

A PHYSICAL AND CHEMICAL STUDY OF
TOFINO INLET, VANCOUVER ISLAND,
BRITISH COLUMBIA

by

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of the Requirements for the Degree of
Master of Science
in the Department
of
Chemistry

We accept this thesis as conforming
to the required standard

The University of British Columbia

September 1964

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ABSTRACT

The distribution of the physical and chemical properties in Tofino Inlet is examined in this study. The presence of shallow thresholds in the entrances to the inlet prevents the exchange of deep water in the inlet with oceanic water of the same depth and restricts the intrusion of oceanic water to that of the surface layer. Replacement of the bottom water of the inlet occurs in the summer, when the density of the oceanic surface water is highest for the year, and accounts for the relatively high bottom temperatures, which are observed throughout the year. Between replacements the bottom water in the upper basins of Tofino stagnates and becomes anoxic. Under these stagnant conditions the oxygen supply of this water is used up. Eventually heterotrophic bacteria use sulphate as hydrogen acceptor for the oxidation of organic matter and produce hydrogen sulphide and carbon dioxide. The production of these substances results in an increase in the alkalinity and a decrease in the pH of the water. Using certain assumptions regarding the oxidative processes, calculations are made which suggest that the observed anomalous increase in alkalinity is mainly due to the dissolution of calcium carbonate in these relatively acidic waters. A rate of oxygen utilization is calculated for the deep basin water and is used to determine whether or not replacement of the bottom water was likely during the summer of 1959.

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CHAPTER I

INTRODUCTION

Annual surveys of some of the British Columbia mainland inlets have been carried out by the Institute of Oceanography at the University of British Columbia since 1951. In 1959 the scope of the survey was expanded to include the inlets in the west coast of Vancouver Island. Many of these inlets, including Tofino Inlet, had not been previously surveyed. It was found that the water in Tofino Inlet exhibited a marked temperature inversion. The temperature decreased from a value of 16.0°C . at the surface to 10.0°C . at 30 meters and then increased to 15.3°C . at the bottom. In addition, the low oxygen content of the deep water indicated stagnation and suggested that the bottom water in the basins further up the inlet might well be anoxic.¹ Ford (1959) found that the same temperature inversion was present in July, 1959 and also that 15.3°C . water was present at 70-75 meters in the basin at Station 1/2. In March, 1960, while the intensity of the inversion had decreased, it was still in evidence. Consequently, a more detailed examination of the inlet was undertaken. The observations that were made were selected with two objects in mind; (1) to determine the physical distribution of

¹ Richards and Benson (1961) have suggested that the word anoxic be used to describe natural waters that contain no dissolved oxygen.

properties and flushing characteristics of the inlet, and (2) to investigate the chemical properties of the anoxic basins.

It is the purpose of this thesis to present the results of these physical and chemical studies in Tofino Inlet and to suggest reasons for the distribution of properties that were found.

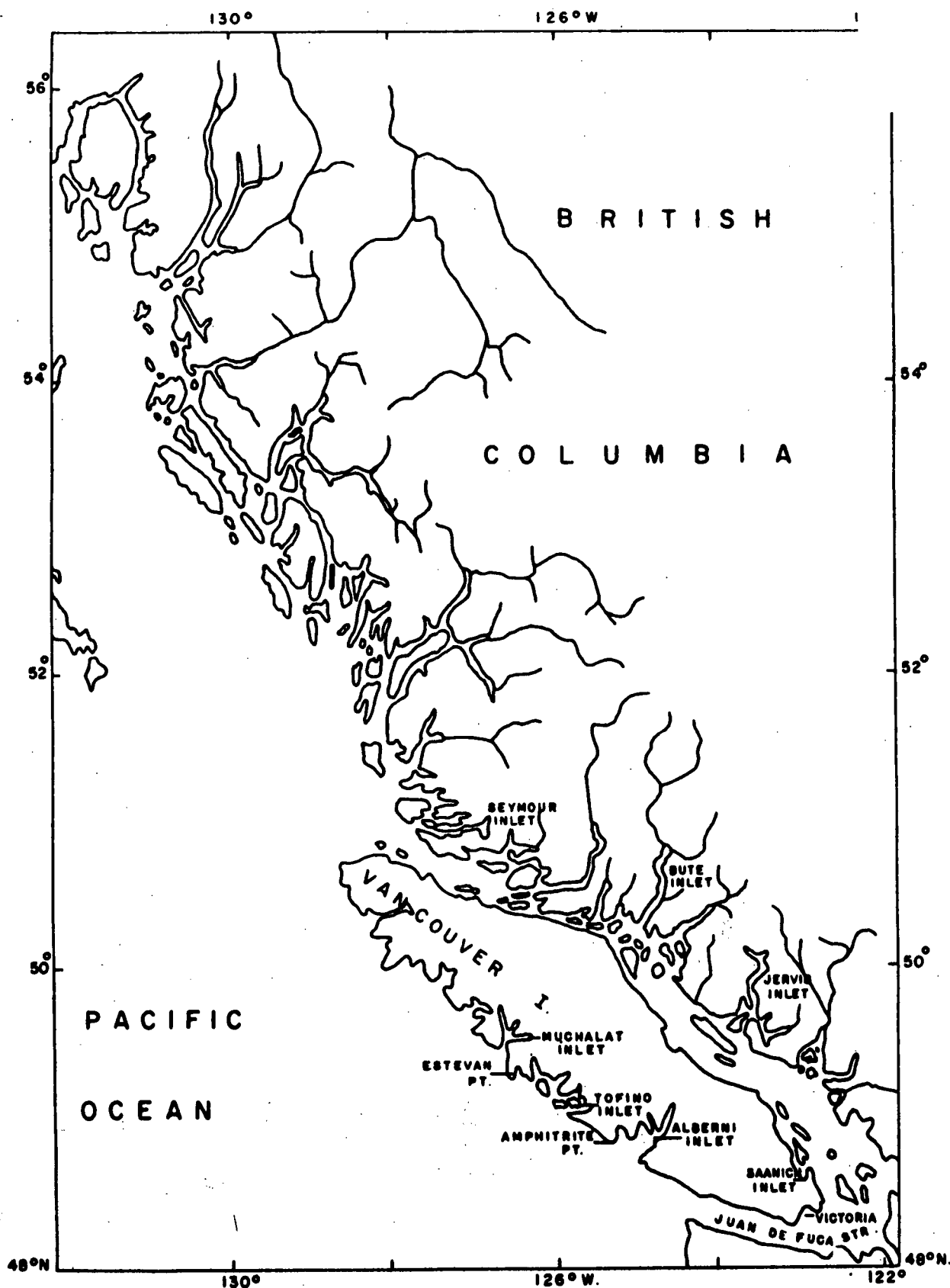


Fig. 1. Coastline of British Columbia, showing the location of Tofino inlet.

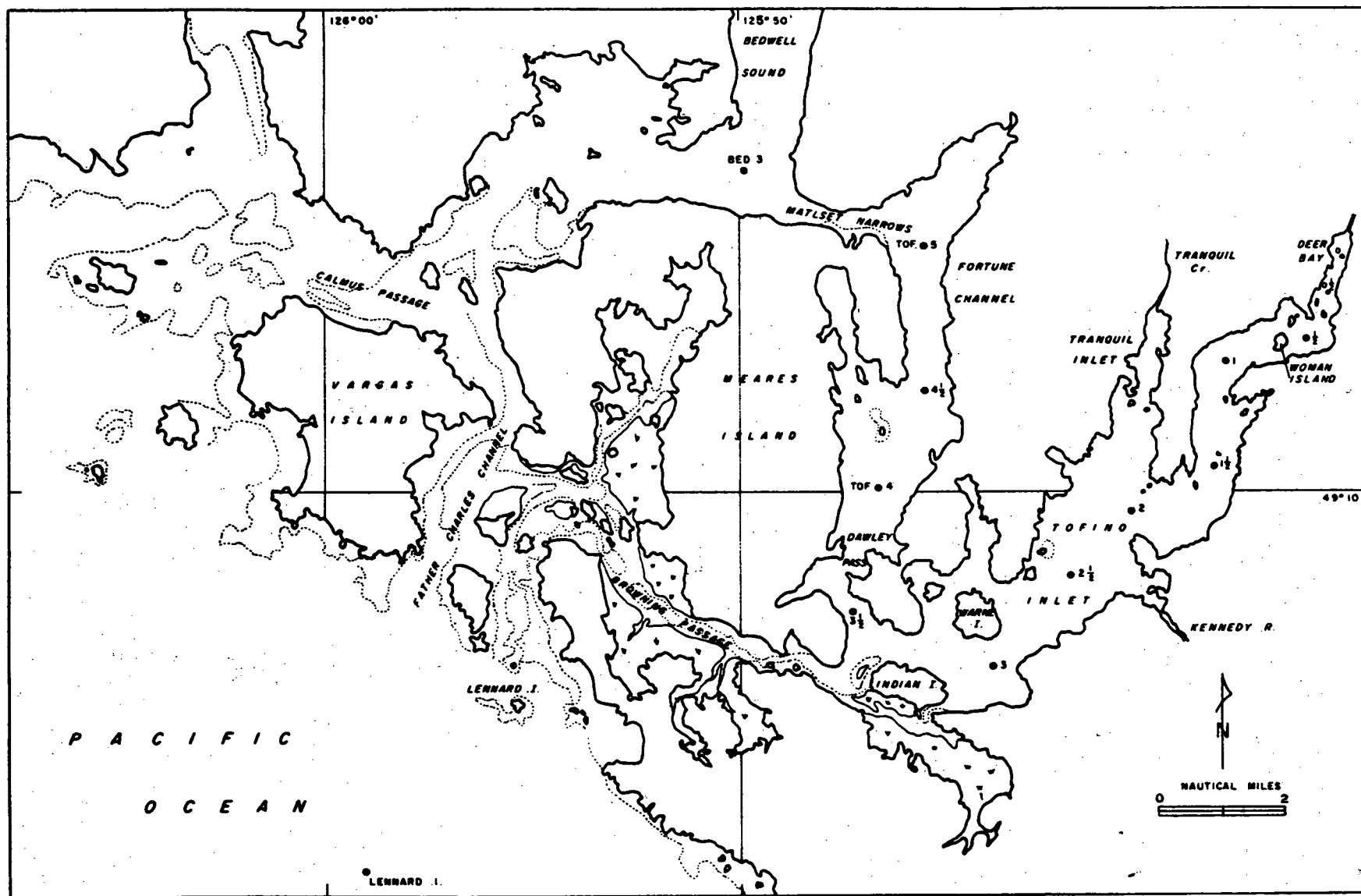


Fig. 2. Map of Tofino Inlet and its approaches showing the location of the oceanographic stations.

CHAPTER II

PHYSICAL DESCRIPTION OF TOFINO INLET

I. GEOGRAPHY AND TOPOGRAPHY

Tofino Inlet is situated in the west coast of Vancouver Island at $49^{\circ}08'N$ and $125^{\circ}47'W$. Figure 1 shows the general location of the inlet. Figure 2 is a map of the inlet and its approaches, containing the location of the oceanographic stations.

The inlet is separated from the coastal shelf region of Clayoquot Sound by Meares Island. Two channels are thus formed, which connect the inlet with the water of the coastal shelf of Vancouver Island. Of these two channels the northern one is deeper. It begins at Dawley Pass and runs through Fortune Channel, Matlset Narrows, the southern portion of Bedwell Sound and Father Charles Channel. Browning Passage forms the shallower, southern channel.

Tofino Inlet is 11.5 nautical miles long. From the two narrow channels of Dawley Pass and Browning Passage the width increases to a maximum of 2.5 miles at Station 2 and then progressively decreases toward the head at Deer Bay. The maximum depth, 130 meters, is at Station 1. In Fortune Channel the maximum depth is 140 meters, at Station 5. The general features of the bottom topography of the inlet and of the northern passage as far as Bedwell Sound are given

in the longitudinal profiles Figures 3-5, pages 14 and 16. The vertical exaggeration is 100 to 1.

Carter (1933), in describing the inlets of British Columbia, classified them as fjords. These are long, narrow winding bodies of water which are connected to the sea over a shallow threshold or sill. Often a series of sills are present which divide the inlet into a number of basins. Tofino Inlet falls into the fjord classification.

The depth in the approaches to Tofino Inlet water is not greater than 11 meters, except through Father Charles Channel, where the depth is 13 meters. From this point, the northern channel deepens into a basin in Bedwell Sound with a maximum depth of 110 meters. In Matlset Narrows there is a 28 meter sill. The basin formed by Fortune Channel has a maximum depth of 140 meters at Station 5 and then shallows to a 33 meter sill in Dawley Pass. The southern channel, which is formed by Browning Passage, is not deeper than 11 meters and the sill depth in this channel is 7 meters.

The main basin of Tofino Inlet gradually deepens from Dawley Pass, until at Station 1, the inlet reaches a maximum depth of 130 meters. Sills of 66 meters, 21 meters and 33 meters separate the three anoxic basins at the head of the inlet. The depth of these basins, at Station 1/2, Station 0 1/2 and Station 0, is 96 meters, 45 meters and 47 meters, respectively.

The depths, cited above, are taken from Chart No. 3640

published by the Canadian Hydrographic Service and from their unpublished field sheet. The depths are reduced to lowest normal tides. At high tide the water level can be 4-5 meters greater.

II. PRECIPITATION AND FRESH WATER INFLUX

Precipitation in the area is heavy. Measurements taken at Estevan Point prior to November 1958 and at Tofino Airport since then indicate the annual rainfall in this region is 120 inches a year (Anon. 1957a - 1960a). Figures 16 to 19, pages 40 to 43, show the monthly rainfall in the region during the years 1957-1960. The rainfall is heavy during the fall, winter and spring and light during the summer. During the summers of 1958 and 1960 there were periods of several weeks of dry weather.

The Kennedy River provides the largest source of fresh water, draining approximately 100 square miles. No discharge figures are available but a rough estimate, using rainfall and drainage area, would place the average flow at 1000 cubic feet per second. The discharge of Tofino Creek, at the head of the inlet, is substantially less than the Kennedy River.

Since the mountains, which are in the Tofino Inlet watershed, are only 2000-3000 feet high, no large snow-storage area exists and maximum run-off occurs during the winter, coinciding with the period of maximum rainfall.

This is true of all the rivers along the west coast of Vancouver Island and differs from conditions on the mainland, where maximum run-off occurs during the summer (Pickard 1963).

CHAPTER III

EXPERIMENTAL METHODS AND TREATMENT OF DATA

I. DESCRIPTION OF CRUISES

The original work carried out by the Institute of Oceanography at the University of British Columbia and by Dr. W. L. Ford in Tofino Inlet, during May and July of 1959, formed the basis for the series of cruises that were subsequently undertaken. Table I contains a list of these cruises, the stations occupied and the observations taken on each cruise. Except for hydrogen sulphide the data taken on these cruises is published in the Data Reports of the Institute of Oceanography at the University of British Columbia (Anon 1959b-1961b). The hydrogen sulphide data are included in Appendix A, page 69.

II. OBSERVATIONAL METHODS

Hydrographic casts were made at each station. Temperatures were measured with reversing thermometers and with a bathythermograph. Meteorological data were recorded. Samples for chemical analysis were withdrawn from the Atlas sampling bottles in an order which minimized the exchange of dissolved gases with the air.

III. METHODS OF ANALYSIS

Except where noted below, the analytical methods used

were those described by Strickland and Parsons (1961).

Total sulphide. Sulphide samples were drawn into 500ml plastic bottles containing 2 mls of 24% zinc acetate solution and were analyzed by the iodine volumetric method. (Standard Methods, 1955). The samples taken during the cruise in September 1960 were kept at ambient laboratory temperature aboard ship and brought back and stored in a refrigerator until analyzed. A fungus growth developed in these samples after about two months but apparently no reaction took place with the precipitated zinc sulphide. Samples taken on later cruises were frozen aboard ship and kept frozen until they were analyzed. These samples were free of fungus growth.

Analysis of sulphate. Sulphate samples were analysed by the method of Bather and Riley (1954). The precision of this method is not sufficient to obtain any worthwhile information from the sulphate observations and no use is made of them in this presentation.

IV. TREATMENT OF DATA

The data is presented graphically in two ways; (1) in longitudinal profile along a section which runs through the center of the inlet, (2) in vertical profile at each station, showing the variation of each property with depth.

