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TITLE

Variation of surface water temperatures at St. Andrews, N.B. Numerical forecasting of temperatures.

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VARIATION OF SURFACE WATER TEMPERATURES AT ST. ANDREWS, N.B.

NUMERICAL FORECASTING OF TEMPERATURES

by

L. M. Lauzier

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INTRODUCTION

The annual mean sea surface temperatures along the Canadian Atlantic Coast show both long and short period variations. The general warming of the waters in the North Atlantic has been discussed at great length as far as its influence on the fisheries is concerned but comparatively little has been said about the short term variations as such.

The temperature variations in the Bay of Fundy area, at St. Andrews, N. B. were compared with those at other points along the Atlantic seaboard and are shown to be a good index of the changes that occur in the area (Hachey and McLellan, 1948). The periodic variations in the temperature of these waters were also studied by Hachey and McLellan, and the intense warming of the recent decades was described by Lauzier (1954). Bailey, MacGregor and Hachey (1954) also studied the temperature variations of the Bay of Fundy waters at intermediate depths and near the bottom. In dealing with warm years and cold years, Hachey and McLellan (1948) have discussed differential warming, the vernal and aestival warming for the waters of Passamaquoddy Bay. Taylor and Graham (1953) have noticed that the increase of winter temperatures for the coastal waters of the Gulf of Maine was greater than the increase of annual mean temperature.

Year-to-year variations in the annual mean, the minimum, the maximum, the warming and the cooling will be considered here, as well as the interrelations of these factors.

DATA

The twice daily observations of surface temperature at St. Andrews since 1921 up to date provide the basis for monthly and annual means. These data have been used by various authors.

Moving averages.

Figure 1 represents the twelve-month moving average of the surface water temperatures at St. Andrews as well as the ten-year moving average. The twelve-month average curve is formed by overlapping means of 12 successive values. This curve is apt to show more periodicities than the annual temperature curve, which is a particular case of the former curve. The purpose of using a twelve-month moving average curve is to have a continuous index of the heat content of the surface waters on a twelve-month basis, independently of the seasonal variations of temperature. It shows the exact location of the extremes. For instance, the lowest annual mean 5.4°C. was recorded in 1923 but the coldest twelve-month period (4.9°C.) was between October 1922 and September 1923. The highest annual mean 8.5°C., was recorded in 1951, but the warmest twelve-month period (8.6°C.) occurred between November 1950 and October 1951. The annual temperature range during the period 1921-1954 is 3.1 degrees, but the range of the twelve-month running average is 3.7 degrees.

The ten-year moving average is used to indicate the trend of the temperature variations after eliminating some of the cyclic variations whose periods are less than 10 years. The ten-year moving average curve was at a low value in 1921-1930, it reached a first maximum in 1929-38 and it was still on the upward trend in 1946-1955.

Annual Means

The annual mean temperature curve is shown in Figure 2A. The two main features of this curve are the upward trend indicating the general warming, very intense since the early forties, and the apparent change in periodicities. From the twenties up to the middle forties, the cyclic variations of a period of approximately 9 years (Hachey and McLellan, 1948) were most prominent. From the middle forties up to date much shorter periods were experienced. Such changes in recurrence are very common in meteorological sequences and are to be expected in oceanography. According to Brooks and Carruthers (1953): "A very large number of such so-called periodicities have been reported from time to time; some of these may be real while they last, but others are probably illusionary, due to chance arrangements". This may be more true for the 12-month average curve than for the annual mean curve.

Maxima and Minima of Monthly Averages

In Passamaquoddy Bay the maximum monthly temperature is normally reached in August, but in some years the September average might be equal to or higher than the August one. The minimum monthly temperature occurs usually in February but in some years it is delayed until March. The variations in the maxima and the minima during the period 1921-1956 are shown in the curves B and C respectively of Figure 2. The curve of maxima shows an upward trend from the early twenties to the middle thirties, a rapid drop during the following four years, and another rise from the early forties to the early fifties. From 1951 to 1955 the maxima have shown a drop of more than 2.5 degrees. From 1946 to 1952, there have been erratic variations not recorded before or after. The curve of minima has different features. The variations seem to be erratic from the beginning of the series to the early forties. After 1942, there was a steady increase up to 1954, with the exceptions of 1948 and 1951 when the minima were somewhat out of line.

The overall extremes recorded in maxima were 11.4°C. and 14.9°C. in 1923 and 1951 respectively. The extreme minima, -1.7°C. and 2.4°C. were also recorded in 1923 and 1951 respectively.

Warming and Cooling

The difference between the monthly maximum temperature and the monthly minimum temperature within a calendar year is considered as the warming during that year. It is also the range of monthly temperatures experienced during that year. The variations in the annual warming from 1921 to 1955 are shown in Figure 3A. The variations through the years show that the extremes could be reached from one year to the next, as in 1933 and 1934. However, after 1934, it seems that the variations were more consistent. There are periods of decreasing and increasing warming. The aestival warming from June to August, may account for as much as 36%, or as little as 18%, of the total.

The cooling is defined as the difference between the maximum of one year and the minimum of the next year. As shown in Figure 3B, the variations through the years are very erratic, the extremes being more widely separated than those of the warming. The winter cooling from December to February, may account for as much as 48%, or as little as 17%, of the total cooling.

It is of some interest to note that, during the last decade, both the warming and the cooling were on a downward trend, indicating a shorter range of seasonal temperature variations.

STATISTICAL APPROACH

Persistence and Variability

In analyzing the data, such observations as annual means, monthly means, maxima, minima, warming and cooling are often treated as if each one was independent of the others, almost disregarding the order in which the events occurred. One is apt to expect that a warm year is more likely to be followed by another warm year than by a cold year. This is due to the fact that the excess amount of heat necessary to produce a warm year seems to persist from year to year. Similarly, excessive cooling seems to persist.

Of the observations of surface water temperatures taken at St. Andrews. N. B. since 1921, five different variables have been given consideration, namely, the maximum, the minimum, the warming, the cooling, and the annual mean which combines the first four. Figures 2 and 3 show that some of the variables are more persistent than others, and also that some vary within wider limits than others. The coefficient of serial correlation(r/a) which is a measure of the persistence, has been calculated for all the variables. It is given in Table I, together with the standard deviation (σ) of the series of observations as a whole, and the standard deviation (σ_d) of the difference from one observation to the next.

In Table I it is shown that the annual mean was the most persistent, and the cooling the least persistent. The annual mean was however, more persistent from 1922 to 1944 than during the last decade. This is shown in shorter periods of variations from the middle forties up to 1955 (Fig. 2A). The same phenomenon was observed in the variation of the maxima (Fig. 3B). Table I also shows that the minimum has a relatively high standard deviation but still it has a fair degree of persistence.

TABLE I

Coefficient of serial correlation and standard deviations

		σ	σ_d	r_a
Annual mean	1921-55	0.77°C.	0.65°C.	0.65
	1921-44	0.67	0.53	0.69
	1944-45	0.92	0.83	0.59
Minimum	1921-55	1.10	1.03	0.56
Maximum	1921-55	0.81	0.83	0.47
Warming	1921-55	0.73	0.89	0.26
Cooling	1921-55	0.96	1.48	-0.19

Correlation Coefficients

After considering the variations of single elements like the minimum, the maximum, the annual mean, etc., and their order of occurrence, the joint variations of two or more elements, or their interdependence, are to be studied. This is done by calculation of correlation coefficients.

The variables used in the correlations may be grouped in four types:

(a) the single elements like the annual mean, T_N; the minimum, Min_N; the maximum, Max_N.

