70.98. Phosphate results include arsenate, 1 μg atom of As as arsenate being determined as 1 μg atom of P as phosphate. Arsenic in sea water at Station E1 *inter alia* has recently been determined by Smales & Pate (1952), by a neutron-irradiation method. 0.024-0.047 μg atom As/l. were found, in confirmation

of figures from 0.013 to 0.041 got by an indirect chemical method by Armstrong & Harvey (1950). The fraction of the arsenic present as arsenate in these water samples is not known, so that the correction to be applied to the phosphate figures is uncertain. Some analyses by Gorgy, Rakestraw & Fox (1948) of Pacific water samples of arsenic contents from 0.43 to 0.53 μg atom As/l. showed that about 10% of the arsenic was present as arsenate.

Arsenic is not included in the 'total' phosphorus figures. The validity of the 'total' phosphorus method has been tested by comparison with the perchloric acid digestion procedure of Hansen & Robinson (1953) which may reasonably be assumed to convert all organic phosphorus to phosphate. Analyses were done in sextuplicate on two samples of filtered sea water, by each of the two methods. The figures got by the autoclave method were 94 and 98% of those by the perchloric acid digestion. Dr B. H. Ketchum has stated (private communication) that he and his associates have also found satisfactory agreement between figures obtained by the autoclave method and by the sulphuric acid-peroxide digestion method of Redfield, Smith & Ketchum (1937).

Estimates of organic phosphorus may be somewhat low if they are computed from these figures by subtracting phosphate (which includes arsenate) from the corresponding 'total' phosphorus figures.

Silicate was determined by the molybdenum-blue method described previously (Armstrong, 1951). The results, which are again inherently not subject to 'salt-error', are given in microgram-atoms of silicon per litre. The factor for conversion to milligrams SiO_2 per cubic metre is 60.06.

The salinities quoted were determined at the Government Laboratory.

It is hoped that the tabulated figures will appear elsewhere in due course. The presentation here is mainly graphical, and is arranged to show the vertical distribution of temperature, phosphate, and silicate for each year. In addition, the variations of the integral mean concentrations in the water column of phosphate, 'total phosphorus' and silicate are tabulated.

OBSERVATIONS

Temperature 1950-53

Temperature diagrams are included for comparison with those for phosphate and silicate (Fig. 1).

Phosphate 1950-53 (Fig. 2)

1950. The water column was homogeneous from January until the end of April, the decrease having been rapid during the latter month. Vertical discontinuity was thereafter apparent until December, though in October and November the decrease in the upper layers was confined to the top 5 m. In July and August there was a mass of water of phosphate-content greater than 0.3 μg atom P/l., below 20 m.

