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CHEMICAL CHANGES IN SEA WATER OFF PLYMOUTH DURING 1960

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(Text-figs. 1–3)

Analyses of sea water collected at approximately monthly intervals during 1960 at the International Hydrographic Station E 1 (lat. 50° 02′ N., long. 4° 22′ W.) are here reported. The results are presented in the same form as in earlier reports (Armstrong, 1954, 1955, 1957, 1958; Armstrong & Butler, 1959, 1960*a*, *b*) but with some of those for the year 1959 they also form part of a series of surveys of an area surrounding Station E 1, the results of which are presented separately (Armstrong & Butler, 1962). We wish again to thank Lt.-Cdr. C. A. Hoodless, D.S.C. and the crew of R.V. 'Sarsia', and Capt. W. J. Creese and the crew of R.V. 'Sula' for their help at sea.

METHODS

Some slight changes in methods have been made. Samples were taken with a Nansen–Pettersson insulated water bottle, or occasionally with Nansen (Copenhagen) type reversing water bottles with paired protected reversing thermometers. Surface samples were normally taken with these bottles at a depth of about 0·5 m, but in rough weather a polythene bucket was used.

Until July, salinities were determined by chlorinity titration by the Government Chemist, Department of Scientific and Industrial Research. After July they were done in this laboratory by an electrical conductivity method, using the Thermostat Salinity Meter of the National Institute of Oceanography. This instrument in our hands appears to give salinities of reproducibility better than ± 0·01 ‰. Some checks against chlorinity titrations showed that the two methods agree at least as well as do replicates by the chlorinity method.

Phosphates were usually determined within 24 h. On the survey cruises, when this was not possible, the samples were preserved with 1 ml. chloroform and kept in a refrigerator before analysis, which was done 60–72 h after collection. The absorptiometric method employed (Harvey, 1948; Armstrong, 1949) was unchanged. The method is calibrated with sea water and there is no salt error.

Silicate samples were kept in polythene bottles and were analysed within a few days. The method used is a molybdenum blue one (Armstrong, 1951) with a modification (C. O. Granger & J. Connor, U.K.A.E.A., Windscale

Works, 1951, unpublished work quoted in private communication). In the original method, after reaction of the sea water with acid molybdate, strong sulphuric acid and oxalic acid are added to inactivate excess molybdate and prevent interference by phosphate. In the modified method tartaric acid is used instead. Blanks are lower and the blue colour is more stable. The part of the blank in sea water due to quinquevalent molybdenum becomes negligible so that a blank determination using silicon-free distilled water is all that is necessary to correct results. Because the reaction between silicate in the sea water and the molybdate reagent is the same as in the original method and also because standardization with known additions of silicate to sea water is done with each batch of analyses, the old and new methods should give comparable results. Direct tests did indeed show that they agree within the limits of experimental error. The modified method is given in the Appendix.

We are sure that these modifications will not affect comparisons of recent figures with those done since 1947.

RESULTS

Temperature and salinity

The vertical distribution of temperature is shown in Fig. 1, and integral mean salinities for the 70 m water column in Table 1. The lowest surface temperature was 9·1° C on 9 February; the highest was 18·30° C on 9 August. Surface water was slightly warmer than that below (by 0·1–0·2° C) in March and April, but a thermocline was not observed until 4 May. It maintained a depth of 15–20 m during the summer, and vertical mixing was completed by 11 October. Salinity was changing throughout the year. Attention may be drawn to the increase between 9 February and 11 March and to a similar decrease between 4 April and 4 May, and the succeeding rather greater decrease which had occurred by 8 July.

Phosphate

The vertical distribution is shown in Fig. 2 and integral mean concentrations in Table 1. The maximum found was 0·59 μg atom P/l. on 4 January. This is higher than in recent years, having been equalled since 1950 only once, in 1955. In the upper layers phosphate had fallen to low values by 4 May and remained low in the summer. Unusually small concentrations of about 0·03 μg atom P/l. were found in August. By 11 October the water column had become uniform, and phosphate then increased until the end of the year.

'Total' phosphorus

Values for January, February and March are given in Table 1. The maximum of 0·71 μg atom P/l. was the same as in 1955.