(b) the differential variables like the warming, W_N, and the cooling C_N.

(c) the adjusted variables like the warming $\frac{T_{N-1}}{\overline{T}} W_N$ and the cooling $\frac{T_{N-1}}{\overline{T}} C_N$ or $\frac{Max_N}{\overline{Max}} C_N$.

These adjusted variables are used in order to show that a certain quantity of cooling, for instance, would have a different effect if the general level was higher than normal or lower than normal.

(d) the year-to-year variations of the previous types, like $T_{N+1} - T_N$, $C_N - C_{N-1}$, etc.

The correlation coefficients are given in Table II.

The correlation coefficients "r" have been based on at least 33 pairs of observations for the period 1921-1955, so that for values of "r" greater than 0.44, the significant level would be better than 1 percent. Only a few of the variables were correlated in pairs, since some of the correlations would not have any physical significance.

From Table II we see that the best correlation exists between the yearly maximum and the annual temperature. This was to be expected as the maximum occurs in the middle of the period for which the annual temperature is considered. In order of decreasing values of "r" there are the following correlations:

(a) between the change in yearly maximum from one year to the next, and the change in annual temperature from one year to the next, (r= 0.83).

(b) between the yearly minimum and the annual temperature, (r = 0.81).

(c) between the change in yearly minimum from one year to the next, and the change in annual temperature between one year and the next, (r = 0.72).

(d) between the adjusted value of cooling in one year and the change in annual temperature from that year and the next, (r = 0.72).

(e) between the maximum and minimum of the same year, (r = 0.71).

The low coefficients show the following lack or weakness of correlations:

(a) between the change in warming from one year to the next, and the change in annual temperature from one year to the next, (r = -0.06).

(b) between the maximum and the warming in one year, (r = 0.13).

(c) between the annual temperature and the warming in one year, (r = -0.21).

(d) between the warming and cooling in one year, (r = 0.30).

(e) between the adjusted value of cooling in one year and the annual temperature of the next year, (r = 0.23).

Generally speaking, the cooling shows better correlation than the warming with any of the other variables. It seems then that the temperature level reached during a year is more closely related to the cooling during the previous autumn and winter seasons than to the vernal and aestival warming of that year.

TABLE II

Correlation coefficients between different variables of the surface waters at St. Andrews, N. B.

	T_N	Min_N	W_N	C_{N-1}	$T_{N-1} - T_N$	$T_N - T_{N-1}$
Min_N	0.81			-0.44		
Min_{N-1}	0.58					
Max_N	0.90	0.71	0.13			
Max_{N-1}	0.43	0.49		0.38		
W_N	-0.21	-0.55				
C_N	-0.44		0.30		-0.63	
$\frac{T_N}{\overline{T}} C_N$					-0.72	
$\frac{T_{N-1}}{\overline{T}} C_N$	0.23					
$\frac{Max_N}{\overline{Max}} C_N$					-0.64	
$\frac{T_{N-1}}{\overline{T}} W_N$	0.47					-0.38
$Min_N - M_{N-1}$						0.72
$Max_N - Max_{N-1}$						0.83
$W_N - W_{N-1}$						-0.06
$C_N - C_{N-1}$					-0.67	

Taylor and Graham (1953) have noted that, for the coastal waters of the Gulf of Maine in recent years, the increase of winter temperatures was more intense than the increase of the annual mean temperatures. However, in Passamaquoddy Bay, the general increase in temperature was of the same order of magnitude for both the average minimum and the average maximum, as well as for the average annual mean from the coldest to the warmest five-year periods on record. This is shown in Table III.

TABLE III

Increased temperatures of surface waters at St. Andrews, N. B.
1922-1953

Period	Abnormality	Minimum	Maximum	Annual Mean
1922-26	Cold	-0.7°C.	12.1°C.	6.0°C.
1949-53	Warm	1.8	14.3	8.2
Warming 1922-26 to 1949-53		2.5	2.2	2.2

Within these cold and warm five-year periods at St. Andrews, the coldest and the warmest individual years had annual mean temperatures of 5.4°C. and 8.5°C. in 1923 and 1951 respectively. During these two years, the warming was 13.1 and 12.5°C. respectively. The low annual mean of 1923 occurred following a period of intense cooling, 14.3°C. and, the high annual mean in 1951, following a period of little cooling, 11.2°C. During the winter of intense cooling in 1923, the monthly temperature reached a minimum of -1.7, while in 1951, presumably because of lack of cooling, the minimum was only 2.4°C. In the two years, the maxima were 11.4° and 14.9° for 1923 and 1951, respectively, but the warming was of the same order as mentioned above.

NUMERICAL FORECASTING OF TEMPERATURES

Annual Temperatures

The study of correlations between the annual temperature and one or two variables has the ultimate purpose of foreshadowing the annual temperatures at least 9 or 10 months in advance. Such a forecast forcibly eliminates the use of correlation between the warming during a year or of the maximum during a year and the annual temperature of the same year, because it would give predictions only 5 months beforehand. The cooling and the minimum, could be used for making such a forecast.

A regression equation relating the change in annual temperatures and the adjusted cooling during the previous winter has been established. The equation is based partly on the persistence of the annual temperature, and also on the cooling, which is not persistent. However, predicted values of annual temperatures were calculated and the probable error of the predicted value was ±0.33°C.

A regression equation based on a more persistent variable than the cooling has also been established, using the minimum temperature. Even, if the minimum temperature varies within wide limits over the years(high standard deviation) it has a fair degree of persistence comparable to that of the annual temperature. Based on the multiple correlation between the annual temperature of year N, the annual temperature of year N-1, and the minimum temperature of year N, the following equation has been established:

$$T_N = 0.49\ M_N + 0.20\ T_{N-1} + 5.4 \qquad (1)$$

where

T_N is the annual temperature of year N, M_N is the minimum temperature which occurs normally in February,

T_{N-1} is the annual temperature of the previous year (N-1).

With this equation one can calculate in advance the annual temperature with a good degree of accuracy since the probable error of the difference between the calculated and observed value is ± 0.28°C. The relationship between observed and calculated values of annual temperatures is given in Figure 4.

Maximum and Minimum Temperatures

Regression equations relating maximum and minimum temperatures to each other, as well as to the preceding values in the time series, have been established in an attempt to foreshadow these temperature levels at least 6 months in advance. They are:

$$\mathrm{Max}_N = 0.46\ \mathrm{Min}_N + 0.17\ \mathrm{Max}_{N-1} + 10.8 \qquad (2)$$

$$\mathrm{Min}_N = 0.34\ \mathrm{Max}_{N-1} + 0.29\ \mathrm{Min}_{N-1} - 4.2 \qquad (3)$$

where

Max_N is the maximum temperature of year N

Min_N is the minimum temperature of year N

Max_{N-1} is the maximum temperature of the previous year (N-1).

Min_{N-1} is the minimum temperature of the previous year (N-1).

The degree of accuracy of the predicted values obtained from these two equations is lower than it was with equation (1). The probable error of the difference between the calculated and observed values are ± 0.39°C. and ±0.57°C, for equations (2) and (3) respectively.