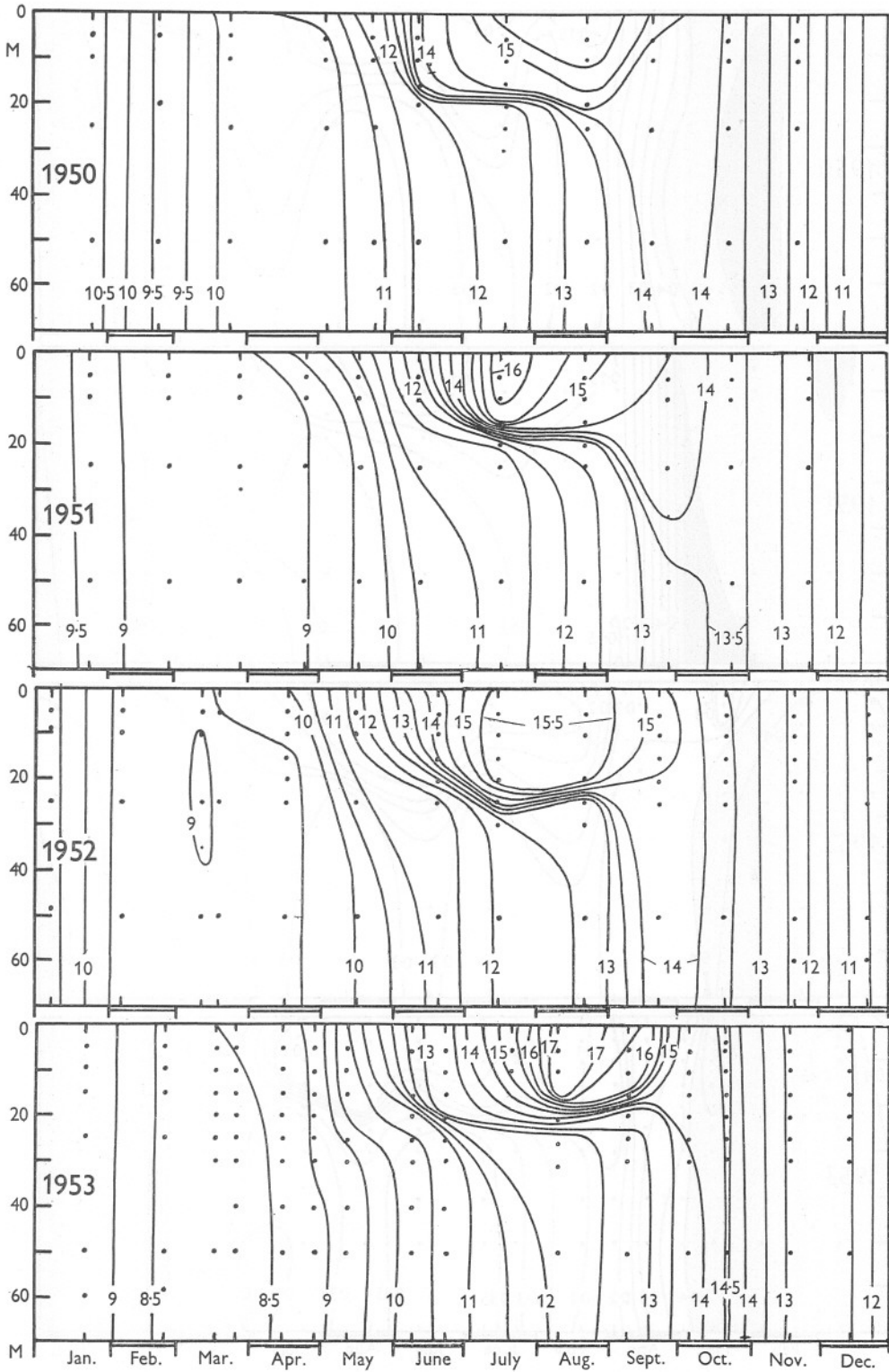


Fig. 1. Vertical temperature distribution at International Hydrographic Station E I, 1950-53. Contour lines at 0.5° C intervals.