TABLE I

OBSERVATIONS TAKEN ON TOFINO INLET CRUISES

Cruise	Date	Stations Occupied	Observations Taken
59/6	May 1959	Bed.3, Tof.5, Tof.4, Tof.3, Tof.2, Tof.1.	Salinity, Temp. Oxygen.
W.L. Ford	May 1959	Tof.3, Tof.2, Tof.1, Tof. 1/2.	Temp. by Bathy- thermograph.
60/3	March	Bed.3, Tof.5, Tof.4, Tof.3 1/2, Tof.3, Tof. 2, Tof.1, Tof. 1/2.	Salinity, Temp.
60/8	June, 1960	Bed.3, Tof.5, Tof.4, Tof.3, Tof.2, Tof.1, Tof. 1/2, Tof. 0 1/2, Tof.0	Salinity, Temp. Oxygen, Phosphate, Silicata, pH, Current Measure- ment. Nitrate, Nitrite.
60/17	Sept. 1960	Tof.4, 3, 2 1/2, 2, 1 1/2, 1, 1/2, 0 1/2, R-2.	Salinity, Temp., Oxygen, Phosphate, Silicate, PH, Alkalinity, Sulphide.
60/26	Dec. 1960	Tof.2 1/2, 2, 1 1/2, 1, 1/2.	Salinity, Temp., Oxygen.
61/3	Feb. 1961	Len 1, Bed.3, Tof.5, 4 1/2, 4, 3 1/2, 3, 2 1/2, 2, 1 1/2, 1, 1/2.	Salinity, Temp., Oxygen, Phosphate, Silicate, pH, Alkalinity, Sulphide, Nitrate.
61/8	April, 1961	Tof.4, 3, 2, 1 1/2, 1, 1/2.	Salinity, Temp., Oxygen, Phosphate, Silicate, pH, Alkalinity, Sulphide.

CHAPTER IV

EXPERIMENTAL RESULTS

In this section the observations of temperature, salinity, density, dissolved oxygen, pH, alkalinity, phosphate and silicate are described. The distribution of these properties, especially temperature and salinity, is indicative of the oceanographic state of the inlet and can be used to follow long-term changes in the water masses of the inlet. Chemical processes occurring in the inlet are reflected in the distribution of the chemical constituents, such as oxygen, hydrogen sulphide, pH, alkalinity, phosphate and silicate.

I. DISTRIBUTION OF TEMPERATURE

The temperature characteristics observed in Tofino Inlet during seven cruises are shown in longitudinal profile, Figures 3-5. Vertical profiles are given for each station in Figure 8, page 20.

The temperature structure in the inlet is complex except in September 1960. The complexity is greatest toward the head and becomes less pronounced toward the mouth at Dawley Pass. In Fortune Channel, the water below the surface thermocline is isothermal at all times. Turbulence, produced by the 3-4 knot currents in the two narrow passages

at either end of Fortune Channel, provides enough mixing to bring about uniformity of temperature. The variation of sea-surface temperature at Amphitrite Point, for the years 1957-1960, is presented in Figures 16-19, pages 40 to 43 (Anon, 1958c-1961c). These temperatures should be representative of seasonal changes occurring in the oceanic surface water, outside Tofino Inlet. Figure 8, page 20, shows that in the spring, summer and fall, a temperature minimum occurs in Tofino Inlet at intermediate depths. The vertical profiles for Station 1, June 1960, illustrate this. The temperature decreases from 15.0°C at the surface to a minimum of 9.0°C at 40 meters and then increases to 13.9°C at 120 meters. In September 1960, the temperature minimum is not pronounced and below 40 meters the temperature remains constant at 13.5°C . In February 1961, winter cooling has reduced the temperature of the surface water below that of the intermediate water and no temperature minimum appears. In April 1961, the surface water has heated up and a temperature minimum is again in evidence. The temperature minimum is due to two conditions; (1) the presence of warm bottom water which remains relatively unchanged in the basins for long periods, and (2) the warming of the surface water during the warmer seasons of the year. Note that between September 1960 and April 1961, the temperature of the 100 meter water, at Station 1, decreased from 13.48°C to 13.40°C ., and the 110 meter water decreased from 13.48°C . to 13.44°C . This is

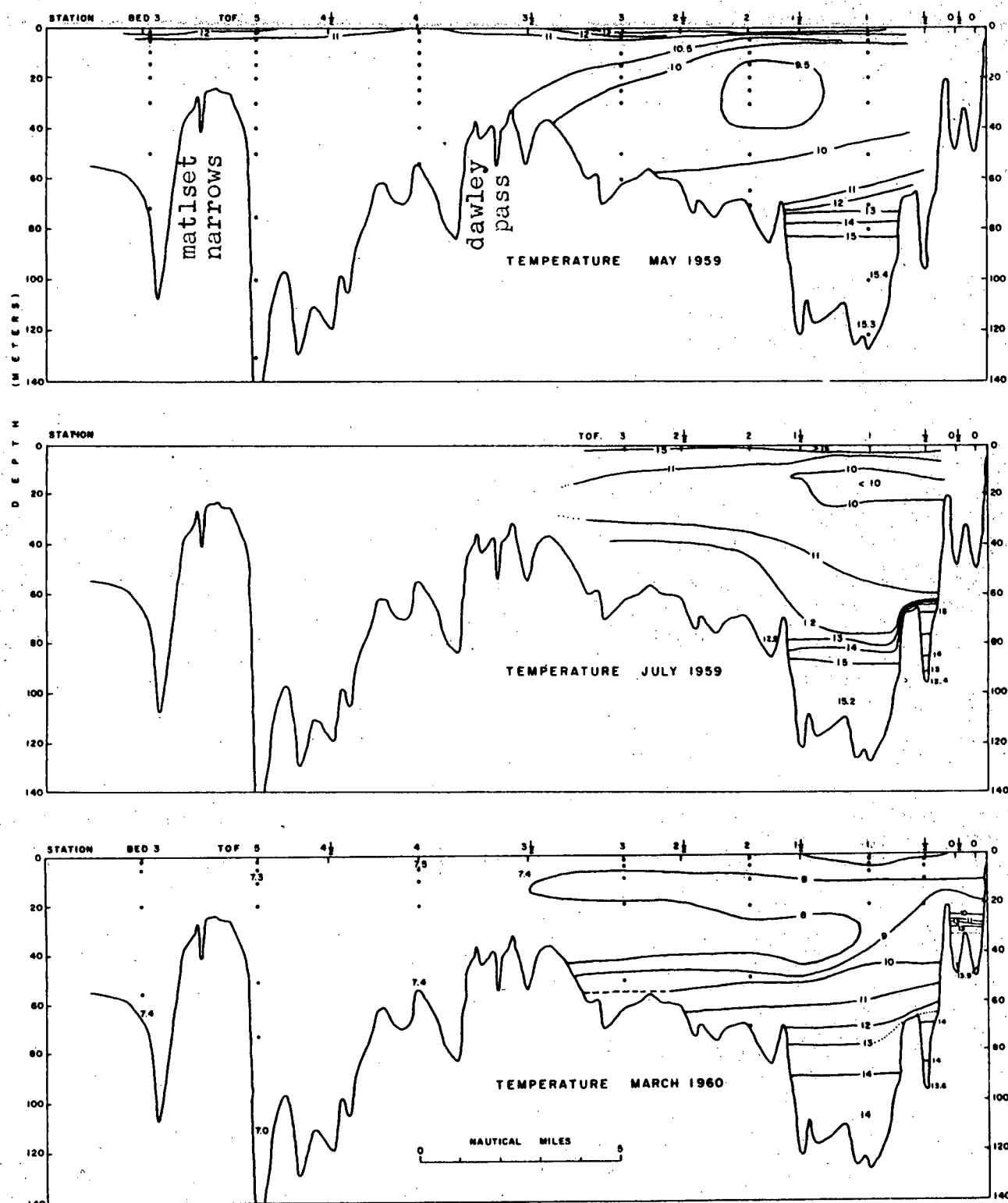


Fig. 3. Longitudinal profiles of temperature ($^{\circ}\text{C}$) for Tofino Inlet in May 1959, July 1959 and March 1960.

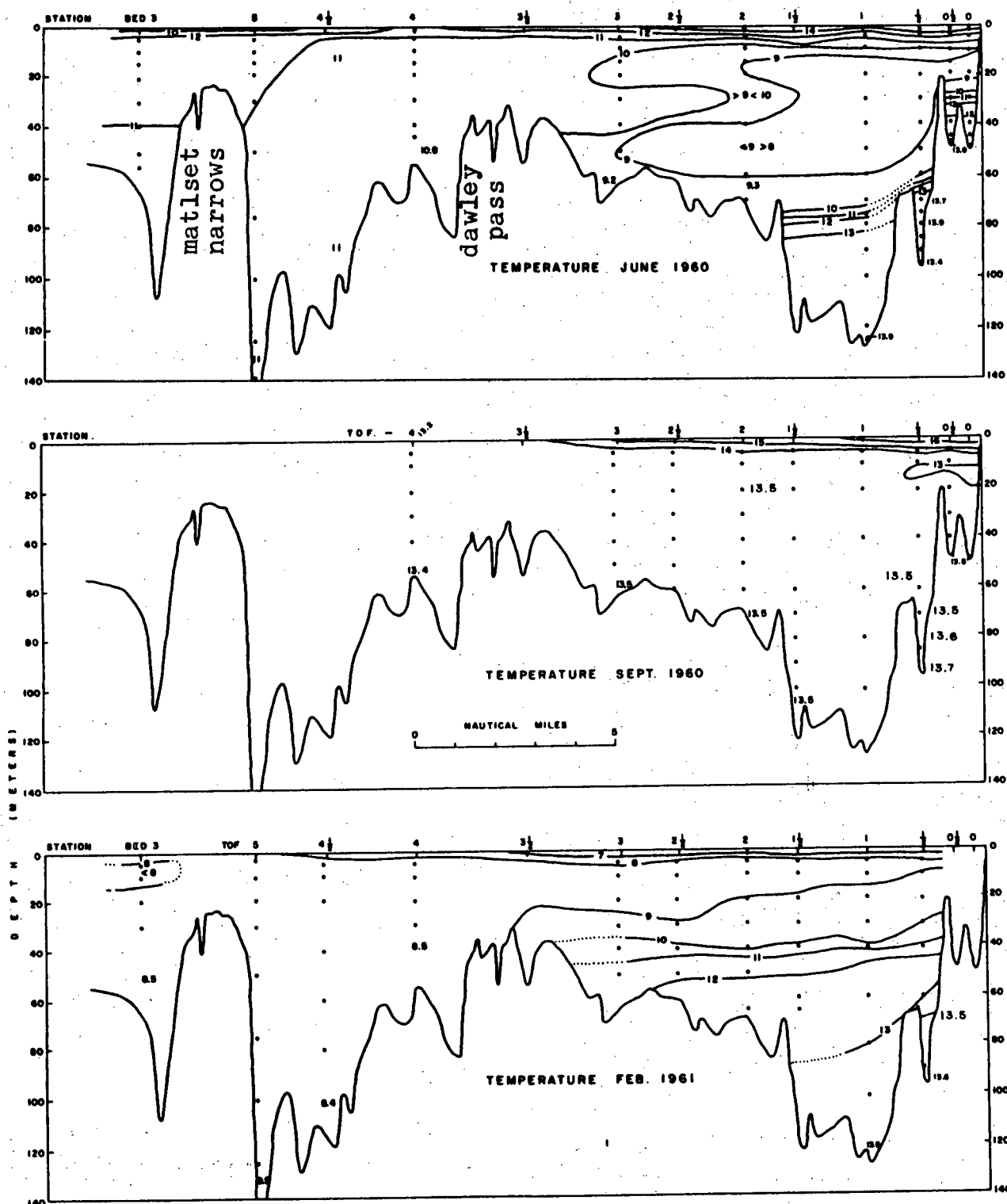


Fig. 4. Longitudinal profiles of temperature ($^{\circ}\text{C}$) for Tofino Inlet in June 1960, Sept. 1960 and Feb. 1961.

in contrast to the period from May 1959 to June 1960; during this time the 100 meter water decreased from 15.4°C . to 13.9°C .

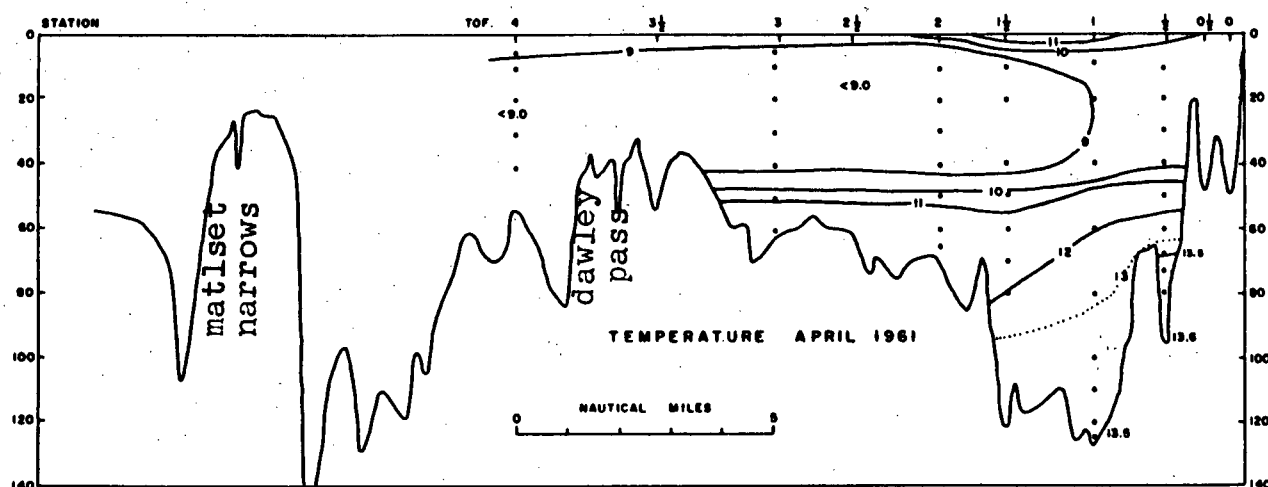


Fig. 5 Longitudinal Profile of Temperature ($^{\circ}\text{C}$) for Tofino Inlet in April 1961.

At Station 1/2, the temperature profiles for July, 1959 and June, 1960, exhibit an additional feature. In July, 1959 the temperature of the water in the basin increased to a maximum of 15.3°C , between 68 meters and 75 meters and decreased to 12.6°C at the bottom. In June, 1960 the temperature increased to 14.0° at 75 meters and decreased to 13.5°C at the bottom.

The two upper basins, Station 0 1/2 and Station 0 were not surveyed on every cruise but when observed, in June 1960 and September 1960, they showed the temperature minimum in the intermediate water.

II. DISTRIBUTION OF SALINITY AND DENSITY

The salinity characteristics observed in Tofino Inlet for six cruises are shown in longitudinal profile, Figures 6 and 7, and in vertical profile in Figure 8. Density is shown in longitudinal profile in Figures 9 and 10. In oceanographic work a quantity called σ_t defined as $1000 \times$ (specific gravity minus one) is used to specify the density of seawater.

As in other British Columbia Inlets the distribution of mass and hence the movement of water in Tofino Inlet depends almost entirely on the salinity distribution (Tully 1949, Pickard 1961, 1963). Comparison of the longitudinal profiles of temperature (Figure 4), salinity (Figure 7), and density (Figure 10), in February 1961, illustrates this. While the temperature increases from the surface to the bottom, the increase in temperature does not overcome the stability in density which follows the distribution of salinity.

Salinity of the surface layer. The longitudinal profiles of salinity show that the value in the surface layer increases from a few parts per thousand at the head, to ten to fifteen parts per thousand at Dawley Pass. At Station 3 there is a decrease in surface salinity associated with the run-off from the Kennedy River. In Fortune Channel the surface salinity increases sharply as a result of mixing.