DISCUSSION

This study of the variations of sea water temperatures at St. Andrews, N. B. was made to relate the various components of the annual temperatures between themselves and also with the annual temperatures. It was possible to evaluate, statistically, the relation of warming and cooling, during the yearly cycle, to the level of the annual mean, the maximum and the minimum temperatures. From the relationship between the different variables, considering the persistence of the variables, it was possible to establish regression equations, and from these make an attempt to forecast annual temperatures, maximum and minimum temperatures. The computed values from the regression equations are very closely related to the observed values. The correlation coefficients between the two sets of data, predicted and observed, for the annual temperatures, maxima and minima are 0.90, 0.71 and 0.63 respectively. The regression equations (1), (2) and (3) are a good fit for the data.

This numerical forecasting is solely statistical. It is not based on the variations of the factors controlling the temperature variations, such as heat transfer across the air-sea boundary, the heat content of the whole body of water under consideration or the advection and mixing. However, the statistical study of the various components of the annual temperature seems to lead to the hypothesis that the cooling has a greater effect than the warming on the year-to-year variations of temperature. One might presume that the factors affecting the water temperature at the time of cooling have a greater effect on the general temperature level than at the time of warming. Also the variability of some of these factors might be greater during the cooling period than the warming period.

SUMMARY

1. Year-to-year variations of water temperatures at St. Andrews, N. B., are presented.
2. The twelve-month and ten-year moving averages show respectively the details of the short term variations and the trend, the general warming, during the last three decades.
3. The annual means, the maxima and the minima, vary in a similar fashion but the range of variations over the 34-year period is the smallest for the annual means and the greatest for the minima. The warming and cooling vary erratically.
4. The variables such as the annual means, the maxima and the minima are shown to be persistent, as compared to the warming and cooling. Of the five variables, the minima have the highest standard deviation.
5. Correlation coefficients have been calculated between several variables. The maxima and minima show respect-

ively significant correlations with the annual temperatures but not so much with the warming and cooling. In general, the cooling shows better correlation than the warming with any of the other variables.

6. Multiple correlation coefficients have been calculated and regression equations established in an attempt to forecast annual temperatures, maxima and minima. The probable errors of the difference between the calculated and observed values were ±0.28°C. for the annual temperature, ±0.39°C. for the maxima, and ±0.57°C. for the minima.

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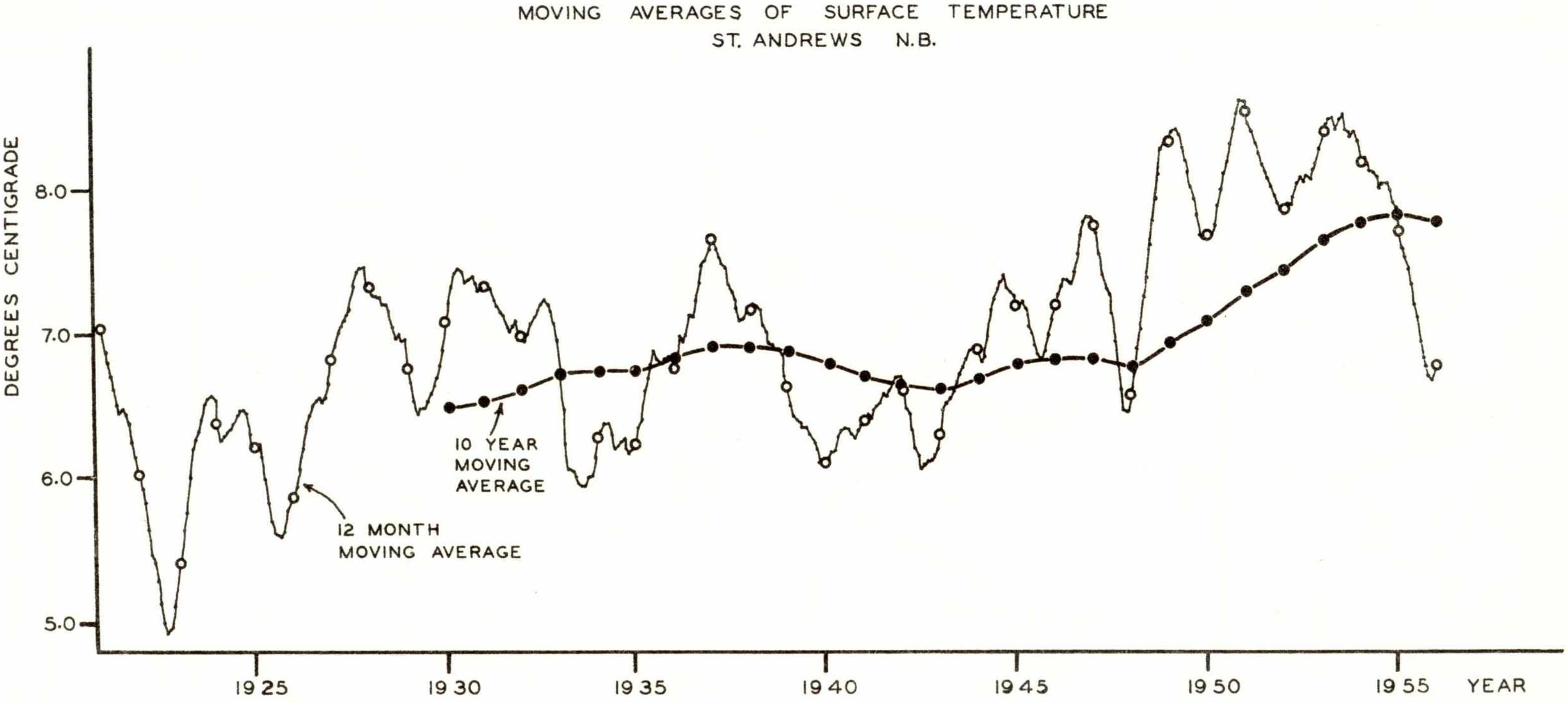

Figure 1. Moving averages of surface water temperatures St. Andrews, N. B.