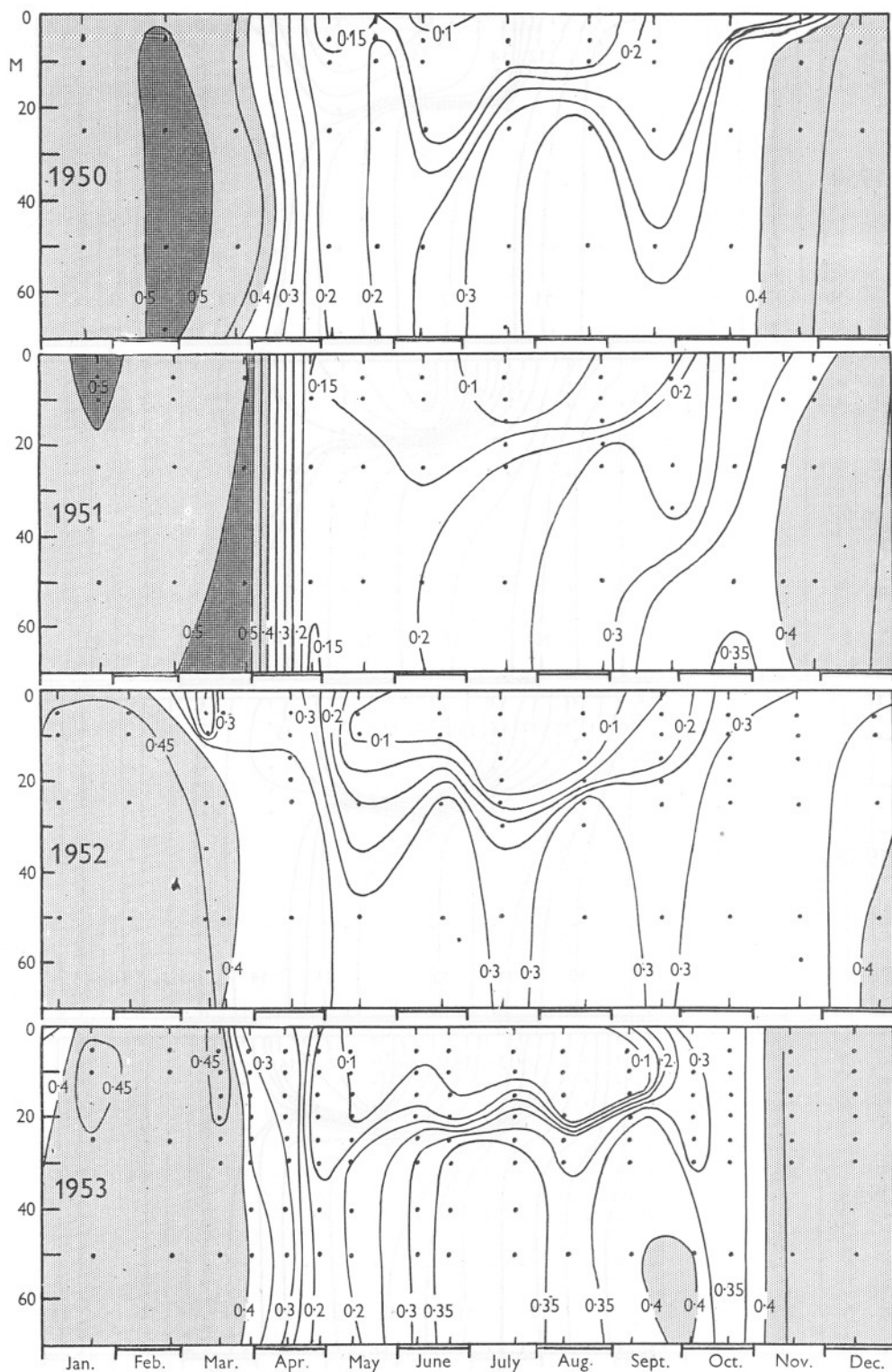


Fig. 2. Vertical distribution of phosphate, as $\mu\text{g atom P/l.}$, at International Hydrographic Station E1, 1950-53. Contour lines at $0.05 \mu\text{g atom P/l.}$ intervals.