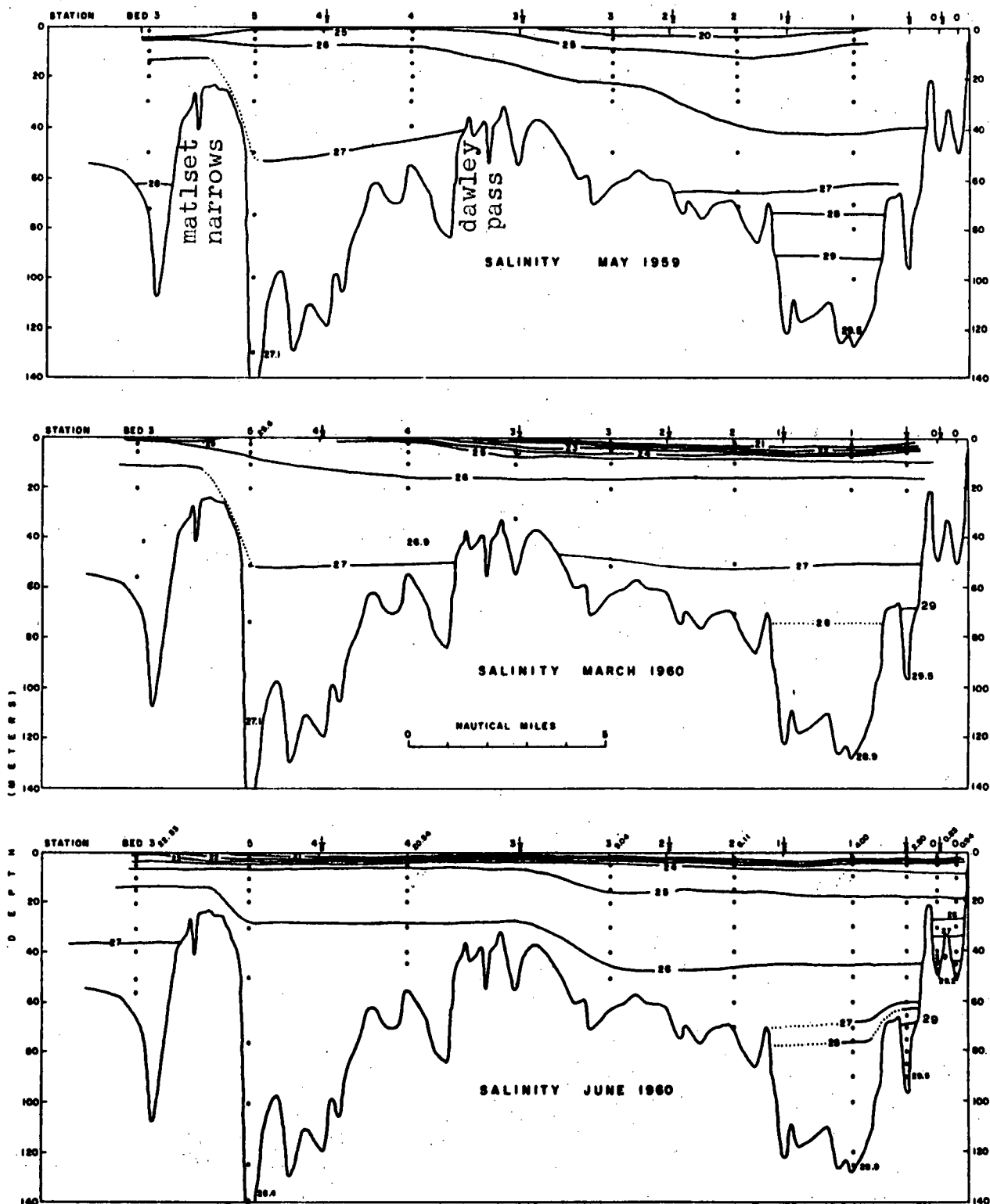


Fig. 6. Longitudinal profiles of salinity (‰) for Tofino Inlet in May 1959, March 1960 and June 1960.

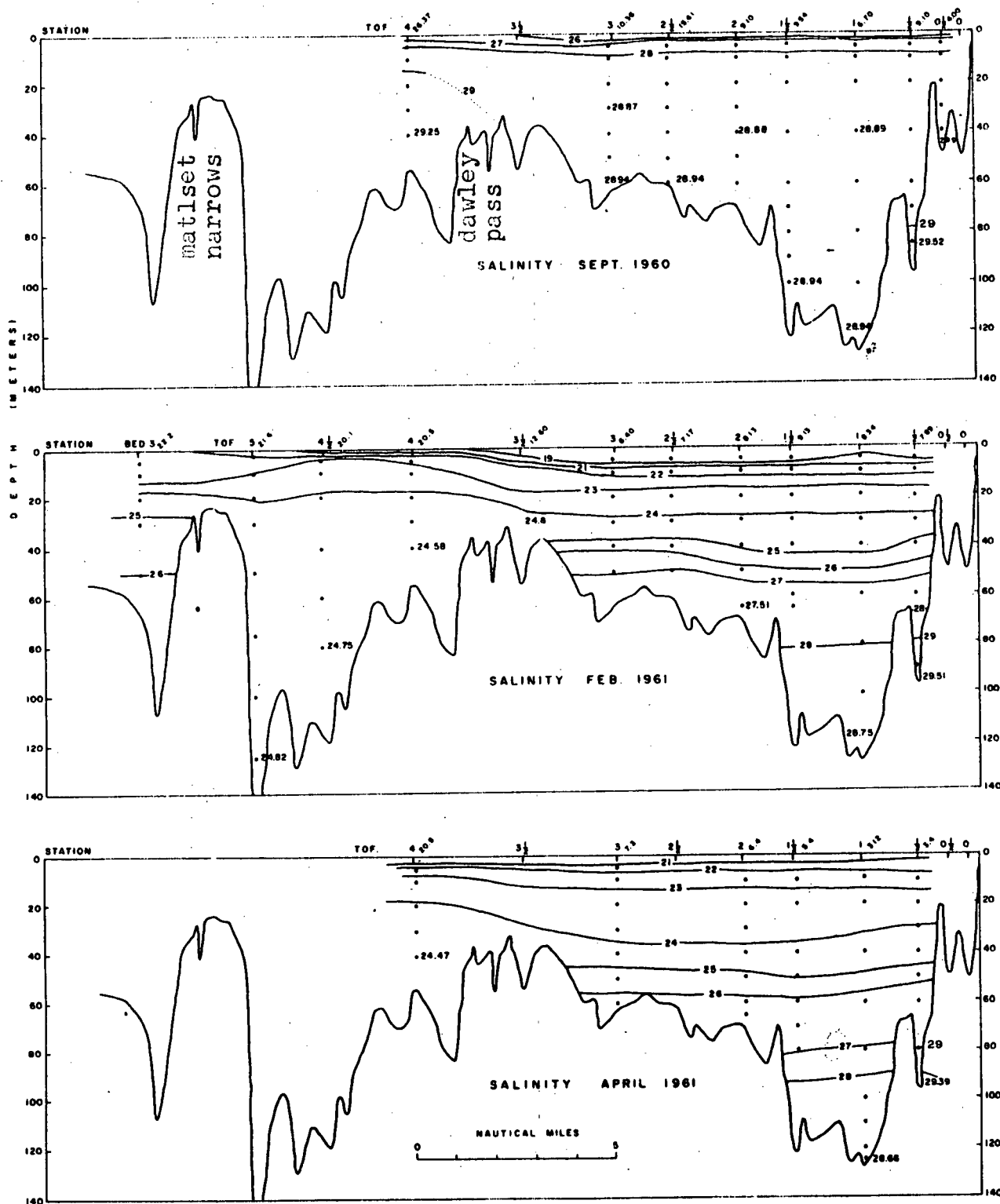


Fig. 7. Longitudinal profiles of salinity (‰) for Tofino Inlet in Sept. 1960, Feb. 1961 and April 1961.

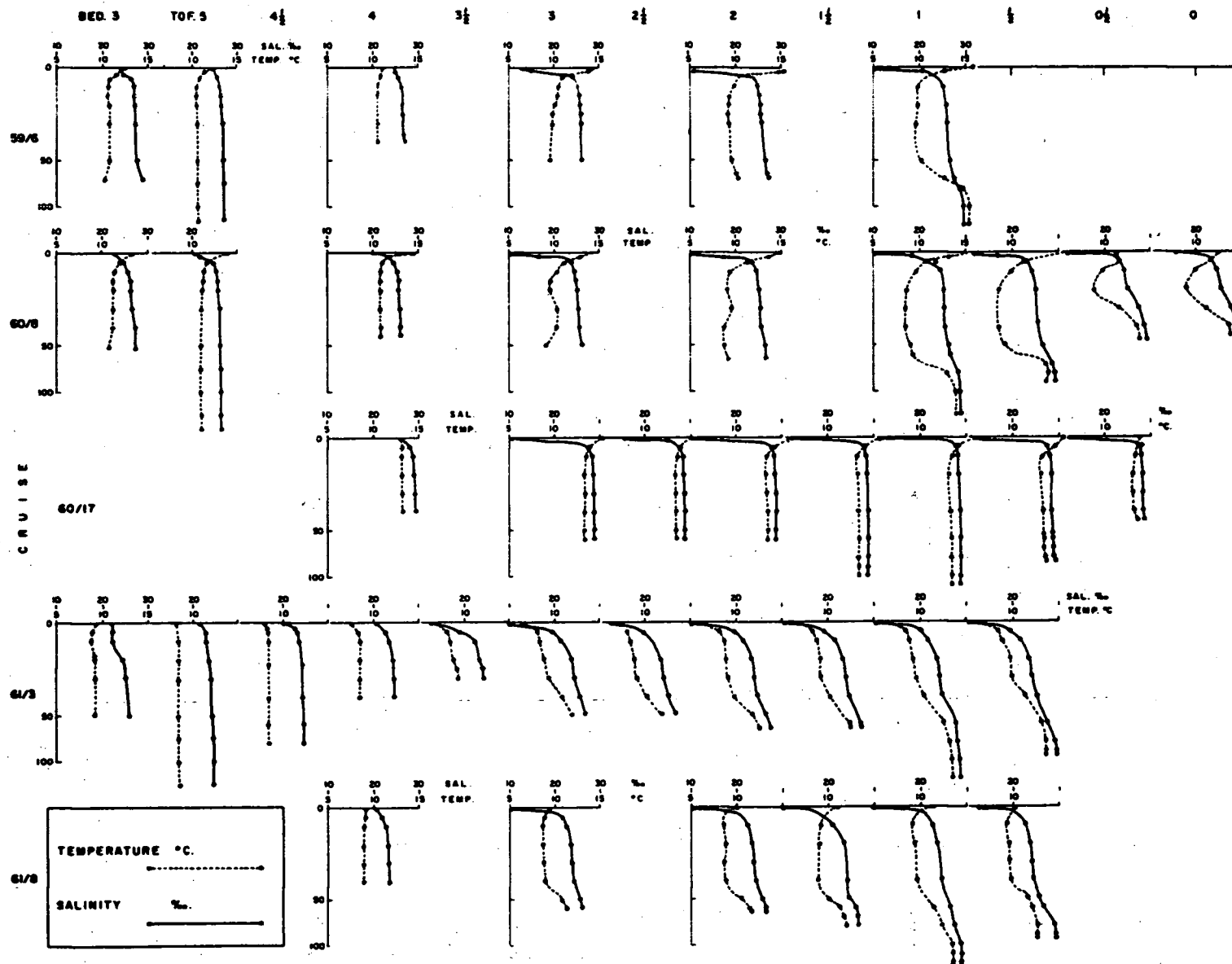


Fig. 8. Vertical profiles of salinity and temperature in Tofino Inlet during cruises; 59/6 May 1959, 60/8, June 1960, 60/17 Sept. 1960 61/3 Feb. 1961, 61/8 April 1961. The stations are shown at the top.

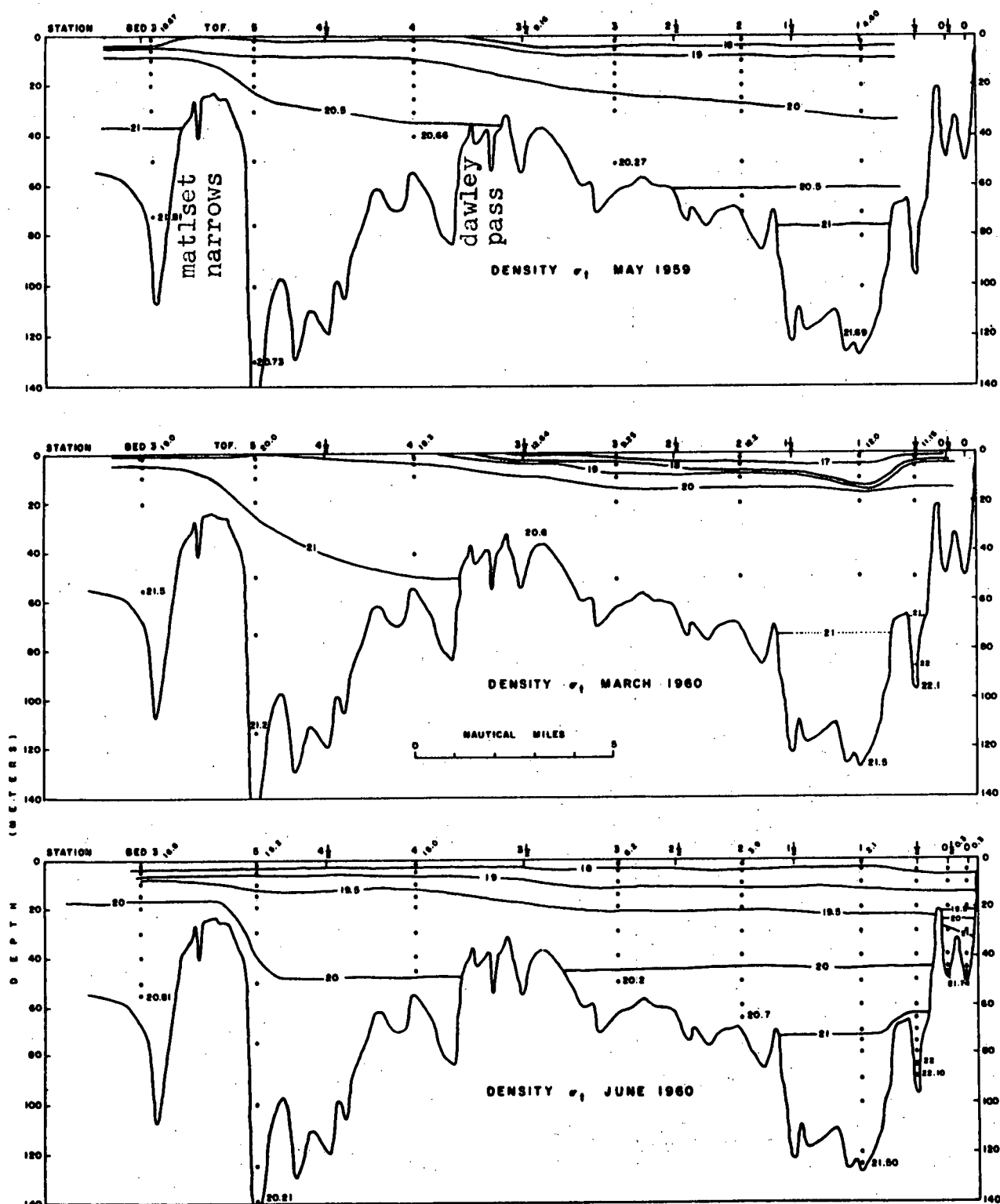


Fig. 9. Longitudinal profiles of density (σ_t) for Tofino Inlet in May 1959, March 1960 and June 1960.

From Fortune Channel through Bedwell Sound the salinity of the surface water increases, approaching the value of coastal surface water. Figures 16 to 19, pages 40 to 43, show the surface salinity variation at Amphitrite Point from 1957-1960 (Anon. 1958c-1961c). They show that the salinity of the coastal surface water is higher in summer than in winter. This feature has been described by Tully (1949), Pickard and MacLeod (1953) and Lane (1962). In summer, the upwelling of high salinity water induced by the prevailing northwest winds, coupled with reduced fresh water run-off gives higher surface salinities. In winter lower surface salinities are due to greater land drainage and to the prevailing southeast winds which hold the light surface water against the shore.

Salinity of the deeper water. The vertical profiles of salinity, Figure 8, show the salinity features in the deeper water. Normally two haloclines can be seen in the depth profiles. An upper halocline having a large gradient extends from the surface to 2.5 meters and has its origin in the estuarine circulation of the inlet. Below 2-5 meters the salinity gradually increases down to 50 to 60 meters. Here a second halocline appears. This deep halocline does not appear in Fortune Channel, where intensive mixing results in constant density below 20 meters. In September, 1960 the deep halocline was absent in the inlet. From June to September the salinity increased from $26.9^{\circ}/\text{oo}$ to $28.9^{\circ}/\text{oo}$

at 60 meters. Below 5 meters, the salinity distribution was homogeneous at $28.9^{\circ}/\text{oo}$ at this time, showing that a major intrusion of dense coastal seawater had occurred.

The main features shown by the salinity distribution are; (1) a shallow surface layer overlying a more saline intermediate zone, (2) high salinity deep water which fills the basins at the head of the inlet (3) uniform salinity in the water below the halocline in Fortune Channel, and (4), that a massive intrusion of oceanic water occurred during the summer of 1960.