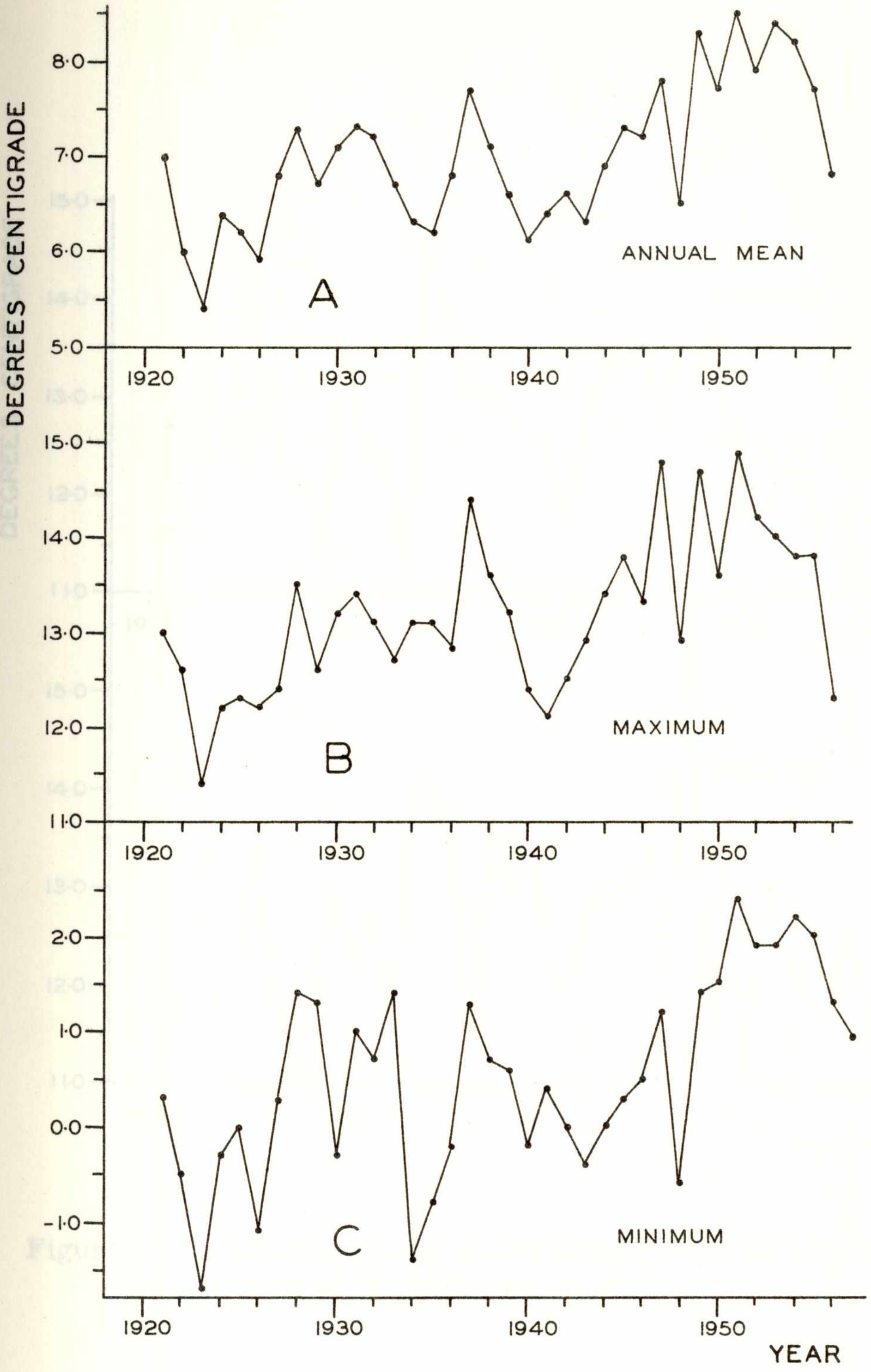

Figure 2. Surface water temperature variations at St. Andrews, N. B.: A. Annual mean, B. maximum, C. minimum.

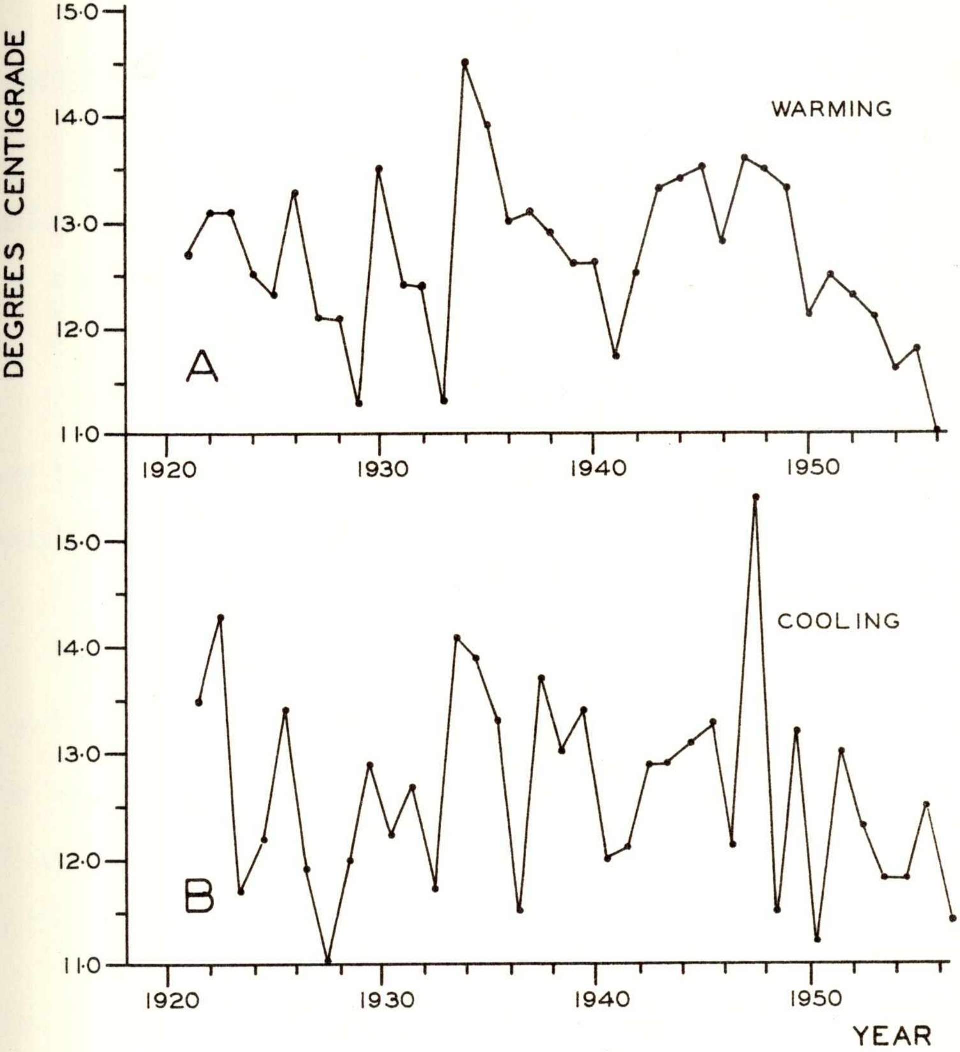

Figure 3. Annual warming A and cooling B of the surface waters at St. Andrews, N. B.