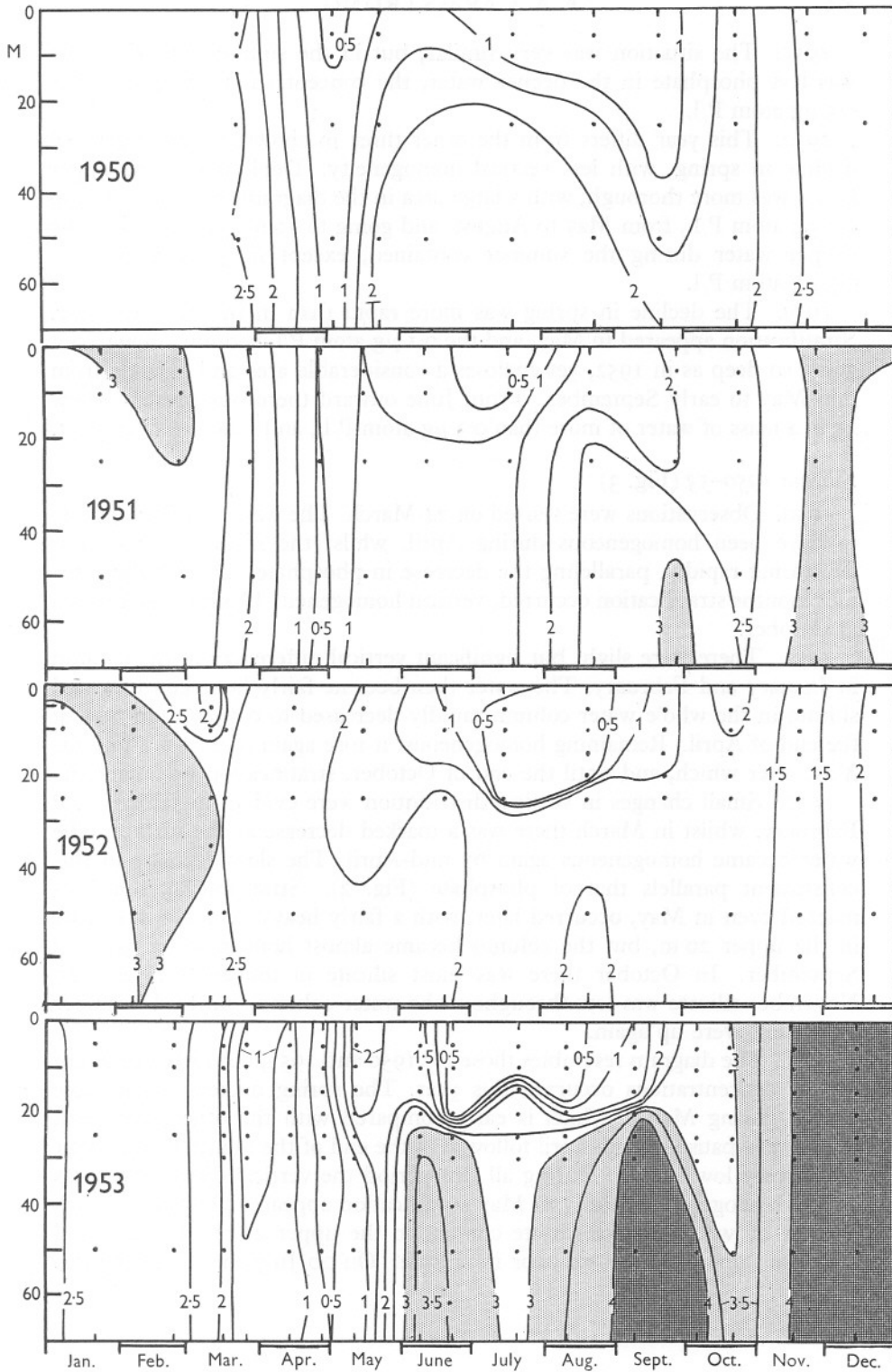


Fig. 3. Vertical distribution of silicate, as $\mu\text{g atom Si/l}$, at International Hydrographic Station E 1, 1950-53. Contour lines at $0.5 \mu\text{g atom Si/l}$ intervals.

1951. The situation was very similar, but in the summer months there was less phosphate in the deeper water, the concentration being less than $0.3 \mu\text{g}$ atom P/l.

1952. This year differs from the other three in showing a more gradual decline in spring, with less vertical homogeneity. Depletion of the upper layers was more thorough, with a large area in the diagram showing less than $0.1 \mu\text{g}$ atom P/l., from May to August, and going to 20 m deep in July. The deeper water during the summer contained, except in July, more than $0.3 \mu\text{g}$ atom P/l.