III. DISTRIBUTION OF DISSOLVED OXYGEN AND HYDROGEN SULPHIDE

Figures 11 and 12, pages 25 and 28, give the longitudinal profiles of dissolved oxygen, in mg/l; for May 1959, June 1960, September 1960, February 1961 and April 1961. Figure 13, page 30, shows the vertical profiles for the same periods.

Oxygen concentration at the surface. The concentration of oxygen in the surface water decreases from the head to the mouth of the inlet. In part, this may be due to the higher solubility of oxygen in the fresh water which enters at the head of the inlet. As salt is entrained by the surface water moving down the inlet, the solubility is decreased. Photosynthesis also contributes to the high

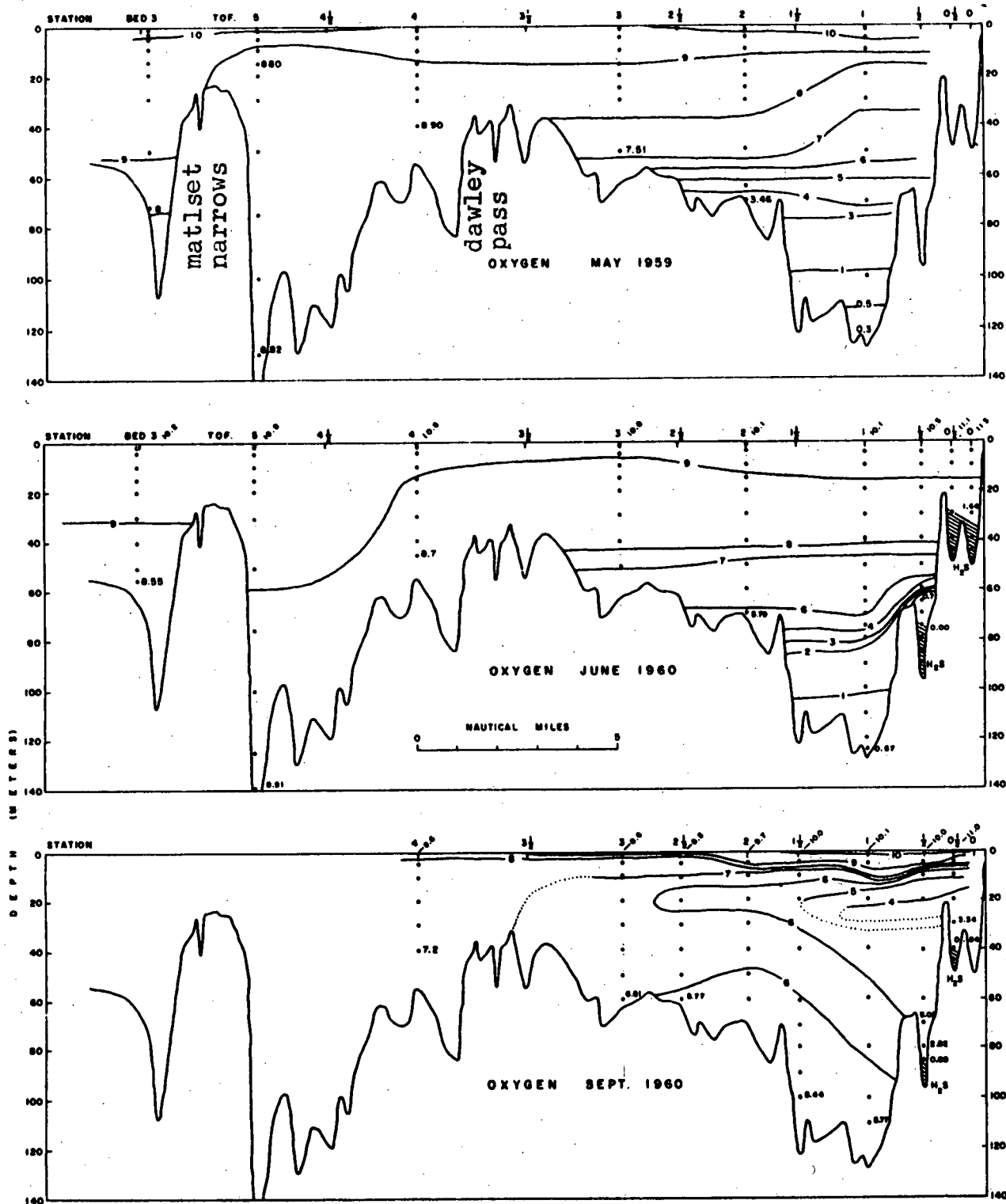


Fig. 11. Longitudinal profiles of dissolved oxygen in mg./l for Tofino Inlet in May 1959, June 1960 and Sept. 1960.

values of oxygen found in the surface layer.

TABLE II
SURFACE OXYGEN VALUES
mg./l

Station Date	Bed 3	Tof.5	4.	3.	2.	1.	1/2.	0.
June 1960	10.2	10.9	10.8	10.0	10.1	10.5	10.5	11.3
Sept. 1960		8.6	9.6	9.7	10.1	10.1	10.1	11.0
Dec. 1960						9.2	9.7	
Feb. 1961	9.7	9.5	9.6	11.2	11.1	11.1	11.2	
April 1961			10.2	11.8	12.1	12.1	12.1	

Oxygen and hydrogen sulphide in the deep water. The concentration of oxygen increases to a maximum 2-5 meters below the surface and then decreases with depth. The maximum is attributable to the production of oxygen by photosynthetic organisms, which are present in greatest numbers at these depths. In the basins, at Station 1/2, Station 0-1/2, and Station 0, the concentration of oxygen decreases to zero. In these basins hydrogen sulphide is present in concentrations up to 13.9 mg./l. The sulphide-containing anoxic zones are shown by cross-hatching, in Figures 11 and 12. The highest concentration of sulphide, 13.9 mg./l, was observed at Station 0-1/2, in September 1960.

In Fortune Channel oxygen is essentially constant in

the water below the halocline. As with temperature and salinity, the mixing caused by the tidal currents maintains uniform oxygen concentrations with depth.

In September 1960, the distribution was markedly different from what it was in June 1960. In the basin at Station 1, the oxygen concentration was between 5.5 - 5.8 mg./l in September 1960, whereas in June it was between 0.9 - 4.0 mg./l. During this same period at Station 1/2, the upper limit of the anoxic zone deepened from 70 meters to 83 meters. The oxygen distribution also exhibited a minimum centred at 20 meters which extends from the head to Station 3 (Figure 13). This feature has been noted in other inlets in British Columbia (Pickard, 1961), (Thompson and Barkey, 1937). Thompson and Barkey attributed the mid-depth oxygen minimum that they observed in Seymour Inlet to the movement of low-oxygen water from over the sediments of Seymour's tributary arms into the mid-depths of Seymour Inlet.

In the deep water of Fortune Channel the oxygen concentration is 7.2 mg./l in September 1960. This is 1.5 mg./l less than the value in June. The saturation value for the deep water in Fortune Channel in September is 8.5 mg./l (Truesdale, Downing and Lowden, 1955). The value of 7.2 mg./l represents an undersaturation of 12⁰o.

These features of the oxygen distribution in September are discussed in Chapter V, page 49, where they

are attributed to an intrusion of coastal surface water.

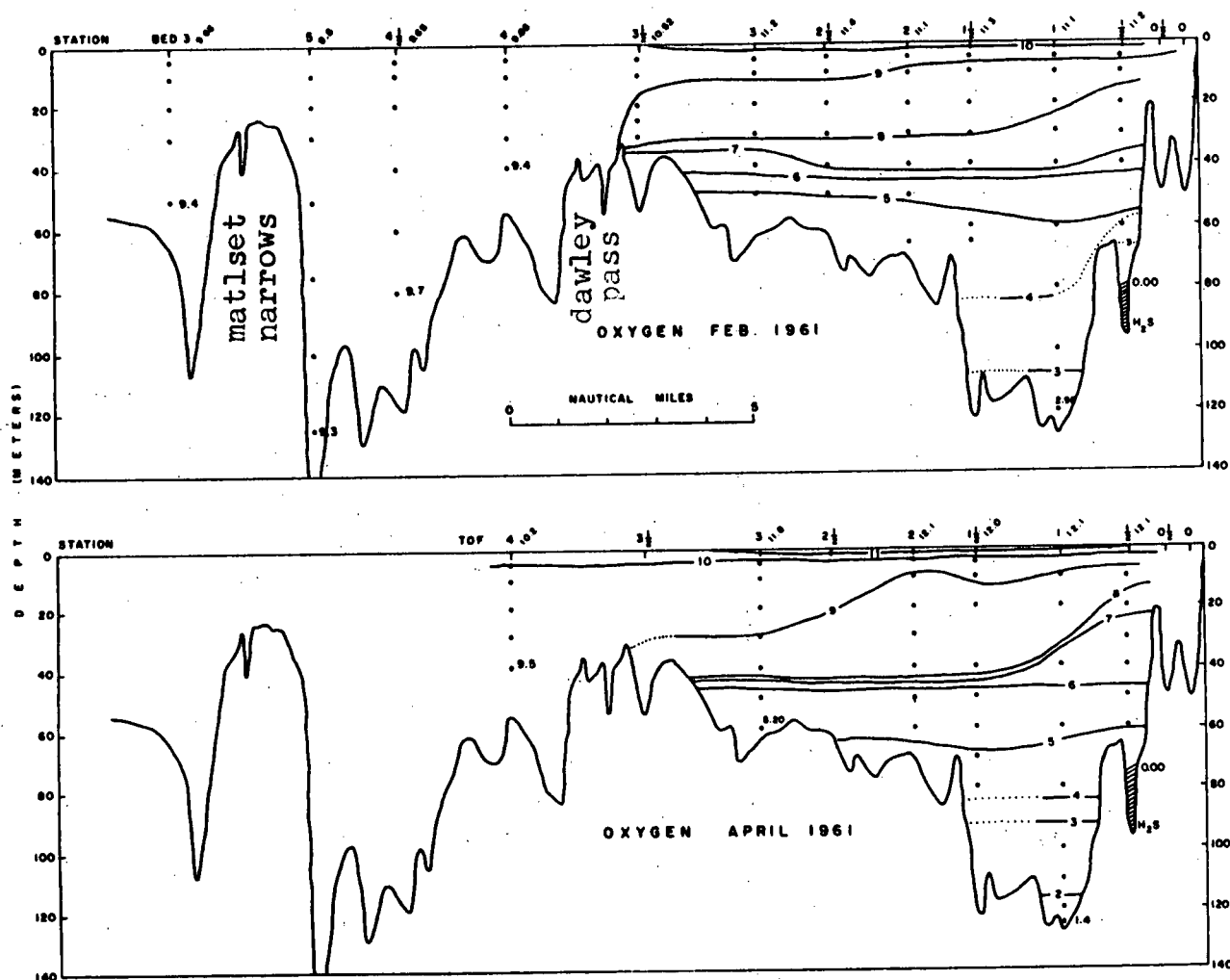


Fig. 12. Longitudinal Profiles of dissolved Oxygen in mg/l, for Tofino Inlet in Feb. 1961 and April 1961.

IV. DISTRIBUTION OF pH AND ALKALINITY

The vertical profiles of pH are shown in Figure 13. Table III contains the alkalinity values found at Station 1/2 in September 1960 and compares them with the values that would result from the dilution of normal seawater with pure water to the chlorinity observed at Station 1/2. Alkalinity has a special oceanographic connotation; it is the amount of strong acid required to titrate all the titrable bases in seawater. The values given in Table III are corrected for borate.¹

TABLE III

A COMPARISON OF OBSERVED ALKALINITY WITH NORMAL
SEAWATER VALUES OF ALKALINITY AT STATION TOFINO
1/2 IN SEPTEMBER 1960

Depth	Chlorinity	Normal Seawater Alkalinity	Observed Alkalinity
0 m.	5.1 ‰	0.63 m. equiv/l	0.69 m. equ
5	15.3	1.86	1.91
10	15.6	1.89	1.92
20	15.8	1.92	1.96
40	16.0	1.94	1.95
60	16.0	1.94	1.95
70	16.0	1.94	1.93
80	16.1	1.95	2.04
85	16.4	1.98	3.03

¹The amount of borate present in seawater is roughly proportional to the chlorinity. Tables have been published which give borate as a function of chlorinity, temperature and pH, allowing corrections to be made. (Strickland and Parsons, 1961).

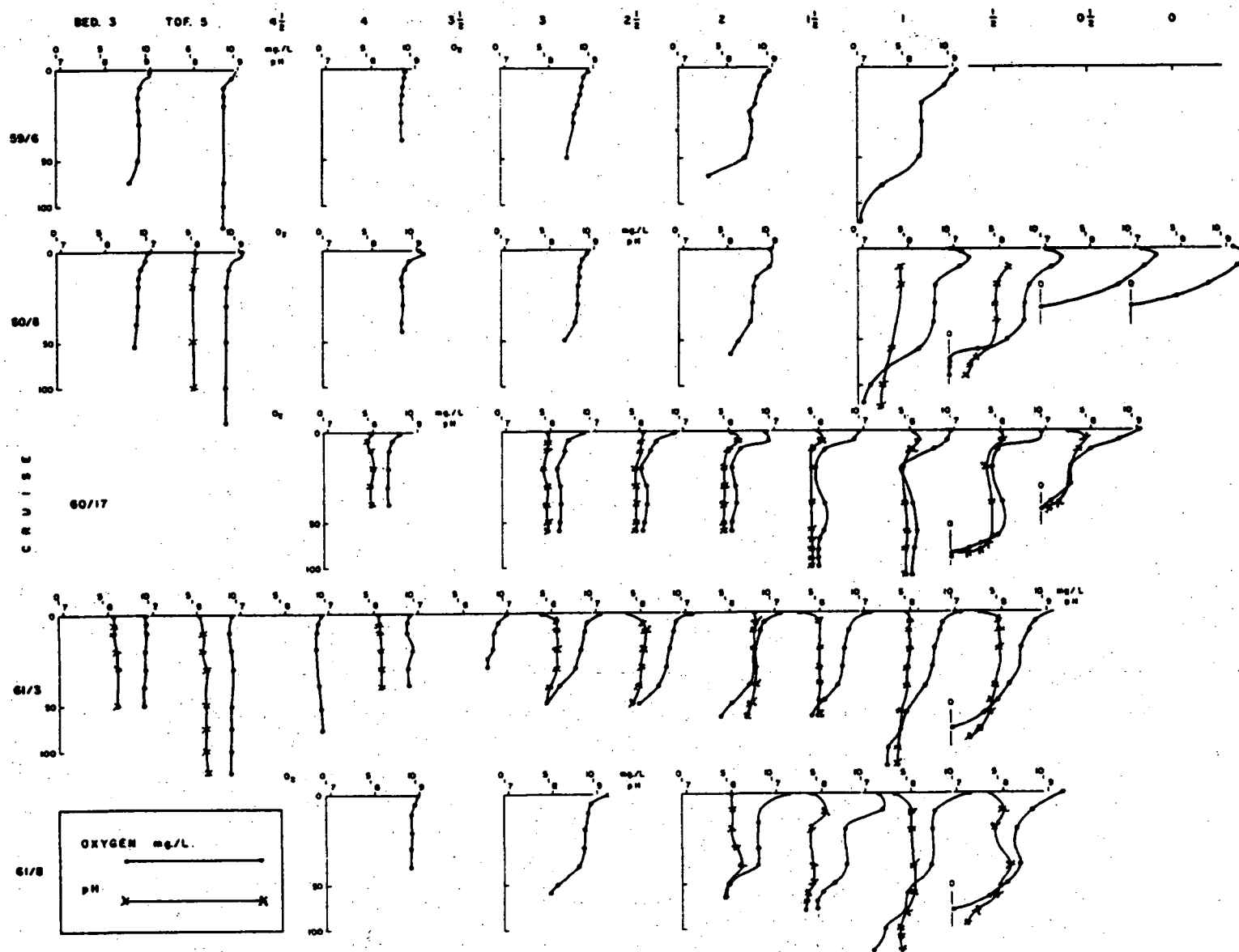


Fig. 13. Vertical profiles of oxygen and pH in Tofino Inlet during cruises 59/6 May 1959, 60/8 June 1960, 60/17 Sept. 1960, 61/3 Feb. 1961, 61/8 April 1961. The stations are shown at the top.