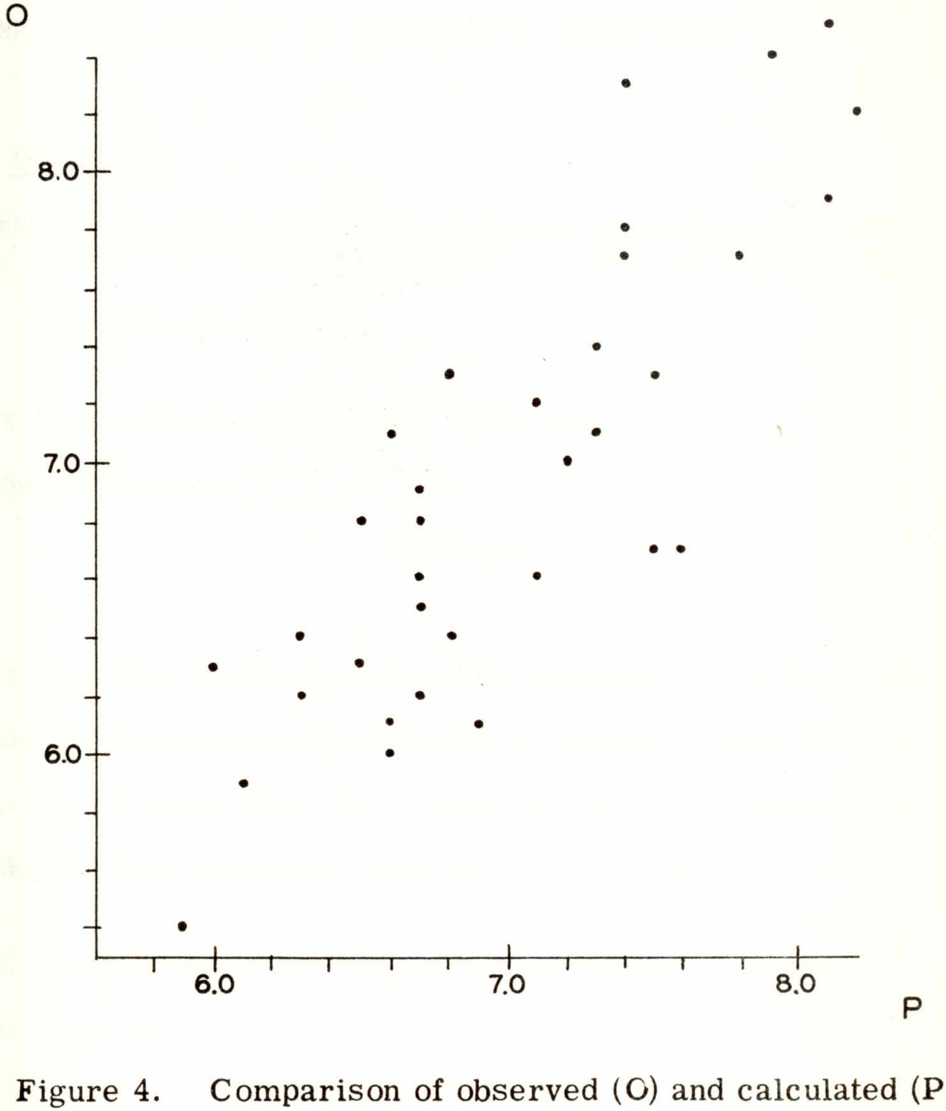

Figure 4. Comparison of observed (O) and calculated (P) values of annual mean temperatures at St. Andrews, N. B.

Addenda to Volume I

Please insert these addenda to the copy of Volume I already in your possession.

Thank you.

Approved December 1957 Standard Method No. Sal. 3.A

Addendum No. 1

DETERMINATION OF SALINITY BY CONDUCTIVITY MEASUREMENT

A. Capabilities of the Method

A statistical treatment of results obtained by skilled operators under sea-going conditions has shown that the precision range quoted in Standard Method No. Sal. 3.A applies unchanged to average sea-going analyses.

Rejection criteria can be relaxed somewhat and duplicate readings accepted if they agree to within 0.12 using the same cell or 0.17 using different cells (ca. S ‰ = 0.006 and 0.0085 respectively).

For shore-base work under exceptionally favourable conditions the range for the mean of duplicate determinations approaches ± 0.003 ‰. It would be unrealistic to assume that this precision can be improved significantly using the existing equipment (ref. Method Sal. 3.A).

Note. Section J. 2 and 3 should be modified as described in Standard Method No. Sal. 3.B.

Approved June 1958 Standard Method No. O. 1.A

Addendum No. 1

DETERMINATION OF OXYGEN IN SEA WATER

Note. Reference is made to Standard Method No. O. 1.A.

A. Capabilities of the Method

For the maximum precision using Standard Method No. O. 1.A, 50 ml. aliquots in 125 ml. Erlenmeyer flasks should be used instead of the 100 or 200 ml. aliquots in 250 ml. Erlenmeyer flasks, specified in Section F. 5. Titrations should be made using a 10 ml. burette graduated in 0.05 ml. divisions and for better end-point detection the Erlenmeyer flask should be painted white on the bottom and down one side. The flask is illuminated from the side during titrations and at least 4 ml. of starch indicator are added for each determination. The precision at the 0.7 mg.at.O_2/l. level given below corresponds to the highest precision considered likely for shore-base laboratory work under near ideal conditions, with thiosulphate standardized by the mean of at least five titrations.

Precision at 0.7 mg.at.O_2/l. level

The correct value lies in the range: Mean of n determinations $\pm \frac{0.005}{n^{1/2}}$ mg.at.O_2/l. Under routine conditions at sea the range will be greater, probably by 50 to 100 per cent. The starch end-point is comparable in precision with an electrometric end-point under sea-going conditions but the starch-iodine complex has an appreciable dissociation resulting in a slight error when starch is used. This error is not allowed for by standardization when low oxygen concentrations are being estimated (i.e. 0.1 mg.at.O_2/l. or less) and results will be up to 0.0015 mg.at.O_2/l. too low.

Approved December 1957 Standard Method No. P. 1.A

Addendum No. 1

DETERMINATION OF INORGANIC PHOSPHORUS (PHOSPHATE) PRESENT IN SEA WATER IN AMOUNTS LESS THAN 0.5 MICROGRAM ATOMS PER LITER

Note. Reference is made to Standard Method No. P. 1.A.

A. Capabilities of the Method

The following method is essentially the same as Standard Method No. P. 1.A except that a different technique is used for the extinction measurements. The technique is designed to minimize the errors that may occur in the estimation of amounts of phosphorus less than about 0.5 μg. atoms P/l that are present in turbid samples. In general it should only be necessary to employ this modification for phosphorus depleted surface waters near to a land drainage area. (In no case should a phosphorus determination be attempted, without filtration of the sample, if the turbidity blank exceeds about 0.1 on a 10 cm. cell.)

Precision at the 0.3 μg.at.P/l level has not been evaluated as conditions can be so variable. The precision should be comparable and generally much higher than that quoted in Standard Method No. P. 1.A instead of much worse, as would be the case were the analysis of low phosphorus high turbidity waters attempted without using the present modification.

The method described in this addendum could be used to determine phosphorus in all samples but the additional complexity of manipulation is not justified except in the circumstances outlined above.

B. Outline of the Method

The seawater sample is allowed to react with molybdate under acidity conditions that permit the formation of phosphomolybdate without the formation of silicomolybdate from any silicic acid present. The extinction of this solution is measured in a 10 cm. cell using light of wavelength near to 7000 A. Stannous chloride is then added to produce a blue reduced complex and the extinction is re-measured. The difference between the second and first extinction value is a measure of the phosphate present in the sample.

C. Special Apparatus and Equipment

See Standard Method No. P. 1.A.

D. Special Reagents Required

See Standard Method No. P. 1.A.

E. Sampling Procedure and Sample Storage

See Standard Method No. P. 1.A. Samples should be vigorously shaken just before the analysis is commenced.

F. Experimental

Procedure

1. Warm the samples to a temperature between 18° C and 23° C in a thermostated water bath or by placing the bottles in warm water to bring them within this temperature range and then storing them in a laboratory which has a uniform temperature between 18° C and 23° C (note a).

2. Add 1.0 ml. of molybdate solution (Reagent No. 1) from an automatic pipette to 100 ml. of sample and mix the solution (note c). Transfer the

solution to a 10 cm. cell that has previously been rinsed several times with distilled water and drained. A little water left behind in the cell before the sample is added does no harm (it should not exceed 1 to 2 ml.) and the cell should <u>not</u> be rinsed with sample. Three minutes after adding the molybdate to the sample (note d) measure the extinction with a Beckman DU Spectrophotometer, at a wavelength of 7000 A and slit width of 0.03 mm. using the red sensitive photocell. If a filter-type absorptiometer is used choose a filter having a maximum transmission in the region of 7000 A (note g). Record extinction values to the nearest 0.001 unit. Let this extinction be E_m.

3. Pour the solution from the cell back into the vessel containing the remainder of the sample and molybdate. Drain the cell but do not wash it. Add 0.5 ml. of dilute stannous chloride (Reagent No. 2) swirling the sample to ensure rapid mixing (note e). Refill the 10 cm. cell with the reduced sample solution, rinsing the cell once, and exactly 10 minutes after adding the stannous chloride re-measure the extinction on the spectrophotometer or absorptiometer (note f). Let this extinction be E_r. Evaluate $(E_r - E_m)_{\text{sample}}$.