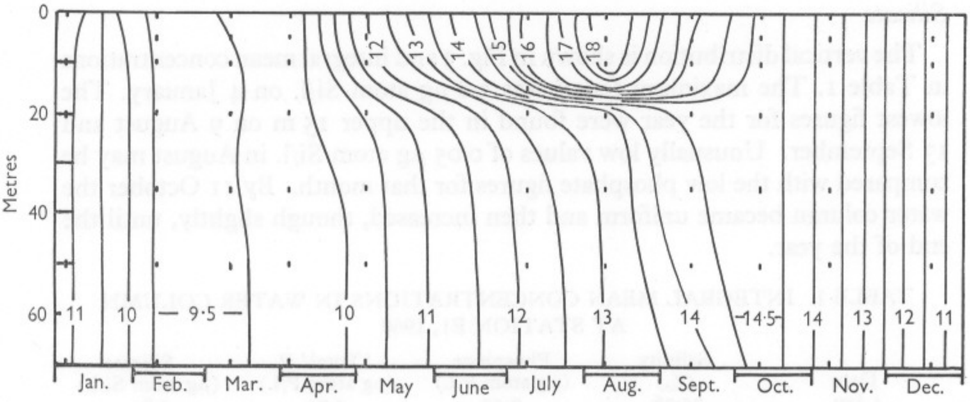

Fig. 1. Vertical temperature distribution at International Hydrographic Station E 1, 1960. Contour lines at 0·5° C intervals.

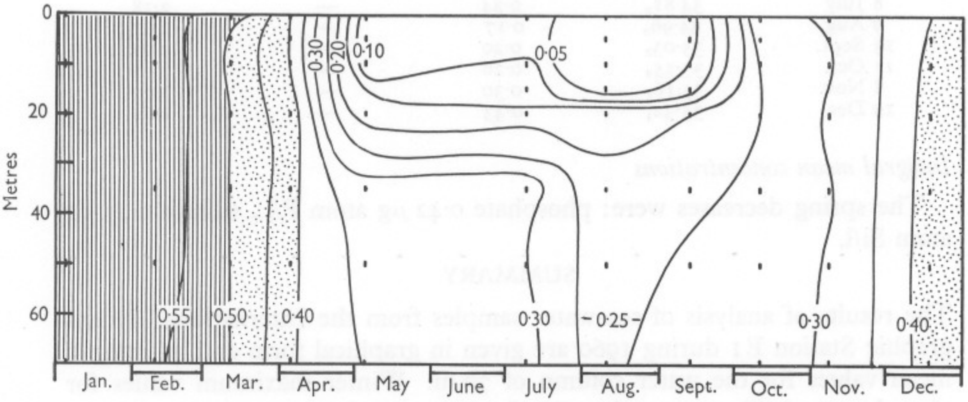

Fig. 2. Vertical distribution of phosphate at International Hydrographic Station E 1, 1960. Contour lines at 0·05 μg atom P/l. intervals.

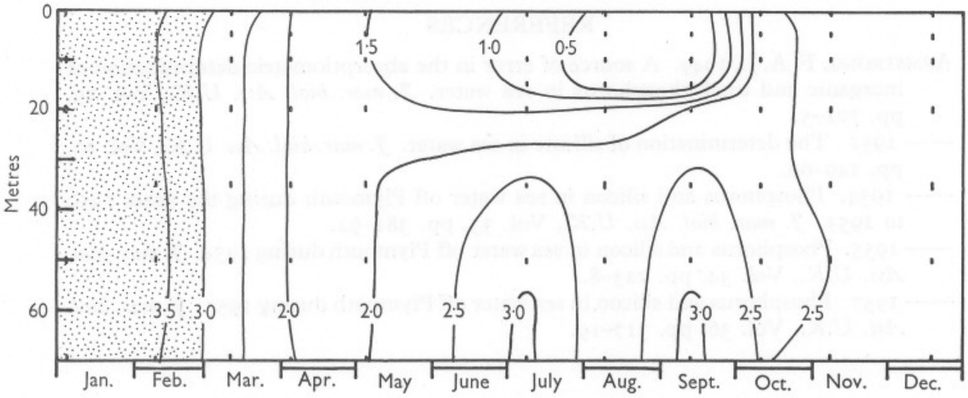

Fig. 3. Vertical distribution of silicate at International Hydrographic Station E 1, 1960. Contour lines at 0·5 μg atom Si/l. intervals.