1953. The decline in spring was more rapid than in the previous year. Stratification appeared in May, and the $0.1 \mu\text{g}$ atom P/l. contour, though not going so deep as in 1952, yet encloses a considerable area and extends from mid-May to early September. From June onward there was present below 25 m a mass of water of more than $0.3 \mu\text{g}$ atom P/l., and much of nearly 0.4.

Silicate 1950-53 (Fig. 3)

1950. Observations were started on 24 March. The water column appears to have been homogeneous during April, whilst the silicate content was decreasing rapidly, paralleling the decrease in phosphate. During the summer months stratification occurred, vertical homogeneity being re-established in October.

1951. There were slight but significant vertical differences in the column in January and February. The water then became fairly homogeneous, and silicate in the whole water column rapidly decreased to $0.5 \mu\text{g}$ atom Si/l. at the end of April. Remaining homogeneous, it rose again to over 1.0 in mid-May, after which, and until the end of October, stratification was marked.

1952. Small changes in vertical distribution were evident in January and February, whilst in March there was a marked decrease at the surface. The water became homogeneous again by mid-April. The slow decrease of this constituent parallels that of phosphate (Fig. 2). Stratification, not very marked even in May, occurred later, with a fairly heavy decrease in silicate in the upper 20 m, but the column became almost homogeneous again in September. In October there was most silicate in the *upper* layers. In November silicate was low throughout the water column, but by December the figures were up again.

1953. The diagram resembles those for 1950 and 1951, but rather different silicate concentrations occurred this year. The spring decrease took place mainly during March, which is early compared with the other years, but there was a pause in mid-April followed at the end of the month by a further fall to very low values. During all this period the vertical distribution was almost homogeneous. Early in May stratification appeared; however, it was marked by water of *high* silicate content in the upper 20 m. In June and after the upper layers were poor in silicate. On 20 July the lowest figures

recorded here so far occurred in the top 10 m. At 0.5 and 5 and 10 m silicate concentrations were below the minimum perceptible with certainty by the method, i.e. were less than 0.05 μg atom Si/l.

In June, and from August onward notably high figures were observed in the deeper water.

Changes in the Integral Mean Concentrations in the Water Column

For each date on which analyses were made, the integral mean concentrations in the water column have been computed, using the formula

$$\frac{1}{2d_n} \{(a_1 + a_2)(d_2 - d_1) + (a_2 + a_3)(d_3 - d_2) + \dots + (a_{n-1} + a_n)(d_n - d_{n-1})\},$$

where a_1, \dots, a_n are observations at depths d_1, \dots, d_n . The results for phosphate, total phosphorus and silicate are given in Table I.

Phosphate

The seasonal variation is well shown; sharp declines in spring occurred in April, except in 1952 when, as noted above, the fall was less abrupt. The recoveries in summer and autumn show considerable irregularity, though that of 1951 is smooth. The difference between the maximum and minimum values for each of the four years in order were 0.34, 0.35, 0.27 and 0.32 μg atom P/l. respectively.

Total Phosphorus

A seasonal variation is evident, although, as shown earlier (Armstrong & Harvey, 1950) it is less marked than that of phosphate. The differences between the maximum and minimum values for each of the four years in order were 0.27, 0.21, 0.27 and 0.15 μg atom P/l. It is not clear where this considerable quantity of phosphorus has gone. Were it used in the growth of plant or animal matter, this would amount to some 1-3 g/m^3 , an amount so far unaccountable in estimates of annual production (Harvey, 1950).

Silicate

The fluctuations in this constituent were considerable, and the only general observation which may safely be made is that a decrease occurs in spring. Even so this decrease was not so steep nor rapid in 1952 as in the other years. There is a rough correspondence between changes in phosphate and silicate. It has been pointed out (Atkins, 1953) that the relative decreases in phosphate and silicate may give an idea whether diatoms or non-siliceous algae have been mainly responsible for a plankton outburst.