Notes

See the notes to Section F of Standard Method No. P. 1.A.

G. Determination of Blanks

Only a reagent blank is necessary with this method as "cell to cell" and "turbidity" blanks are eliminated by the nature of the procedure. The reagent, however, may constitute an appreciable fraction of the total extinction due to phosphorus in the sample and should be determined <u>each</u>

time samples are analysed. Carry out the method exactly as described in Section F above using distilled water in place of the 100 ml. of seawater sample. Evaluate $(E_r - E_m)_{\text{distilled}}$.

H. Calibration

This is carried out exactly as described in Stzndard Method No. P. 1.A and samples may conveniently be analysed by the procedure described in this addendum at the same time as a batch of analyses is undertaken by the main method. The same factor, F, is used for both methods.

I. Calculations

$$\mu\text{g.at.P/l} = \left[(E_r - E_m)_{\text{sample}} - (E_r - E_m)_{\text{distilled}}\right] \times F.$$

Approved December 1957 Standard Method No. P. 2.A

Addendum No. 1

DETERMINATION OF TOTAL PHOSPHORUS IN SEA WATER

(AND ORGANIC PHOSPHORUS BY DIFFERENCE)

Addition to Section E

It appears to be impossible to prevent a very small, but detectable, pick-up of phosphorus from glassware over a sufficient period of time but pyrex boiling tubes, 200 mm. x 25 mm. holding about 80-90 ml., have proved satisfactory for storing samples for total phosphate for a period exceeding a month. The tubes are cleaned thoroughly in hot chromic-sulphuric acid for several hours, rinsed thoroughly with distilled water and conditioned by being allowed to stand full of slightly acidic water (1 drop of concentrated hydrochloric acid) for several months. When not in use the tubes should be kept nearly full of acidic water and covered with a clean square of Parafilm. In no circumstances should a cork or rubber stopper be used as either can introduce contamination. This water is emptied, and the tube drained as dry as possible, immediately before 50 ml. of sample are placed in it for storage on the ship. One to 2 drops of concentrated hydrochloric should be added to each sample to acidify the sea-water sample during storage, and the tubes should be re-stoppered by Parafilm sheeting. The very slight phosphorus pick-up which may still occur during a cruise (ca. 0.1 μg.at.P/l.) can be minimized by storing tubes in a deep-freeze and by assessing a mean blank correction. This is obtained by storing synthetic sea water of known total phosphorus content in 3 to 4 tubes selected at random and redetermining the total phosphorus at the end of the cruise.

Addition to Section F

(ca. 0.1 µg.at.P/l.) The extinction of samples should not exceed 1.5, equivalent to about 6 µg.at.P/l., or readings may be in appreciable error owing to optical defects in the spectrophotometer used. If extinction values exceed about 1.2 the slit width of the Beckman DU Spectrophotometer should be increased to 0.05 mm. to allow greater sensitivity of response in the instrument.

For quantities of phosphorus exceeding about 5 µg.at.P/l. the six minutes reduction time, Standard Method No. P. 2.A, Section F. 7, is too near the safe upper limit and the reduction time should be reduced to 4 minutes. (For 7 µg.at.P/l. the stable maximum extinction persists from 2.5 to 6.0 minutes at 23° C.) Occasionally total phosphorus extinction values may exceed 1.5. When this occurs dilute 25 ml. of the reduced solution to 50 ml. in a stoppered graduated 50 ml. measuring cylinder by pouring the sample into a cylinder containing exactly 25 ml. of distilled water. Mix and re-measure the extinction *at once*. If this *final* extinction measurement is made no longer than 6 minutes after the addition of stannous chloride the extinction obtained after dilution may be doubled to give the correct initial extinction value. In this manner the maximum total phosphorus that can be determined by Standard Method No. P. 2.A is extended to about 8 µg.at.P/l.

Correction to Section A

At the top of page 67 $\pm \frac{0.16}{n}$ should read $\pm \frac{0.16}{n^{1/2}}$.

Approved December 1957 Standard Method C. 1.A

Addendum No. 1

DETERMINATION OF CARBONATE, BICARBONATE AND FREE CARBON DIOXIDE IN SEA WATER FROM PH AND ALKALINITY MEASUREMENTS

Introductory Remarks

Re-determination of the dissociation constants of boric acid and carbonic acid in sea water by Dr. J. Lyman (J. Lyman Ph.D. thesis, U.C.L.A. 1957. Buffer Mechanism of Sea Water) has substantiated the Buch values (K. Buch, Das Kohlensäure gleichgewichtssystem im Meerwasser. Havsforskn Inst. Skr. Helsingf. No. 151. 1951) used to compute the Tables in Standard Method C. 1.A, except for the second dissociation constant of carbonic acid. pK values for this dissociation are now considered to be some 0.15 units higher than previously supposed. The data in Tables VI, VII and IX are consequently subject to revision.

The constant K defined on page 108 of Standard Method C. 1.A and reported in Table IX should be defined as:

$$K = \frac{a_H \times \left(CO_3^{2-}\right)}{\left(HCO_3^{1-}\right)}$$

Tables VI, VII and IX are to be deleted and replaced by the following Tables.

Table VI

Factor, F_T, in the equation II 2.d.

Total carbon dioxide content = carbonate alkalinity x F_T

°C $pH_{s.d.}$	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
			Cl = 15 ‰							S = 27 ‰						
7.3	1.07	1.06	1.06	1.06	1.05	1.05	1.05	1.05	1.04	1.04	1.04	1.04	1.03	1.03	1.03	1.03
7.4	1.05	1.05	1.04	1.04	1.04	1.04	1.03	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.02	1.02
7.5	1.04	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.00
7.6	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.00	1.00	1.00	1.00	.99	.99
7.7	1.01	1.01	1.01	1.01	1.00	1.00	1.00	1.00	1.00	.99	.99	.99	.99	.99	.98	.98
7.8	1.00	1.00	1.00	1.00	.99	.99	.99	.99	.99	.98	.98	.98	.98	.97	.97	.97
7.9	.99	.99	.99	.99	.98	.98	.98	.98	.98	.97	.97	.97	.97	.96	.96	.96
8.0	.98	.98	.98	.98	.97	.97	.97	.97	.96	.96	.96	.96	.95	.95	.95	.94
8.1	.97	.97	.97	.97	.96	.96	.96	.96	.95	.95	.95	.94	.94	.93	.93	.93
8.2	.96	.96	.96	.95	.95	.95	.94	.94	.94	.93	.93	.93	.92	.92	.91	.91
8.3	.95	.95	.94	.94	.94	.93	.93	.93	.92	.92	.91	.91	.90	.90	.89	.89
8.4	.93	.93	.93	.92	.92	.92	.91	.91	.90	.90	.89	.89	.88	.88	.87	.86
8.5	.92	.91	.91	.91	.90	.90	.89	.89	.88	.88	.87	.86	.86	.85	.85	.84
8.6	.90	.89	.89	.89	.88	.88	.87	.87	.86	.85	.85	.84	.83	.83	.82	.81

Table VI (cont'd)

Factor, F_T, in the equation II 2.d.