Silicate

The vertical distribution is shown in Fig. 3 and integral mean concentrations in Table 1. The maximum found was 3·8 μg atom Si/l. on 4 January. The lowest figures for the year were found in the upper 15 m on 9 August and 13 September. Unusually low values of 0·05 μg atom Si/l. in August may be compared with the low phosphate figures for that month. By 11 October the water column became uniform and then increased, though slightly, until the end of the year.

TABLE 1. INTEGRAL MEAN CONCENTRATIONS IN WATER COLUMN AT STATION E1, 1960

Date	Salinity (‰)	Phosphate (μg atom P/l.)	'Total' P (μg atom P/l.)	Silicate (μg atom Si/l.)
4 Jan.	$35{\cdot}26_7$	0·59	0·71	3·84
9 Feb.	$35{\cdot}22_5$	0·57	0·71	3·60
11 Mar.	$35{\cdot}38_8$	0·50	0·57	2·62
4 Apr.	$35{\cdot}35_6$	0·41	—	2·00
4 May	$35{\cdot}21_3$	0·25	—	1·85
8 July	$34{\cdot}81_9$	0·24	—	2·18
9 Aug.	$34{\cdot}96_0$	0·17	—	1·61
13 Sept.	$35{\cdot}03_3$	0·20	—	2·07
11 Oct.	$35{\cdot}15_9$	0·26	—	2·41
8 Nov.	$35{\cdot}16_6$	0·30	—	2·60
19 Dec.	$35{\cdot}32_1$	0·43	—	2·68

Integral mean concentrations

The spring decreases were: phosphate 0·42 μg atom P/l., silicate 2·23 μg atom Si/l.

SUMMARY

The results of analysis of sea-water samples from the International Hydrographic Station E1 during 1960 are given in graphical form and as integral mean values for the water column of 70 m. Winter maximum values for phosphate and silicate were found in January, and the spring decreases were 0·42 μg atom P/l. and 2·23 μg atom Si/l.

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APPENDIX

Determination of silicate

Reagents

1. Ammonium molybdate 5% (w/v)
2. Hydrochloric acid approx. 1 N.

These solutions should be kept in polyethylene bottles.

3. Mixed molybdate.

Prepare just before use by mixing 2 volumes molybdate and 3 volumes acid and keep in a polyethylene bottle.

4. Tartaric acid 10% (w/v).
5. Stannous chloride approx. 0·05 N.

Prepare just before use by dilution of a stock solution of 40 g $SnCl_2 . 2H_2O$ in 100 ml. 50% (v/v) HCl, and check by titration with standard iodine. The strength should lie between 0·04 and 0·06 N.

6. Standard silicate.

Fuse 0·1201 g silica with 0·6 g Na_2CO_3 in a platinum crucible. Dissolve melt, when cold, in water and make the volume to 100 ml. This stock solution contains 20 μg atom Si/ml. and should be diluted serially for use. If kept in a stoppered polyethylene bottle it is stable for at least a year, but dilutions do not keep well. Finely ground 'Vitreosil' is suitable for use as silica. It should be heated to redness and cooled in a desiccator before weighing, and contains over 99·8% SiO_2.

Determination

1. Place 3 ml. of the mixed molybdate in a 100 ml. Pyrex conical flask and add 50 ml. of sample with mixing.

2. After 15 min add 2 ml. tartaric acid reagent and measure the absorbance of the solution at about 700 mμ in a cuvette of length appropriate to the expected silicon concentration. Return the solution in the cuvette to the flask.

3. Add 1 ml. approx. 0·05 N stannous chloride, with mixing, and measure the absorbance as before, after 5 min and within 1 h.

4. Carry through a blank determination with distilled water (silicon free).

5. Parallel with the series of samples, carry through a calibration with a sample of sea water (preferably filtered) without and with a known addition of standard silicate. The quantity added should match the samples under analysis. The increase in absorbance can be used to find a factor for calculation of silicon contents of samples after correction for blank.

Note (*a*) The following cuvette lengths are suitable:

0–10 μg atom Si/l.	10 cm
2·5–25 μg atom Si/l.	4 cm
10–100 μg atom Si/l.	1 cm

(*b*) The quantity of stannous chloride specified is sufficient for quantities of silicate up to about 60 μg atom Si/l. For higher concentrations the stannous chloride may be increased in concentration or quantity. This will slightly increase blanks and will require an appropriate calibration.