The most interesting of these figures were for 20 November 1952, and for 8 June and 8 September 1953 onward. Between 21 October and 20 November 1952 the mean value in the water column fell from 1.93 to 1.24 μg atom Si/l.,

TABLE I. INTEGRAL MEAN CONCENTRATIONS IN WATER COLUMN
AT STATION E I

Date	Phosphate-P (μg atom P/l.)	'Total-P' (μg atom P/l.)	Silicate (μg atom Si/l.)
18. i. 50	0.46	0.57	—
22. ii. 50	0.51	0.63	—
24. iii. 50	0.46	0.54	2.53
3. v. 50	0.17	0.52	0.64
25. v. 50	0.20	0.36	1.91
12. vi. 50	0.20	—	1.60
19. vii. 50	0.28	0.42	1.88
23. viii. 50	0.32	0.48	1.68
20. ix. 50	0.28	0.46	1.07
23. x. 50	0.36	0.46	1.77
22. xi. 50	0.43	0.58	2.66
18. xii. 50	0.47	0.56	2.60
24. i. 51	0.49	0.58	2.78
26. ii. 51	0.49	0.59	2.92
28. iii. 51	0.51	0.62	1.94
25. iv. 51	0.16	0.45	0.43
17. v. 51	0.17	0.44	1.19
12. vi. 51	0.17	0.41	1.07
17. vii. 51	0.19	0.42	1.13
22. viii. 51	0.23	0.49	2.40
27. ix. 51	0.28	0.51	2.50
24. x. 51	0.33	0.46	2.39
15. xi. 51	0.40	—	—
27. xi. 51	0.40	0.53	3.19
7. i. 52	0.46	0.56	2.79
5. ii. 52	0.46	0.57	3.02
11. iii. 52	0.39	0.58	2.73
17. iii. 52	0.40	0.57	2.55
16. iv. 52	0.37	0.50	2.20
15. v. 52	0.23	0.48	2.01
19. vi. 52	0.28	0.43	1.88
15. vii. 52	0.19	0.31	1.07
20. viii. 52	0.26	0.35	1.41
22. ix. 52	0.25	0.39	1.52
21. x. 52	0.33	0.40	1.93
20. xi. 52	0.33	0.46	1.24
22. xii. 52	0.40	0.52	2.29
21. i. 53	0.45	0.56	2.69
23. ii. 53	0.43	0.56	2.72
16. iii. 53	0.44	0.53	1.96
25. iii. 53	0.36	0.53	0.86
13. iv. 53	0.30	0.51	1.13
27. iv. 53	0.15	0.41	0.26
11. v. 53	0.16	0.48	1.22
8. vi. 53	0.25	0.49	3.02
22. vi. 53	0.29	0.51	2.31
20. vii. 53	0.31	0.52	2.08
10. viii. 53	0.23	0.41	2.36
8. ix. 53	0.32	0.42	3.41
5. x. 53	0.34	0.49	3.50
20. x. 53	0.32	0.42	3.06
17. ix. 53	0.47	0.52	4.05
14. xii. 53	0.47	0.54	3.90

with no corresponding change in phosphate. This fall in silicate cannot readily be ascribed to a late autumn outburst of diatoms because at the same time the total amount of chlorophyll in the water column decreased (Atkins, Jenkins & Warren, 1954).

On 8 June and on and after 8 September 1953, silicate figures were notably higher than at the beginning of the year. These high integral mean concentrations do not of course include any silicate sequestered by diatoms, yet silicate in solution has increased in the column as a whole.

The salinity determinations give little support to the idea that these results are caused by changes in the body of water sampled at E1. It is, however, possible that enrichment (not the impoverishment noted in November 1952) could be caused by solution of siliceous matter suspended in the water. Proximate analyses of this matter have shown (Armstrong & Atkins, 1950) that at the surface it may account for 1.3–14.7 μg atom Si/l., thus solution of a fraction only of this silica would account for the increases found. It has indeed been shown (Armstrong, 1950; Atkins, unpublished) that the soluble silicate content of sea water increases on standing (in non-siliceous bottles).