Total carbon dioxide content = carbonate alkalinity x F_T

°C / $pH_{s.d.}$	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
	Cl = 17 ‰								S = 30.5 ‰							
7.3	1.06	1.06	1.06	1.05	1.05	1.05	1.04	1.04	1.04	1.04	1.04	1.03	1.03	1.03	1.03	1.03
7.4	1.05	1.04	1.04	1.04	1.04	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.02	1.02	1.02	1.01
7.5	1.03	1.03	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.01	1.00	1.00
7.6	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.00	1.00	1.00	1.00	1.00	.99	.99	.99
7.7	1.01	1.01	1.01	1.00	1.00	1.00	1.00	1.00	.99	.99	.99	.99	.98	.98	.98	.98
7.8	1.00	1.00	1.00	.99	.99	.99	.99	.98	.98	.98	.98	.98	.97	.97	.97	.96
7.9	.99	.99	.99	.98	.98	.98	.98	.97	.97	.97	.97	.96	.96	.96	.95	.95
8.0	.98	.98	.97	.97	.97	.97	.96	.96	.96	.96	.95	.95	.95	.94	.94	.94
8.1	.97	.97	.96	.96	.96	.95	.95	.95	.95	.94	.94	.94	.93	.93	.92	.92
8.2	.96	.95	.95	.95	.94	.94	.94	.93	.93	.93	.92	.92	.92	.91	.91	.90
8.3	.94	.94	.94	.93	.93	.92	.92	.92	.91	.91	.90	.90	.90	.89	.88	.88
8.4	.93	.92	.92	.92	.91	.91	.90	.90	.89	.89	.88	.88	.87	.87	.86	.86
8.5	.91	.91	.90	.90	.89	.89	.88	.88	.87	.87	.86	.86	.85	.84	.84	.83
8.6	.89	.89	.88	.87	.87	.86	.86	.85	.85	.84	.84	.83	.82	.82	.81	.80

Table VI (cont'd)

Factor, F_T, in the equation II 2.d.

Total carbon dioxide content = carbonate alkalinity x F_T

°C	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
$pH_{s.d.}$				Cl = 19 ‰						S = 34 ‰						
7.3	1.06	1.06	1.05	1.05	1.05	1.04	1.04	1.04	1.04	1.03	1.03	1.03	1.03	1.03	1.02	1.02
7.4	1.04	1.04	1.04	1.03	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01
7.5	1.03	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.00	1.00	1.00	1.00
7.6	1.02	1.02	1.01	1.01	1.01	1.01	1.00	1.00	1.00	1.00	1.00	.99	.99	.99	.99	.98
7.7	1.01	1.00	1.00	1.00	1.00	1.00	.99	.99	.99	.99	.99	.98	.98	.98	.98	.97
7.8	1.00	.99	.99	.99	.99	.99	.98	.98	.98	.98	.97	.97	.97	.97	.96	.96
7.9	.99	.98	.98	.98	.98	.97	.97	.97	.97	.96	.96	.96	.96	.95	.95	.94
8.0	.98	.97	.97	.97	.96	.96	.96	.96	.95	.95	.95	.94	.94	.94	.93	.93
8.1	.96	.96	.96	.96	.95	.95	.95	.94	.94	.94	.93	.93	.93	.92	.92	.91
8.2	.95	.95	.95	.94	.94	.94	.93	.93	.92	.92	.92	.91	.91	.90	.90	.89
8.3	.94	.93	.93	.93	.92	.92	.91	.91	.91	.90	.90	.89	.89	.88	.88	.87
8.4	.92	.92	.91	.91	.90	.90	.90	.89	.89	.88	.88	.87	.86	.86	.85	.84
8.5	.90	.90	.89	.89	.88	.88	.87	.87	.86	.86	.85	.85	.84	.83	.83	.82
8.6	.88	.88	.87	.87	.86	.86	.85	.84	.84	.83	.83	.82	.81	.81	.80	.79

Table VI (cont'd)

Factor, F_T, in the equation II 2.d.

Total carbon dioxide content = carbonate alkalinity x F_T

°C / pH s.d.	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
				Cl = 21 ‰						S = 38 ‰						
7.3	1.06	1.05	1.05	1.04	1.04	1.04	1.04	1.04	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.02
7.4	1.04	1.04	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.00
7.5	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.00	1.00	1.00	1.00	1.00	.99
7.6	1.01	1.01	1.01	1.01	1.01	1.00	1.00	1.00	1.00	.99	.99	.99	.99	.99	.98	.98
7.7	1.00	1.00	1.00	1.00	.99	.99	.99	.99	.99	.98	.98	.98	.98	.97	.97	.97
7.8	.99	.99	.99	.99	.98	.98	.98	.98	.97	.97	.97	.97	.96	.96	.96	.95
7.9	.98	.98	.98	.97	.97	.97	.97	.97	.96	.96	.96	.95	.95	.95	.94	.94
8.0	.97	.97	.97	.96	.96	.96	.96	.95	.95	.95	.94	.94	.94	.93	.93	.92
8.1	.96	.96	.95	.95	.95	.95	.94	.94	.93	.93	.93	.92	.92	.91	.91	.90
8.2	.95	.94	.94	.94	.93	.93	.93	.92	.92	.91	.91	.90	.90	.89	.89	.88
8.3	.93	.93	.92	.92	.92	.91	.91	.90	.90	.89	.89	.88	.88	.87	.86	.86
8.4	.91	.91	.91	.90	.90	.89	.89	.88	.88	.87	.87	.86	.85	.85	.84	.83
8.5	.89	.89	.89	.88	.88	.87	.86	.86	.85	.85	.84	.84	.83	.82	.81	.80
8.6	.87	.87	.86	.86	.85	.85	.84	.83	.83	.82	.82	.81	.80	.79	.78	.77

Table VII

Factor, F_p, in the equation II 3.c.

Partial pressure of carbon dioxide (P_{CO_2}) = carbonate alkalinity x F_p

°C $pH_{s.d.}$	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
				Cl = 15 ‰						S = 27 ‰						
7.3	1.12	1.14	1.17	1.19	1.22	1.26	1.29	1.32	1.36	1.39	1.42	1.45	1.49	1.54	1.59	1.64
7.4	.89	.90	.92	.94	.97	1.00	1.02	1.05	1.07	1.10	1.12	1.15	1.17	1.21	1.25	1.29
7.5	.70	.71	.73	.74	.77	.79	.81	.83	.85	.87	.88	.90	.93	.96	.99	1.01
7.6	.56	.56	.58	.59	.60	.62	.64	.65	.67	.68	.70	.71	.73	.75	.78	.80
7.7	.44	.44	.45	.46	.48	.49	.50	.51	.53	.54	.55	.56	.57	.59	.61	.62
7.8	.35	.35	.36	.36	.37	.39	.39	.40	.41	.42	.43	.44	.45	.46	.47	.49
7.9	.27	.27	.28	.29	.29	.30	.31	.31	.32	.33	.33	.34	.35	.36	.37	.38
8.0	.21	.21	.22	.22	.23	.24	.24	.25	.25	.26	.26	.26	.27	.28	.29	.29
8.1	.17	.17	.17	.17	.18	.18	.19	.19	.20	.20	.20	.20	.21	.21	.22	.22
8.2	.13	.13	.13	.14	.14	.14	.15	.15	.15	.15	.16	.16	.16	.16	.17	.17
8.3	.10	.10	.10	.10	.11	.11	.11	.11	.12	.12	.12	.12	.12	.12	.13	.13
8.4	.08	.08	.08	.08	.08	.08	.09	.09	.09	.09	.09	.09	.09	.09	.10	.10
8.5	.06	.06	.06	.06	.06	.06	.06	.07	.07	.07	.07	.07	.07	.07	.07	.07
8.6	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05

Note. Multiply the figure in the table by 10^{-3} to get F_p

Table VII (cont'd)

Factor, F_p, in the equation II 3.c.