Distribution of pH. The pH of the surface water is 8.0-8.1 except toward the head of the inlet where it falls to 7.4 near the outlet of Tofino Creek. The pH rises to a maximum of 8.2-8.3 at a depth of 2-5 meters as a result of photosynthesis in the water immediately below the surface layer. Below this the pH falls to 7.8-7.9. In the anoxic basins the pH falls to values between 7.0-7.6. At Station 1/2, in September 1960, the pH is 7.7 at 20 meters. This is the depth at which an oxygen minimum of 4.7 mg./l occurs. At Station 0-1/2, where the 20 meter minimum is 3.3 mg./l, the pH associated with it is 7.6. Where oxygen values are low the pH is also low. In the anoxic basin at Station 0-1/2, the pH decreases to a minimum value of 7.0. This is due to the production of carbon dioxide by the bacterial oxidation of organic matter. (See Chapter V).

Distribution of alkalinity. The variation of alkalinity with depth, shown in Table III, is typical of the inlet. The alkalinity increases with depth. It reaches high values in the anoxic basins; 3.03 m. equiv./l at 85 meters at Station 1/2 in September 1960. This is 1.05 m. equiv./l greater than would be expected from the dilution of normal seawater. The reasons for this increase in alkalinity are discussed in chapter V.

V. DISTRIBUTION OF PHOSPHATE AND SILICATE

Vertical profiles of phosphate and silicate are given

in Figure 15. Figure 14 depicts the longitudinal profiles of total phosphate² and silicate for September 1960.

Distribution of phosphate. The concentration of inorganic phosphate is lowest in the surface layer, ranging from 0.3-1.0 ug.at./l. Between 5 meters and 50 meters the concentration increases to 1.5-2.0 ug.at./l. In the deeper water, but still above the anoxic zones, phosphate increases to 2.0-3.0 ug.at./l. In the anoxic zone the concentration rapidly increases. A maximum value of 14.7 ug.at./l is observed at 90 meters in September 1960 at Station 1/2. In September 1960, and again in April 1961, there is a phosphate maximum in the oxygenated zone. In September the maximum is at 20 meters and is present at all stations except 1-1/2, and in April the maximum varied between 40 - 60 meters.

Distribution of silicate. The distribution of silicate is similar to that of phosphate. It is relatively low, 10 - 30 ug.at./l, in the surface layer, and gradually

²The inorganic phosphates determined in September 1960 were preserved with chloroform aboard ship and analyzed later on shore. This method of preservation was not successful and many erratic and low results were obtained. The total phosphate assays have been used to illustrate the phosphate maximum at 20 meters in September 1960. Most of the observations indicate there is relatively constant difference between the two forms.

increases in concentration with depth to 50 - 60 ug. at ./.1 in the deeper water. In the anoxic basins the silicate values rise to over 100 ug. at ./.1. The highest observed value was 284 ug. at ./.1, at 85 meters, Station 1/2, in September.

The regeneration of phosphate and silicate in the anoxic basins and the 20 meter maxima is discussed in chapter V.

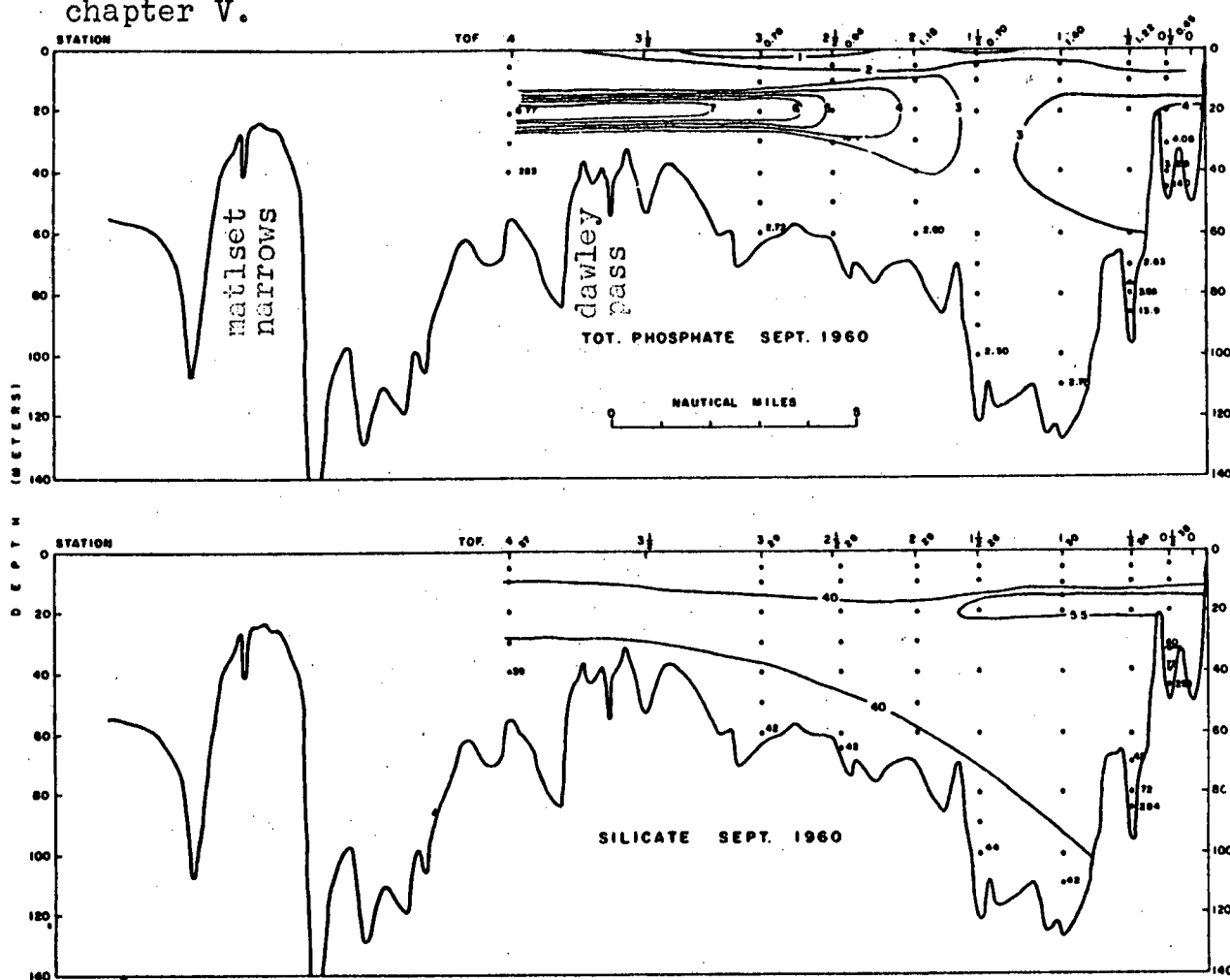


Fig. 14. Longitudinal Profiles of total Phosphate and Silicate (ug. at /.1) for Tofino Inlet in Sept. 1960.

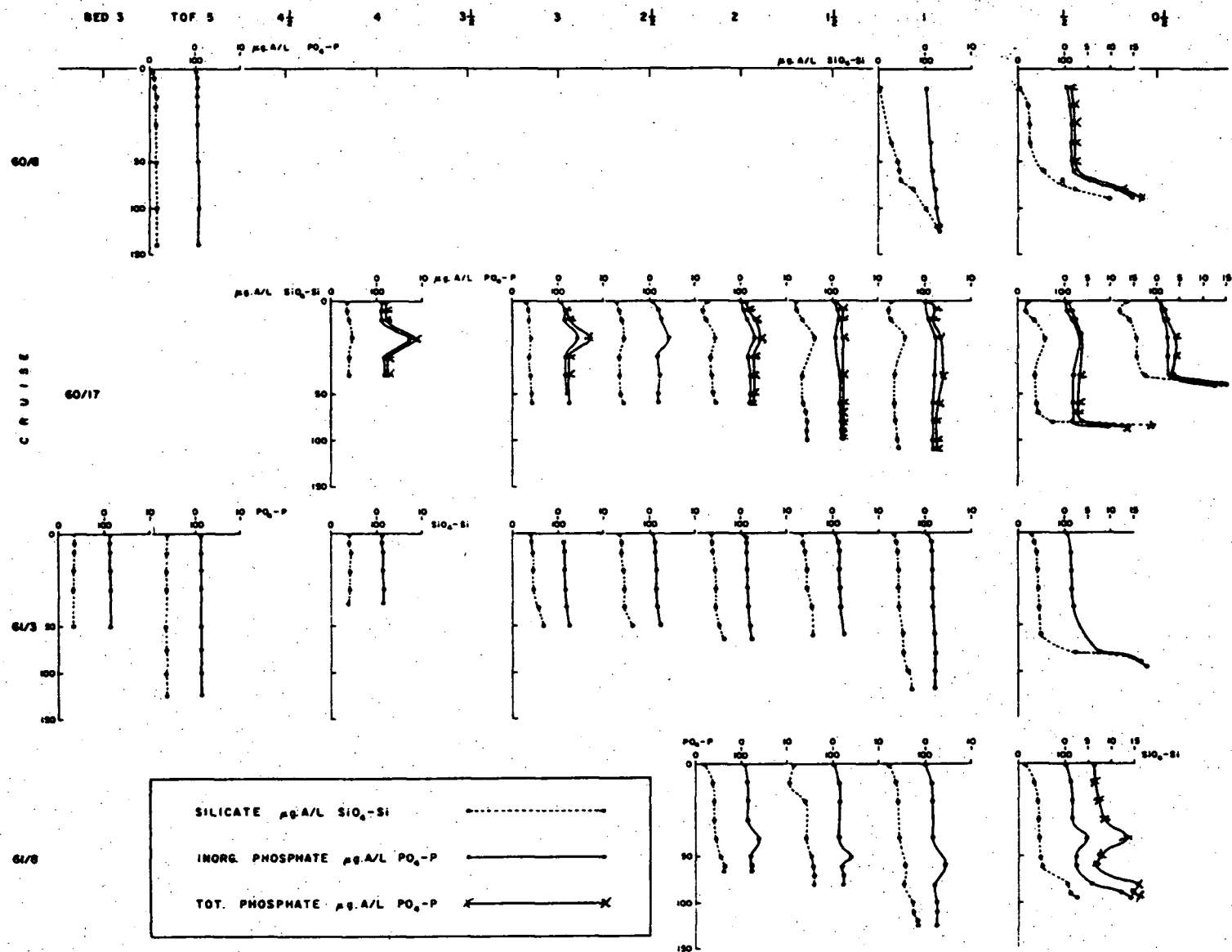


Fig. 15. Vertical profiles of silicate, inorganic phosphate and total phosphate in Tofino Inlet; cruise 60/8 June 1960, 60/17 Sept. 1960, 61/3 Feb. 1961, 61/8 April 1961. The stations are shown at the top.

CHAPTER V

DISCUSSION OF RESULTS

The data presented in the previous sections bring out a number of features which are discussed in this chapter. The distribution of properties, observed in September 1960, indicate that a replacement of the bottom water in Tofino Inlet took place in the summer of 1960. During the succeeding winter, this bottom water stagnated, as shown by decreasing oxygen concentrations. The change in oxygen allows an oxygen utilization rate to be calculated. High phosphate, silicate, alkalinity, and low pH in the anoxic bottom water of the upper basins of Tofino Inlet provide information about the oxidation of organic matter and regeneration of nutrients in these basins.

I. ESTUARINE CHARACTERISTICS OF TOFINO INLET

Cameron and Pritchard (1963) define an estuary as "a semi-enclosed coastal body of water having a free connection with the open sea and within which the seawater is measureably diluted with fresh water deriving from land drainage." They recognize the fjord as a special type of estuary. Tofino Inlet is a fjord-type inlet, with shallow sills and narrow connecting passages which restrict connection with the open sea. The shallow sills restrict

the incoming seawater to that of the upper 11 - 13 meters of the oceanic surface layer. The narrow connecting passages of Fortune Channel and Browning Passage, which have 3-4 knot tidal currents in their entrances, form mixing regions, where the incoming seawater is reduced in salinity by admixture with brackish surface water from the inlet.

One of the first quantitative studies of an inlet of the fjord-type is that made by Tully (1949) in Alberni Inlet, Vancouver Island. He finds that it has a vertical structure which can be related to the dynamic forces within the inlet; tidal mixing and fresh water influx. This structure consists of three layers or zones of water that are distinguishable by their salinity characteristics. The upper zone, some 4 meters thick, contains seaward-moving, low salinity water, which becomes progressively more saline towards the mouth of the inlet. The middle zone, about 12 meters thick, contains higher salinity oceanic water which has a net movement towards the head of the inlet. It has a similar, though less pronounced, salinity gradient extending from the head to the mouth of the inlet. The bottom zone, which extends downward from the sill depth of 16 meters, contains essentially unmodified coastal seawater.

In Alberni Inlet, lateral salinity gradients exist only in the vicinity of the river mouth at the head of the inlet. These lateral gradients disappear a short distance down the inlet. In a narrow inlet, such as Tofino, lateral

gradients can be neglected.

Tully also finds that the vertical salinity gradient between the upper and middle zone is the result of the turbulent mixing of salt between these zones and is maintained by tidal action and river run-off. As a result of this mixing, salt is entrained in the outflowing water of the upper zone and a compensating flow of higher salinity water occurs in the middle zone. This circulation, generated by the entrainment process, is the estuarine circulation. In a fjord-type estuary the net flow is out of the inlet and is equal to the fresh water influx less evaporation.

The bottom zone, on the other hand contains essentially unmodified coastal seawater which tends to remain unchanged for relatively long periods of time, though a gradual modification is observed in this bottom zone due to a slow exchange of salt with the less saline middle zone.

On the basis of an estuarine circulation the vertical structure of Tofino Inlet can be divided into three zones; (1) an upper, brackish zone extending 2 to 3 meters below the surface, salinity range 3 - 15 ‰, (2) an intermediate zone extending below this to sill depth in each of the basins, (3) a bottom zone that lies below sill depth in each basin.

The most important factor involved in replacing the bottom water is the density of the coastal seawater outside the inlet. If the outside seawater, at or above the

depth of the sill, is denser than the bottom water within the inlet, it flows in over the sill and fills the basin of the inlet. If, however, the seawater at sill depth is lighter than the bottom water in the inlet, no such flow occurs and the bottom water becomes isolated. Upwelling, which occurs predominantly during the summer months along the west coast of Vancouver Island (Tully 1949, Pickard and MacLeod 1953, Lane 1961) is capable of causing annual fluctuations in salinity. During periods of up-welling the in-shore surface salinities are higher and the water more dense than at other times. In a fjord, which is protected by a shallow sill the replacement of the bottom water is confined to these periods. In Alberni Inlet an annual flushing of the bottom water is inferred by Tully. In Tofino Inlet an additional factor may be involved in the replacement of the bottom water. The reduction in salinity of the intruding seawater, by admixture with low salinity surface water in the two connecting channels, may restrict the time of the replacement to periods of low run-off. As discussed in the next section, there is some evidence to suggest that this is so.

II. REPLACEMENT OF THE BOTTOM WATER IN TOFINO INLET

In July of 1959 Dr. W. L. Ford's temperature data, (Ford 1959a), Figure 3, show that 15.3°C water was present

below 90 meters at Station 1 and that this water formed a 7 meter layer, sandwiched between colder water at Station 1/2. Ford (1959) suggested that the 15.3°C water had entered the inlet during the summer of 1958, replacing colder water of 12.5°C . Local residents had informed him that the summer of 1958 had been unusually warm and dry. These factors led him to postulate that:

" . . . High surface temperatures and low run-off, hence high surface salinity, last Summer permit the hypothesis that the 15° water was generated in the shallow and narrow passages in the approaches through mixing of high salinity warm ocean water probably 31 (‰) with the exceptionally warm and saline upper layer waters. If so this water is only one year old. . . ."

The annual variations of salinity and temperature of the surface coastal water at Amphitrite Point, (Anon. 1958C - 1961c) for the years 1957-1960, are presented in Figures 16-19. These Figures also show the annual variation of monthly rainfall for the Tofino region. The highest salinities and temperatures in the coastal surface water occur during the June to September period. Rainfall is lowest during this period.

In the summer of 1958 there was 0.2" of rain in June and 0.1 inches in July. In mid-July the surface temperature of the coastal water was 15° - 16°C . Ford's suggestion that the 15° water, which he observed in July 1959, had intruded in the summer of 1958, during a dry period, is substantiated by this data.