During 1953, such a process of solution would need to have been rapid to cause the changes seen between 11 May and 8 June and between 10 August and 8 September. It is odd too that this is the only year in which the effect is seen.

Changes in Salinity

Small changes in salinity occur frequently in the records for these four years, and do not necessarily show that different water masses have been sampled at different times. Since the water at E1 is only some 70 m deep, measurable changes in salinity throughout the water column may be caused by heavy rainfall.

At the end of 1952 and in the latter half of 1953, the integral mean salinities were as shown in Table II.

TABLE II. SALINITIES AT E1 IN 1952 AND 1953

Date	Integral mean salinity (%)	Number of observations for computation
21. x. 52	35.22 ₃	8
20. xi. 52	35.14 ₈	8
22. xii. 52	35.17 ₆	7
11. v. 53	35.15 ₉	10
8. vi. 53	35.16 ₅	10
22. vi. 53	35.14 ₂	10
20. vii. 53	35.12 ₈	10
10. viii. 53	35.12 ₁	9
8. ix. 53	35.16 ₁	9
5. x. 53	35.20 ₆	9
20. x. 53	35.21 ₀	9
17. xi. 53	35.21 ₀	9
14. xii. 53	35.26 ₁	9

It is probably justifiable to assume that the water mass sampled in November 1952 was different from that sampled in October. Evidence from salinity measurements in 1953 is inconclusive, but the increase in salinity from October onward was accompanied by a change in silicate content to values greater than at the previous winter maximum.

Attention has been given to the possibility of change in the water body at E1, because changes of water masses, possibly with different stocks of nutrient salts, may invalidate arguments based on the apparent utilization of these nutrients.

On 11 March 1952 (the year which was unusual in showing a slower decrease in phosphate and silicate in spring) there were plainly two water masses, of different densities, one above the other at the Station. This is shown by the figures of Table III.

TABLE III. SALINITY AND DENSITY AT E1 ON 11 MARCH 1952

Depth (m)	Temperature (°C)	Salinity (‰)	Density <i>in situ</i> (σ_t)
0.0	9.1	35.13	27.22
5	9.04	35.09	27.20
10	9.00	35.09	27.20
25	8.95	35.21	27.20
35	8.98	35.27	27.35
50	9.11	35.26	27.33
68	9.11	35.28	27.34

TABLE IV. ALTERNATE SILICATE OBSERVATIONS, E1, 1953

Date	$\mu\text{g atom Si/l.}$	Date	$\mu\text{g atom Si/l.}$
21. i. 53	2.69	21. i. 53	2.69
23. ii. 53	2.72	23. ii. 53	2.72
25. iii. 53	0.86	16. iii. 53	1.96
27. iv. 53	0.26	13. iv. 53	1.13
11. v. 53	1.22	11. v. 53	1.22
22. vi. 53	2.31	8. vi. 53	3.02
20. vii. 53	2.08	20. vii. 53	2.08
10. viii. 53	2.36	10. viii. 53	2.36
8. ix. 53	3.41	8. ix. 53	3.41
5. x. 53	3.50	20. x. 53	3.06
17. xi. 53	4.05	17. xi. 53	4.05
14. xii. 53	3.90	14. xii. 53	3.90

It is instructive also to consider an aspect of the silicate figures for 1953. Analyses were done more frequently than usual since samples were taken when the ships were at the Station for other purposes. It is possible to choose alternate dates at roughly monthly intervals, to make two series of observations (Table IV). Each series gives twelve observations in 12 months, but the conclusions drawn from the two series might be very different. Phosphate and 'total phosphorus' do not show such marked differences.

The desirability of making frequent and complete observations is obvious, even in so simple a task as logging the changes at a single station.

SUMMARY

Samples taken at the International Hydrographical Station E I during the last four years have been analysed by recently developed methods.

The results for phosphate, 'total phosphorus', and silicate are presented graphically, showing the seasonal changes in vertical structure and integral mean concentration in the water column.

The figures are discussed, particular note being made of unusual silicate values in 1952 and 1953.

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