Partial pressure of carbon dioxide (P_{CO_2}) = carbonate alkalinity x F_p

°C	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
$pH_{s.d.}$				Cl = 17 ‰						S = 30.5 ‰						
7.3	1.09	1.10	1.13	1.16	1.19	1.23	1.26	1.29	1.31	1.34	1.37	1.41	1.44	1.49	1.54	1.57
7.4	.86	.87	.89	.91	.94	.97	1.00	1.02	1.04	1.06	1.08	1.11	1.14	1.18	1.22	1.24
7.5	.68	.69	.71	.72	.74	.77	.79	.80	.82	.84	.85	.87	.90	.93	.96	.97
7.6	.54	.54	.56	.57	.59	.60	.62	.63	.64	.66	.67	.69	.70	.73	.75	.76
7.7	.42	.43	.44	.45	.46	.48	.49	.50	.51	.52	.53	.54	.55	.57	.59	.60
7.8	.33	.34	.35	.35	.36	.37	.38	.39	.40	.40	.41	.42	.43	.44	.46	.46
7.9	.26	.26	.27	.28	.28	.29	.30	.31	.31	.32	.32	.33	.34	.35	.36	.36
8.0	.21	.21	.21	.22	.22	.23	.23	.24	.24	.25	.25	.25	.26	.27	.27	.28
8.1	.16	.16	.17	.17	.17	.18	.18	.18	.19	.19	.19	.20	.20	.21	.21	.21
8.2	.12	.13	.13	.13	.13	.14	.14	.14	.14	.15	.15	.15	.15	.16	.16	.16
8.3	.10	.10	.10	.10	.10	.10	.11	.11	.11	.11	.11	.11	.12	.12	.12	.12
8.4	.07	.07	.08	.08	.08	.08	.08	.08	.08	.08	.09	.09	.09	.09	.09	.09
8.5	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06	.07	.07	.07	.07
8.6	.04	.04	.04	.04	.04	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05	.05

Note. Multiply the figure in the table by 10^{-3} to get F_p

Table VII (cont'd)

Factor, F_p, in the equation II 3.c.

Partial pressure of carbon dioxide (P_{CO_2}) = carbonate alkalinity x F_p

°C / $pH_{s.d.}$	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
	Cl = 19 ‰								S = 34 ‰							
7.3	1.05	1.07	1.10	1.12	1.14	1.18	1.21	1.24	1.28	1.30	1.33	1.36	1.40	1.43	1.48	1.52
7.4	.83	.84	.87	.89	.90	.93	.96	.98	1.01	1.02	1.05	1.07	1.10	1.13	1.17	1.20
7.5	.66	.67	.69	.70	.71	.74	.76	.77	.80	.81	.82	.84	.87	.89	.92	.94
7.6	.52	.53	.54	.55	.56	.58	.60	.61	.63	.63	.65	.66	.68	.70	.72	.74
7.7	.41	.41	.43	.44	.44	.46	.47	.48	.49	.50	.51	.52	.53	.54	.56	.58
7.8	.32	.33	.33	.34	.35	.36	.37	.37	.39	.39	.40	.41	.42	.42	.44	.45
7.9	.25	.26	.26	.27	.27	.28	.29	.29	.30	.30	.31	.32	.32	.33	.34	.35
8.0	.20	.20	.20	.21	.21	.22	.22	.23	.23	.23	.24	.24	.25	.25	.26	.27
8.1	.15	.16	.16	.16	.16	.17	.17	.18	.18	.18	.18	.19	.19	.19	.20	.20
8.2	.12	.12	.12	.13	.13	.13	.13	.14	.14	.14	.14	.14	.15	.15	.15	.15
8.3	.09	.09	.10	.10	.10	.10	.10	.10	.11	.11	.11	.11	.11	.11	.11	.12
8.4	.07	.07	.07	.07	.07	.08	.08	.08	.08	.08	.08	.08	.08	.08	.09	.09
8.5	.05	.05	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06
8.6	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.05	.05	.05

Note. Multiply the figure in the table by 10^{-3} to get F_p

Table VII (cont'd)

Factor, F_p, in the equation II 3.c.

Partial pressure of carbon dioxide (P_{CO_2}) = carbonate alkalinity x F_p

pHs.d. \ °C	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
	Cl = 21 ‰								S = 38 ‰							
7.3	1.02	1.04	1.07	1.08	1.11	1.15	1.18	1.20	1.24	1.26	1.29	1.32	1.36	1.39	1.44	1.47
7.4	.81	.82	.84	.85	.88	.91	.94	.95	.98	.99	1.01	1.04	1.07	1.09	1.13	1.15
7.5	.64	.65	.67	.67	.69	.72	.74	.75	.77	.78	.80	.82	.84	.86	.89	.90
7.6	.50	.51	.53	.53	.55	.57	.58	.59	.60	.61	.63	.64	.66	.67	.70	.71
7.7	.40	.40	.41	.42	.43	.44	.46	.46	.47	.48	.49	.50	.51	.53	.54	.55
7.8	.31	.32	.32	.33	.34	.35	.36	.36	.37	.37	.38	.39	.40	.41	.42	.43
7.9	.24	.25	.25	.26	.26	.27	.28	.28	.29	.29	.30	.30	.31	.32	.33	.33
8.0	.19	.19	.20	.20	.20	.21	.22	.22	.22	.23	.23	.23	.24	.24	.25	.25
8.1	.15	.15	.15	.15	.16	.16	.17	.17	.17	.17	.18	.18	.18	.19	.19	.19
8.2	.11	.12	.12	.12	.12	.13	.13	.13	.13	.13	.14	.14	.14	.14	.14	.14
8.3	.09	.09	.09	.09	.09	.10	.10	.10	.10	.10	.10	.10	.10	.11	.11	.11
8.4	.07	.07	.07	.07	.07	.07	.07	.07	.08	.08	.08	.08	.08	.08	.08	.08
8.5	.05	.05	.05	.05	.05	.05	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06
8.6	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04	.04

Note. Multiply the figure in the table by 10^{-3} to get F_p

Table IX

Values for K, the quasi-thermodynamic second dissociation constant of carbonic acid in sea water.

Note. Multiply the figures in the table by 10^{-9} to get K

S ‰	°C Cl ‰	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
27	15	0.33	0.35	0.36	0.38	0.40	0.42	0.45	0.47	0.50	0.53	0.56	0.60	0.63	0.67	0.72	0.76
28	16	0.35	0.37	0.38	0.41	0.43	0.45	0.47	0.50	0.53	0.56	0.59	0.63	0.66	0.71	0.75	0.79
30.5	17	0.36	0.38	0.40	0.43	0.45	0.48	0.50	0.53	0.55	0.59	0.62	0.65	0.69	0.73	0.78	0.83
32.5	18	0.38	0.40	0.42	0.45	0.47	0.50	0.53	0.55	0.58	0.62	0.65	0.69	0.73	0.77	0.83	0.88
34	19	0.40	0.42	0.44	0.47	0.50	0.52	0.55	0.58	0.61	0.65	0.68	0.72	0.76	0.81	0.86	0.93
36	20	0.42	0.44	0.46	0.49	0.53	0.55	0.58	0.61	0.65	0.68	0.71	0.76	0.80	0.85	0.91	0.98
38	21	0.44	0.47	0.48	0.52	0.54	0.56	0.60	0.63	0.67	0.71	0.74	0.79	0.84	0.90	0.97	1.05