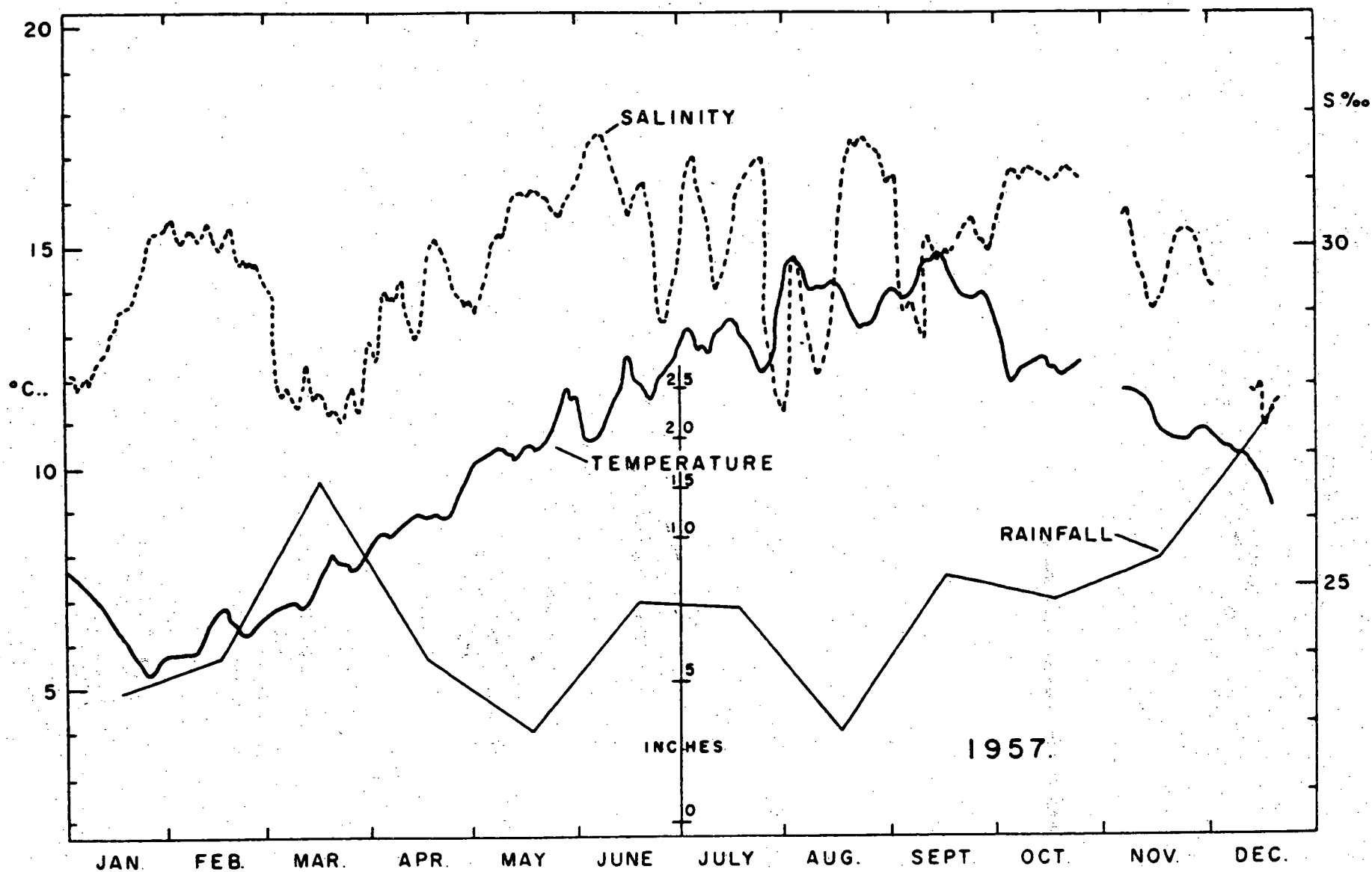


Fig. 16. Variation of sea-surface salinity and temperature at Amhitrite Point. Monthly rainfall at Estevan Point for 1957.

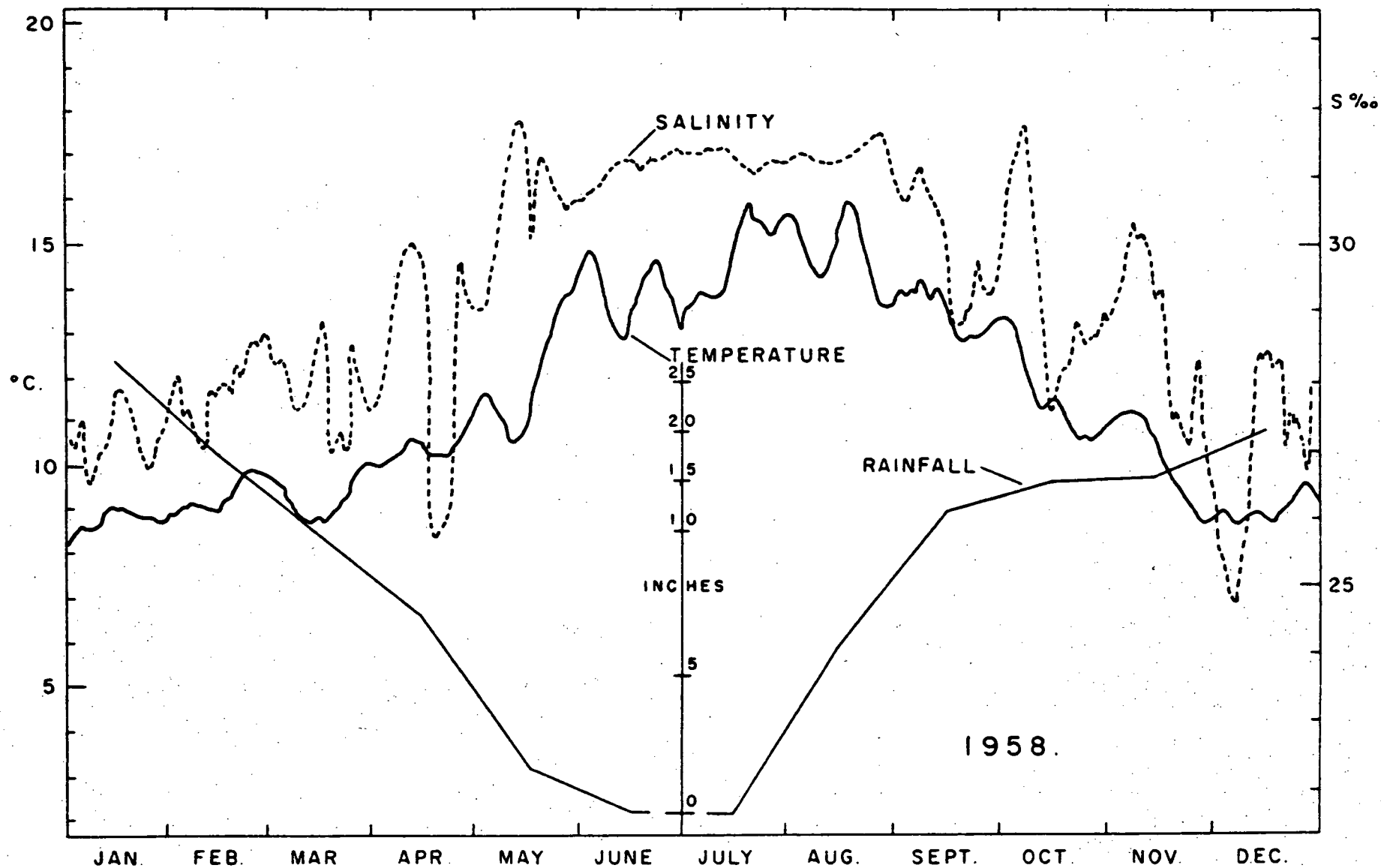


Fig. 17. Variation of sea-surface salinity and temperature at Amphitrite Point. Monthly rainfall at Estevan Point until Nov. 1958. Monthly rainfall at Tofino Airport, Dec. 1958.

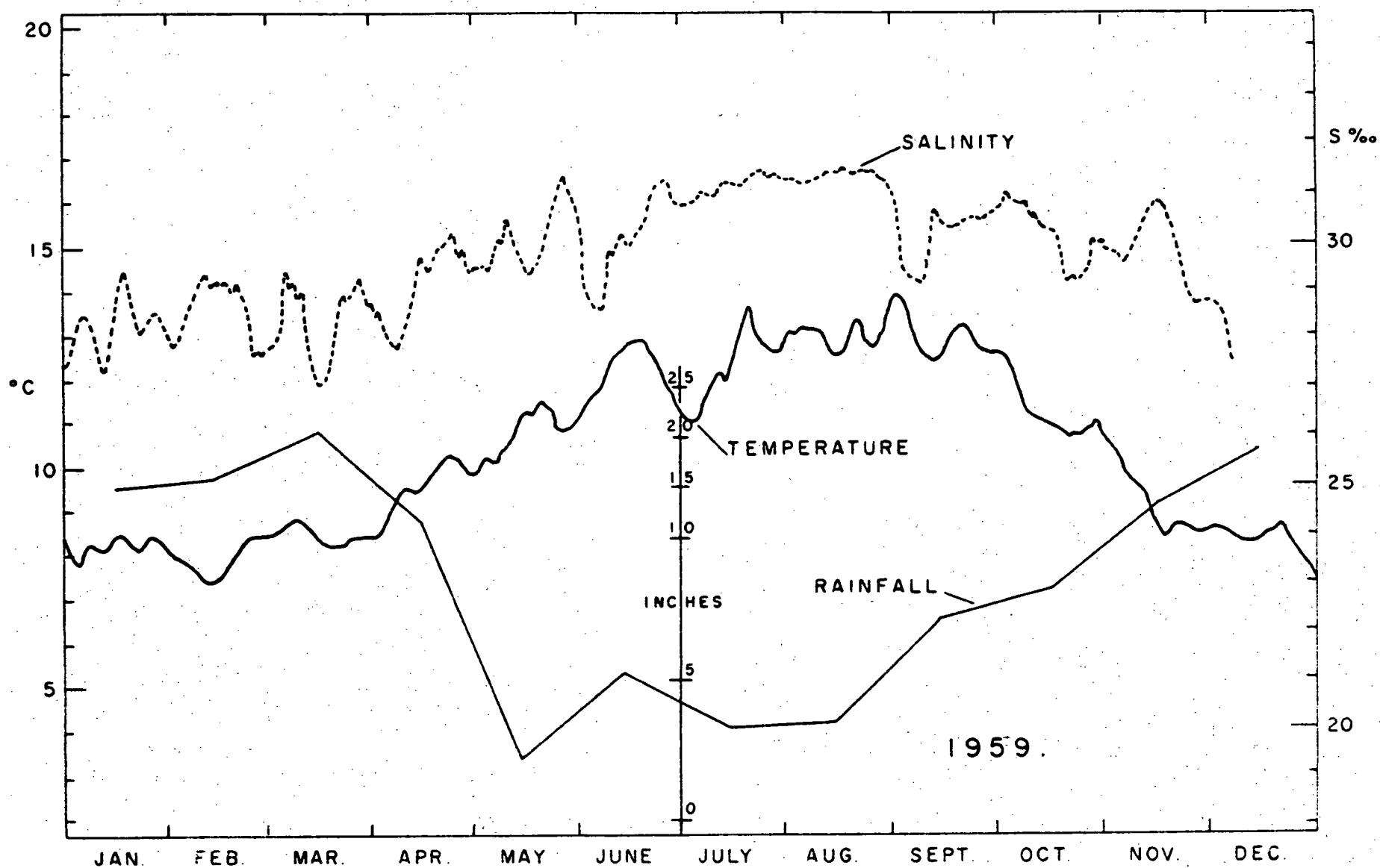


Fig. 18. Variation of sea-surface salinity and temperature at Amphitrite Point for 1959. Monthly rainfall at Tofino Airport 1959.

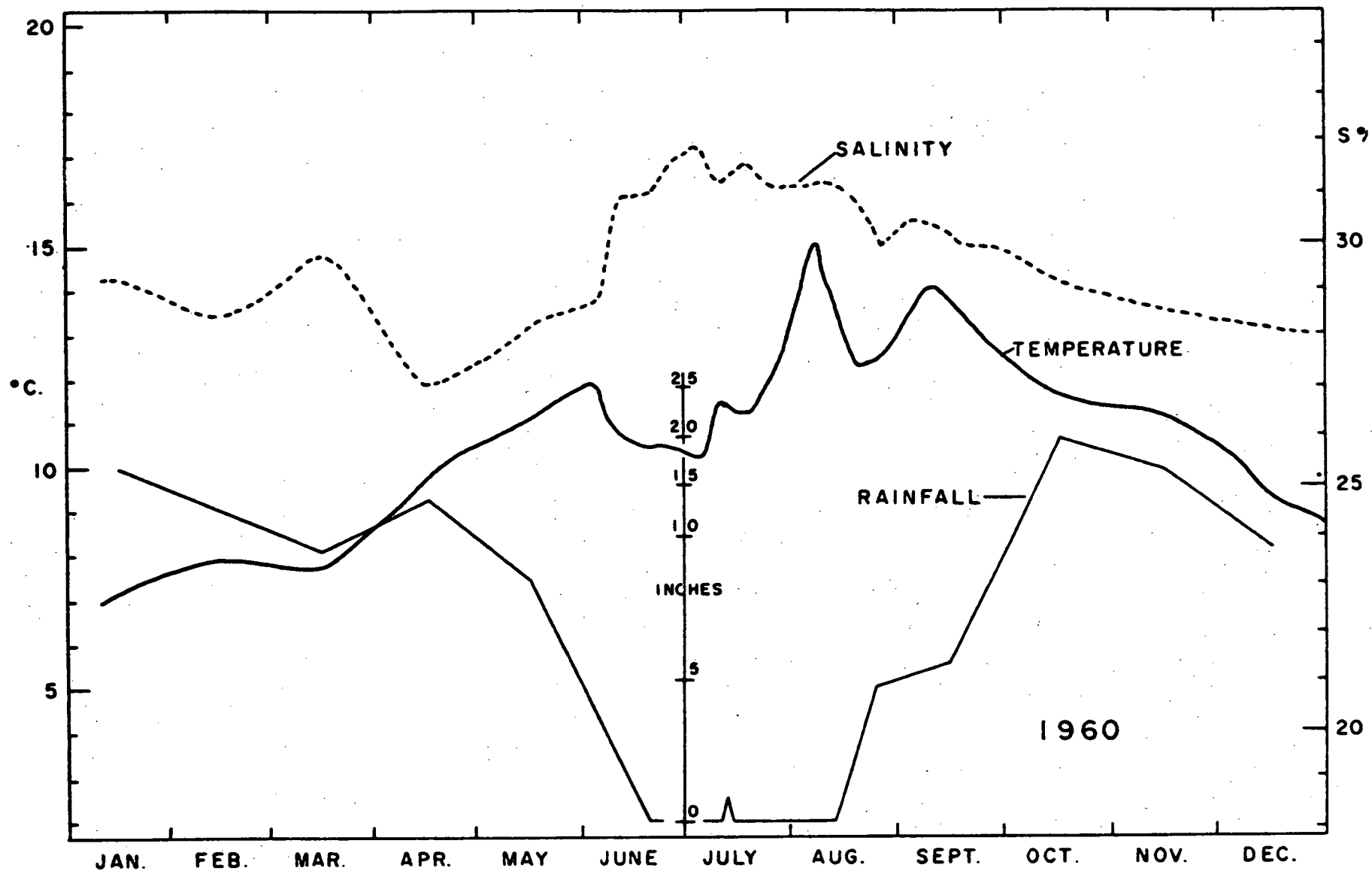


Fig. 19. Variation of sea-surface salinity and temperature at Amphitrite Point. Monthly rainfall at Tofino Airport in 1960.

An intrusion of dense coastal water took place during the summer of 1960. This is supported by the marked changes in temperature, salinity and oxygen distributions from June 1960 to September 1960. (Figures 4, 7 and 11). This intruding water replaced all the bottom water in the inlet, with the exception of part of the anoxic basin water at Stations 1/2 and 0-1.2. Water having a density greater than $\sigma_t = 21$ is confined below the sill-depth of these basins in June, while in September 1960, water having this density or greater is present below 5 meters throughout the inlet (Figures 9 and 10). This could only have resulted from a massive intrusion of dense coastal seawater. The rainfall between July 15 and August 15 was 0.1 inches. The temperature of the coastal surface water was $13.5 - 15.0^\circ\text{C}$. during the first two weeks of August (Figure 18). This corresponds to the essentially homogeneous 13.5°C .-water found throughout the inlet in September 1960 and would place the date of the intrusion at this time.

An intrusion of coastal seawater has since been observed in August 1961 (Anon. 1961b). This intrusion also occurred during a period of low rainfall (See Appendix B).

Thus there is direct evidence of dense coastal surface water intruding into Tofino Inlet, during the summers of 1960 and 1961. The intrusions appear to coincide with periods of dry weather. Examination of sea-surface temperature and salinity at Amphitrite Point,

indicates that a similar intrusion occurred during a dry period in the summer of 1958 (Figure 11). Ford (1959b), suggested that replacement of Tofino bottom water might not occur during the wet summer of 1959, when rainfall, for June, July and August, was 12 inches or 2 inches above normal (Anon. 1959a). However, even during this wetter than normal summer there was a three-week dry period.

The oxygen data observed in the stagnant basins of Tofino Inlet can be used to determine if an intrusion of coastal seawater was likely in the summer of 1959. At 100 meters, at Station 1, the oxygen concentration is 1.3 mg./l, in June 1960, before the intrusion, and 5.0 mg./l in September 1960, after the intrusion. (Figure 11). Using the oxygen utilization rate of 0.015 mg./l/day, which is calculated in the next section, an estimate can be made of what the oxygen concentration was in September 1959, subsequent to a postulated intrusion. This value is calculated to be 5.4 mg./l. It is close to the value found in September 1960 and indicates replacement of the bottom water in the summer of 1959. However, no conclusion can be drawn as to whether or not this intrusion was as extensive as that of the summer of 1960.

III. RATE OF OXYGEN UTILIZATION IN THE STAGNANT BASINS OF TOFINO INLET

Using the oxygen data, collected in the stagnant basins of Tofino Inlet between September 1960 and April 1961,

the rate of oxygen utilization can be calculated. Figure 20 plots oxygen concentration against time for five selected depths in the inlet, where oxygen was observed to decrease.

At Station 1, 100 meters, the concentration of oxygen decreased for the whole period September to April. The oxygen at Station 1/2, 80 meters, decreased to zero in early January 1961 and after this the water became anoxic. The other plots, for Stations 1/2 and 1-1/2, show that at 60 - 70 meters the oxygen decreased from September to February and then increased between February and April 1961. This results from an intrusion of water, of higher oxygen content, into the inlet at these intermediate depths. Deeper water in the basins at Stations 1 and 1/2 is not affected.

The calculated rate of oxygen consumption for the stagnant basins in Tofino Inlet is 0.015 mg./l/day. This value agrees with Barnes and Collias (1958), who found consumption rates ranging from 0.007 - 0.024 mg./l/day in Puget Sound. From Lazier's (1963) data, for Princess Louisa Inlet, a value of 0.015 mg./l/day is obtained.

IV. REGENERATION OF PHOSPHATE AND SILICATE

The vertical profiles of phosphate and silicate (Figure 15) show an inverse relationship to those of oxygen (Figure 13). Richards and Vaccaro (1956) have demonstrated that the regeneration of phosphate is quantitatively related to the oxygen consumed during the oxidation of

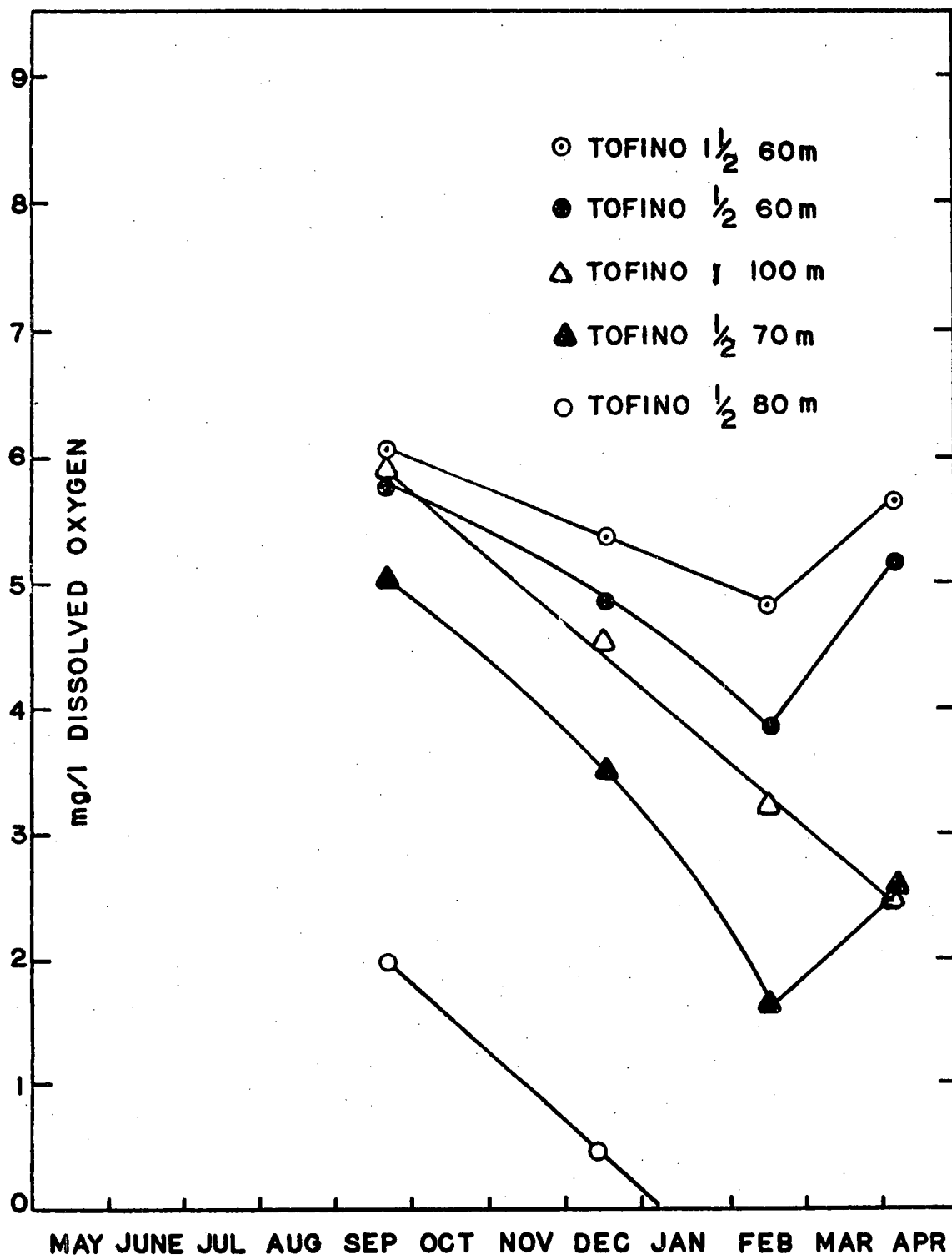


Fig. 20. Oxygen consumption at five selected depths in Tofino Inlet between Sept. 1960 and April 1961.

organic matter. In the oxygenated water of the Cariaco Trench they found that 270 atoms of oxygen were consumed for each atom of phosphorous released. In the anoxic zone the ratio was 235 to 1 in terms of the oxygen equivalent of the sulphate utilized. The ratio they found for the oxygenated zone was close to the theoretical for the complete oxidation of plankton having the average carbon to phosphorous ratio of 106:1. The ratio of 235:1, found in the anoxic zone, results from the fact that amine nitrogen is not oxidized to nitrate but is released as ammonia while any preformed nitrate originally present is reduced to nitrogen in these waters (Richards and Benson 1961). The high phosphate concentrations found in the anoxic basins result from the release of phosphate during the oxidation of organic matter.

The regeneration of silicate does not seem to be directly associated with the consumption of oxygen (Redfield et al. 1963). Lewin (1961) has shown that iron and aluminium may be responsible for the resistance of diatom skeletons to dissolution, since she found that chelating agents, which complex iron, accelerate the release of silicate. She also suggested that in anoxic environments hydrogen sulphide could combine with iron and aid in the dissolution of silica from diatom walls. In Tofino Inlet, silicate increases from 30 - 40 ug. at./l in the oxygenated zone to 100 - 300 ug. at./l in the anoxic basins. This evidently

results from soluble silicate derived from diatom tests and supports Lewin's suggestion. However, this may be only an accumulation accompanying stagnation.

V. OXYGEN MINIMA AND PHOSPHATE-SILICATE MAXIMA IN THE OXYGENATED ZONE

In September 1960, oxygen minima and phosphate-silicate maxima appear in the oxygenated zone at 20 meters. These features appear in the longitudinal profiles (Figures 4 and 14) and in the vertical profiles (Figures 13 and 15).

Lazier (1963) postulated that the intrusion of dense, high-salinity water into inlets with shallow sills takes place in the form of successive tidal jets. This water flows under the lighter water inside the inlet. The lighter water is thus raised to intermediate depths, where it flows out of the inlet. If this mechanism operates in Tofino Inlet, the oxygen minima and the phosphate-silicate maxima at 20 meters, can be a tracer of this type of circulation. The low oxygen, high phosphate-silicate water of the anoxic basins presumably is raised to 20 meters depth by the intruding water.

In addition to the anoxic basins at the head of Tofino Inlet, there is an anoxic basin in Tranquil Inlet (Figure 2, page 4), which has a 16 meter sill. It is anoxic below 40 meters (Anon. 1960b). Thus there are two geographically separated sources of anoxic water, one of which is situated close to the mouth of Tofino Inlet.

An alternate source for the high phosphate-silicate water is in the sediments, which could be stirred into suspension by the intruding water. The sediments in Tofino are anoxic even when the overlying water contains oxygen. Rittenberg, Emery and Orr (1955) have shown that active regeneration of phosphate and silicate occurs in basin sediments. The phosphate maxima, which appeared between 40-60 meters in April 1961, could possibly have a sediment source, since a mid-depth intrusion of water took place between February and April, as evidenced by an increase in oxygen.

The 20 meter depth appears to be a depth of minimum motion in the inlet. This is supported not only by the oxygen, phosphate and silicate data, but also by temperature data in September 1960 and at other times (Figures 3 and 4). The 20 meter depth is about the depth of the temperature minimum in the inlet.

VI. ALKALINITY - pH RELATIONSHIPS IN THE ANOXIC ZONE OF TOFINO INLET

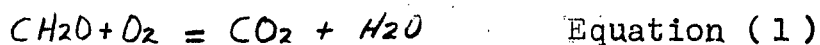
Oxygen is supplied to seawater by exchange with the atmosphere and by photosynthetic organisms. It is consumed in seawater by the oxidative processes of respiring organisms, which in the deeper water are mainly heterotrophic bacteria. In basins, such as exist in Tofino Inlet, into which oxygenated seawater enters and is subsequently trapped in a manner described in Section V, the following events

occur; (1) the oxygen is depleted by bacterial respiration producing carbon dioxide, (2) when the oxygen has disappeared, other hydrogen acceptors such as nitrate and sulphate are utilized by bacteria producing hydrogen sulphide and carbon dioxide (Zobell (1946), Postgate (1951), McKinney and Conway (1957), (3) in extreme cases, when the entrapment lasts many years, methane is produced (Williams et al., 1961).

Representative equations, necessarily oversimplified, covering these oxidation reactions which are carried on by the heterotrophic bacteria, are given by Redfield, Ketchum and Richards (1963). In this work, they cite evidence from the Black Sea and the Cariaco Trench, that sulphate is the source of the sulphide found in anoxic basins and that the reaction products, carbon dioxide and hydrogen sulphide, accumulate in proportions that are in accordance with the stoichiometry of equations 7 and 8, given below. The equations covering these reactions are:

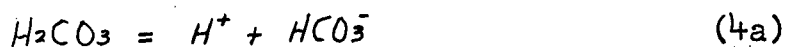
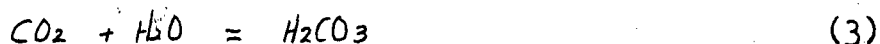
Equations for the oxygenated zone.

(i) Biochemical Oxidation

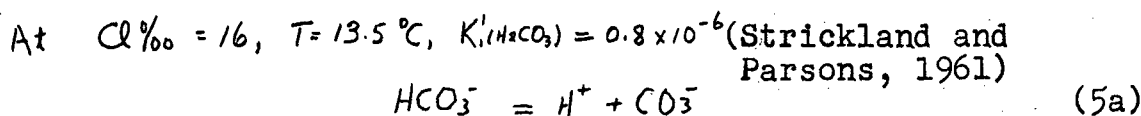


where CH_2O represents carbohydrate, which is presumed to be the average oxidation state of carbon in the organic matter being oxidized.

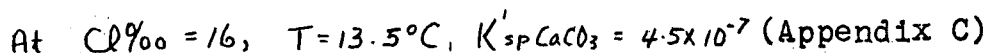
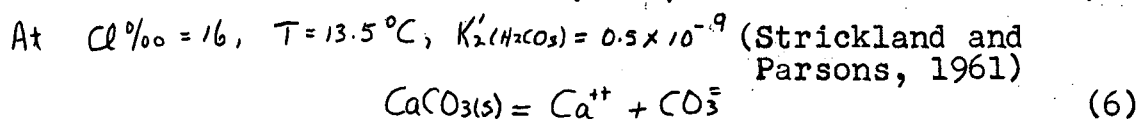
(ii) Carbon Dioxide Equilibria



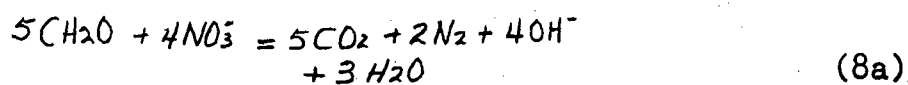
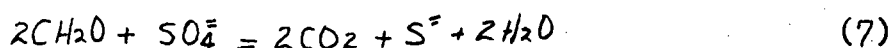
$$K'_{1(H_2CO_3)} = \frac{[H^+](HCO_3^-)}{(H_2CO_3)} \quad (4b)$$



$$K'_{2(H_2CO_3)} = \frac{[H^+](CO_3^{--})}{(HCO_3^-)} \quad (5b)$$

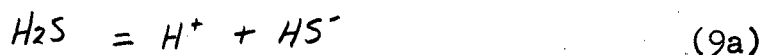
Equations for the anoxic zone.

(i) Biochemical Oxidation



(ii) Carbon Dioxide Equilibria (as in A (ii) above)

(iii) Hydrogen Sulphide Equilibria



$$K'_1(\text{H}_2\text{S}) = \frac{[\text{H}^+](\text{HS}^-)}{(\text{H}_2\text{S})} \quad \text{Equation (9b)}$$

At $\text{Cl}\%_0 = 16$, $K'_1(\text{H}_2\text{S}) = 1.8 \times 10^{-7}$ (Skopintsev, 1957)

$$\text{HS}^- = \text{H}^+ + \text{S}^{2-} \quad (10a)$$

$$K'_2(\text{H}_2\text{S}) = \frac{[\text{H}^+](\text{S}^{2-})}{(\text{HS}^-)} \quad (10b)$$

At $\text{Cl}\%_0 = 16$, $K'_2(\text{H}_2\text{S}) = 9.8 \times 10^{-15}$ (Skopintsev, 1957)

In equations 4b, 5b, 9b and 10b above, the various K' values represent "apparent" dissociation constants and not thermodynamic constants. The terms in square brackets in these equations are activities, while those in round brackets are concentrations. The values of K'_1 and K'_2 for hydrogen sulphide are taken from a paper by Skopintsev (1957). As far as is known these are the only values available for seawater but their temperature dependence is not known.

Titration alkalinity of the anoxic zones. In normal seawater the titration alkalinity is given by

$$\text{Titration Alkalinity} = \frac{(\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + (\text{H}_2\text{BO}_3^-) + (\text{OH}^-) - (\text{H}^+)}{(\text{Harvey, 1955})} \quad (11)$$

In the anoxic waters of Tofino Inlet the titration alkalinity includes the hydrolysis products of sulphide ion and denitrification reactions in addition to the normal components. About 20 $\mu\text{g.at./l}$ $\text{NO}_3\text{-N}$ is available for denitrification (Anon. 1961, April). This represents an increase in alkalinity of 0.02 m. equiv./l, according to equation (8b), and

is allowed for in the following discussion. In the anoxic water equation 11 becomes

$$\begin{aligned} \text{Anoxic Titration Alkalinity} = \text{T.A.A.} = \\ (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + (\text{H}_2\text{BO}_3^-) + (\text{OH}^-) - (\text{H}^+) + \\ (\text{HS}^-) + 2(\text{S}^{2-}) + 0.02 \end{aligned} \quad \text{Equation (12)}$$

After correcting for borate (Harvey, 1955) and denitrification, and neglecting (H^+) , (OH^-) and (S^{2-}) , which are negligible at the pH of the anoxic water, equation 12 becomes

$$\text{T.A.A.} = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + (\text{HS}^-) \quad (13)$$

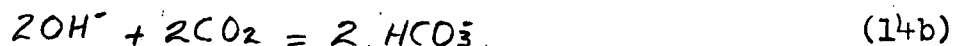
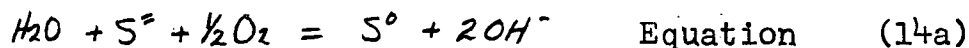
Examination of the T.A.A. values found in the anoxic waters of Tofino Inlet shows that they are higher than would be expected after allowing for the contributions of borate, denitrification and sulphate reduction. For example, Station 1/2, at 80 meters, had an alkalinity corrected for borate of 2.04 m. equiv./l in September 1960. By February, 1961, the T.A.A. had increased to 2.33 m. equiv./l, accompanied by the reduction of 0.114 m. equiv./l of sulphate. This represents an anomalous increase in alkalinity of 0.18 m. equiv./l. Table III lists sulphide concentrations, T.A.A., anomalous alkalinity increases, and pH, observed in the anoxic basins of Tofino Inlet, as well as oxygen for Station 1/2, 80 meters, in September 1960.

TABLE IV

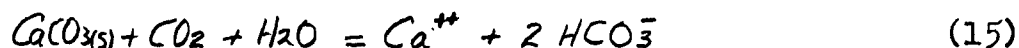
OXYGEN, TOTAL SULPHIDE, T.T.A., ANOMALOUS
ALKALINITY INCREASE AND pH FOR THE
ANOXIC BASINS OF TOFINO INLET

Sta- tion	Depth	Date	Oxygen	Total Sulphide			T. T.A.	ANOMALOUS ALKALINITY INCREASE	pH
			mg./l	mg./l	m. mols/l	m. equiv./l	m. equiv./l		
1/2	80m.	Sept. 1960	2.02	0.0	0.0	0.0	2.04	0.00	7.57
1/2	80m.	Feb. 1961	0	1.82	0.057	0.114	2.33	0.18	7.55
1/2	80m.	Apr. 1961	0	2.22	0.069	0.138	2.44	0.26	7.46
1/2	85m.	Sept. 1960	0	9.53	0.293	0.59	3.01	0.37	7.29
0 1/2	45m.	Sept. 1960	0	13.89	0.435	0.87	3.11	0.20	7.01
1/2	90m.	Feb. 1961	0	11.5	0.360	0.72	3.21	0.45	7.31
1/2	90m.	Apr. 1961	0	11.1	0.345	0.67	3.17	0.43	7.35
1/2	95m.	Apr. 1961	0	12.98	0.405	0.81	3.33	0.49	7.36

There are two possible sources for this anomalous increase in alkalinity; (1) diffusion of oxygen down into the anoxic zone could result in an alkalinity increase according to the following reactions:



(2) the increase could result from the solution of calcium carbonate, according to



It is possible to determine the alkalinity components that would be present under either of the above conditions. King (1954) reports a means of calculating the concentrations of species present in complex buffer mixtures. To calculate the pH of such a buffer system, the concentrations of all the charged species are determined by substituting a "knowledgeable guess" of the equilibrium hydrogen ion activity into the analytical expression for the concentration of each species. If the pH selected is correct the sum of the charged species satisfies the electroneutrality rule. If not, succeeding approximations are made until the electroneutrality condition is satisfied. In the calculations presented here, the sum of the calculated alkalinity components must equal the alkalinity of the anoxic water (Equation 13).

The generalized expression for the concentration of each charged species given by King is:

$$(H_k B^j) = C_j \times \frac{K_1 K_2 \dots K_{m-k} [H^+]^{k-m}}{1 + \sum_{n=1}^m K_1 K_2 \dots K_n [H]^{-n}} \quad \text{Equation (16)}$$

where $(H_k B^j)$ = the concentration of the k^{th} member of the polybasic acid $H_m B^j$

C_j = the total concentration of species containing B^j

$K_1 K_2$ = the ionization constants of the various weak acids.

The numerator of the fraction is the ratio of the concentrations of all the species containing the base B^j to the concentration of $H_m B^j$. This fraction is therefore the fraction which is present as $H_k B^j$. This is illustrated by deriving the expressions for $(H_k B^j)$ in the case of (HCO_3^-) and (CO_3^{2-}) , as follows: Rearranging equation (5b) we obtain

$$(HCO_3^-) = K'_1 (H_2CO_3) [H]^{-1} \quad \text{Equation (17)}$$

Now C_{CO_3} is the concentration of all species containing the base CO_3^{2-} so that

$$\begin{aligned} C_{CO_3} &= (H_2CO_3) + (HCO_3^-) + (CO_3^{2-}) \\ &= \left\{ 1 + K'_1 [H]^{-1} + K'_1 K'_2 [H]^{-2} \right\} (H_2CO_3) \quad (18) \end{aligned}$$

Combining equations 17 and 18 we find:

$$(HCO_3^-) = C_{CO_3} \times \frac{K'_1 [H]^{-1}}{1 + K'_1 [H]^{-1} + K'_1 K'_2 [H]^{-2}} \quad (19)$$

$$(CO_3^{2-}) = C_{CO_3} \times \frac{K'_1 K'_2 [H]^{-2}}{1 + K'_1 [H]^{-1} + K'_1 K'_2 [H]^{-2}} \quad (20)$$

For hydrogen sulphide a similar expression is obtained:

$$(HS^-) = C_{S^{2-}} \times \frac{K'_1 [H]^{-1}}{1 + K'_1 [H]^{-1}} \quad (21)$$

Where $K'_1 K'_2 [H]^{-2}$ has been left out of the denominator, since it approximately equals 10^{-8} at the pH's found in the anoxic basins. The sulphide ion concentration is negligible for the same reason.

The alkalinity calculation is illustrated here for equations 14 and 15, Station 1/2, at 80 meters, in February 1961. The following quantities, needed for the calculation are known or were measured.

1. K'_1 (H_2S) equation (9b)
2. K'_1 (H_2CO_3) and K'_2 (H_2CO_3) equations (4b and 5b)
3. $C_{S^=}$ is known analytically and is given in Table IV.
4. $[H^+]$ was measured aboard ship and corrected to its in situ value (Strickland and Parsons, 1961).

The quantity $C_{CO_3^-}$ is not known analytically and must be obtained by making the following assumption:

$$C_{CO_3^-} = C'_{CO_3^-} + C^2_{CO_3^-} + C^3_{CO_3^-} + C^4_{CO_3^-} \quad (22)$$

where

$C'_{CO_3^-}$ = the total CO_2 present in September 1960 obtained from the tables of Strickland and Parsons (1961).

and where

$C^2_{CO_3^-}$ = the CO_2 production resulting from the utilization of 2.02 mg./l (0.063 m.mols./l) of oxygen according to equation (1).

$C^3_{CO_3^-}$ = the CO_2 production resulting from the utilization of 0.037 m. mols./l of sulphate according to equation (7).

$C^4_{CO_3^-}$ = the amount of the base $CO_3^{=}$ introduced by; (1) the oxidation of sulphide³ and reaction of hydroxyl ion with CO_2 , 0.18 m. mols./l in this case, or (2) the amount of the base $CO_3^{=}$ introduced by the solution of 0.09 m. mols./l of $CaCO_3$, according to equation (15), it is half the alkalinity increase.

Substituting the appropriate values into equation (22) in case (1),

$$\begin{aligned} C_{CO_3^{2-}} &= 2.06 + 0.063 + 0.114 + 0.18 \\ &= 2.45 \text{ m. mols/l} \end{aligned}$$

while in case (2),

$$\begin{aligned} C_{CO_3^{2-}} &= 2.06 + 0.063 + 0.114 + 0.09 \\ &= 2.33 \text{ m. mols/l} \end{aligned}$$

On solving for the various alkalinity components, using equations (19), (20) and (21), the observed pH of 7.55, $C_S = 0.057$ m. mols/l and the values of $C_{CO_3^{2-}}$ obtained above, we find that for case (1),

$$\begin{aligned} \text{T.A.A.} &= (\text{HS}^-) + (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) \\ &= 0.05 + 2.32 + 0.08 \\ &= 2.45 \text{ m. equiv./l} \end{aligned}$$

while in case (2),

$$\begin{aligned} \text{T.A.A.} &= 0.05 + 2.21 + 0.08 \\ &= 2.34 \text{ m. equiv./l} \end{aligned}$$

For the alkalinity value, obtained using the observed pH, total sulphide measurement, and the assumptions regarding the production of carbon dioxide and solution of calcium carbonate, case (2) is closest to the observed value 2.33 m.equiv./l. Table V, which contains a comparison between the observed and calculated values of alkalinity at other depths in the anoxic basins, shows that the calculations involving

the assumption of the solution of calcium carbonate obtain the closest agreement with the observed alkalinities. In making the other calculations in Table V, in the absence of more precise knowledge, it is assumed that the initial oxygen and alkalinity are the same as for Station 1/2, at 80 meters in September 1960.

TABLE V

COMPARISON OF CALCULATED AND OBSERVED ALKALINITY
IN THE ANOXIC BASINS OF TOFINO INLET

Sta- tion	Depth	Date	Observed pH	Case (1)	Alkalinity m.equiv./l	
					Case (2)	Observed
1/2	80m	Feb. 1961	7.55	2.45	2.34	2.33
1/2	80m	Apr. 1961	7.46	2.51	2.38	2.44
1/2	85m	Sept. 1960	7.29	3.28	3.01	3.01
0 1/2	45m	Sept. 1960	7.01	3.13	3.05	3.11
1/2	90m	Feb. 1961	7.31	3.42	3.20	3.21
1/2	90m	Apr. 1961	7.35	3.39	3.18	3.17
1/2	95m	Apr. 1961	7.36	3.60	3.37	3.33

The effect of experimental errors in the determination of pH and hydrogen sulphide on these calculations can be estimated. The pH affects the results in two ways, in the measurement of the alkalinity, and in the calculation of the

alkalinity components. An error of 0.02 in pH causes an alkalinity error of 0.02 in each of these. An error of 10 % in the determination of sulphide causes an error of 0.12 in the calculation of alkalinity.

The differences between the observed and calculated values is less than 0.1 in each instance. Four values differ by 0.01. Two of the observed values in Table V, Station 1/2 at 80 meters, in April and Station 0-1/2 in September, fall between calculated values according to cases (1) and (2). While the possibility of experimental error exists, both these values, 2.44 m.equiv./l and 3.11 m.equiv./l, are 0.06 m.equiv./l greater than can be accounted for by the solution of calcium carbonate. The observation depth in each instance is 5 meters or less below the oxygenated zone so that turbulent diffusion of oxygen into the anoxic water would not be difficult. In both instances, prior to the observations, water had intruded into the inlet as described previously. There is some indication, from these calculations, that oxygen diffusing across the anoxic boundary results in an increase in alkalinity of the anoxic water just below.

In the deeper water of the anoxic zone, the alkalinity increase appears to be explained by the solution of calcium carbonate in the water, made relatively acid by the production of carbon dioxide. There is other evidence to suggest that this is so. If ion products for calcium carbonate are calculated according to the method of Wattenburg (1933) for

normal seawater and for the anoxic waters of Tofino Inlet, it is found that the anoxic zone is unsaturated with respect to calcium carbonate. An outline of Wattenburg's method for determining ion products, a revised table of his log C' values and a table of the apparent second dissociation constant of carbonic acid (Lyman, 1957) is given in Appendix C. This enables apparent solubility products to be calculated for seawater ranging in salinity from 0-20 ‰ and in temperature from 4-20°C. Table VI contains the ion products for the anoxic zone, and three values for the oxygenated zone. It shows slight supersaturation at 60 meters and 70 meters in the oxygenated zone and undersaturation at 80 meters, where the oxygen was 2.02 mg./l in September, 1960. The anoxic zone is undersaturated with respect to calcium carbonate.

TABLE VI

ION PRODUCTS OF CALCIUM CARBONATE AT STATION 1/2
IN TOFINO INLET

Sta- tion	Depth	Date	Ion Product
1/2	60m*	Sept. 1960	5.7×10^{-7}
1/2	70m*	"	6.0×10^{-7}
1/2	80m*	"	3.2×10^{-7}
1/2	85m	"	2.5×10^{-7}
0-1/2	45m	"	1.4×10^{-7}
1/2	80m	Feb. 1961	3.5×10^{-7}
1/2	90m	"	2.9×10^{-7}

4.5×10^{-7} for all depths shown since salinity and temperature changes are insignificant.

* Oxygenated water.

Calcareous shells are found in the sediments of Vancouver Island inlets in greater number than in the mainland inlets (Pickard 1963), but calcareous species of foraminifera are not found in the upper basin sediments of Tofino Inlet (Cockbain, personal communication). In the highly anoxic Powell Lake, no inorganic carbonates are present in the bottom sediments (Williams, personal communication). From these observations it seems likely that calcium carbonate, possibly derived from falling organisms or river sediment, has dissolved in the low pH water of the basins leading to the observed increase in alkalinity. This has the effect of raising the pH of the anoxic waters.

CHAPTER VI

CONCLUSIONS

The study of the chemical characteristics of the anoxic basins in Tofino Inlet shows that the pH and alkalinity changes which occur in them, result from the production of carbon dioxide and hydrogen sulphide. These products arise from the bacterial oxidation of organic matter. The resulting pH is lower and the alkalinity is higher than in normal seawater. The alkalinity is anomalously high in the anoxic basins. Two proposals are advanced to explain this feature. Near the anoxic boundary, the mixing of oxygen down into the anoxic zone, where it oxidizes sulphide to free sulphur, could be responsible for at least part of the increase. Deeper in the anoxic zone the solution of calcium carbonate accounts for the anomalous increase in alkalinity. The regeneration of phosphate and silicate that takes place in the anoxic zone results in high values of these constituents. In the case of silicate, hydrogen sulphide may aid in its regeneration by combining with iron, which is present in the siliceous skeletons of diatoms.

The replacement of bottom water takes place annually in the summer, when meteorological conditions produce high salinities in the water at sill depth at the entrance to the inlet. While the bottom water in the upper basins of the inlet is not completely replaced every year, in each year for

which there is adequate data, extensive replacement of the bottom water occurs. During the winter following the intrusion the bottom water is isolated. The oxygen then decreases to low values. The mechanism of replacement is still obscure. The intruding water may come in through Fortune Channel, Browning Passage or both. In order to determine the path of the intrusion, moored observational instruments are required. When these facilities are not available it is possible to use the chemical properties, oxygen, phosphate and silicate, to trace the water movements.

The oxygen utilization rate for the stagnant basins is calculated and it agrees with published values obtained in other inlets. This rate has been used to calculate the age of bottom water in order to determine a replacement time.

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APPENDIX

APPENDIX A

OBSERVATIONS OF SULPHIDE IN TOFINO INLET

Station	Depth	Date	Concentration of Sulphide mg./l
0 1/2	45m	Sept. 1960	13.89
1/2	85m	Sept. 1960	9.53
1/2	80m	Feb. 1961	1.82
1/2	90m	Feb. 1961	11.5
1/2	80m	April 1961	2.22
1/2	90m	April 1961	11.1
1/2	95m	April 1961	12.98

APPENDIX B

OBSERVATIONS MADE IN TOFINO INLET IN AUGUST 1961

Two cruises were made to Tofino Inlet in August 1961, on August 15 - 16, and on August 30 - 31. On both these occasions there is evidence from salinity and oxygen data that dense water is intruding into the inlet (Anon. 1961b). Oxygen observations show similar conditions to that prevailing in September 1960. At Station 1, the oxygen is again high in the bottom water. While dense water shows up in both Browning Passage and Fortune Channel, the density distribution for August 15 - 16 indicates more continuity structure between Tofino Inlet and Fortune Channel than between Tofino Inlet and Browning Passage. This suggests that the major portion of the intruding water may come in through the deeper northern channel. Why this should be is certainly not clear. The elucidation of the replacement mechanism for bottom water of Tofino Inlet will undoubtedly require direct current observations.

APPENDIX C

WATTENBURG'S METHOD FOR THE DETERMINATION OF THE APPARENT SOLUBILITY PRODUCT OF CALCIUM CARBONATE IN SEAWATER

Wattenburg (1933) determined the apparent solubility product of calcium carbonate in seawater experimentally by equilibrating solid calcium carbonate with seawater of different chlorinities. In each case he chose a constant and high partial pressure for each determination of CO_2 . This was done to reduce the analytical concentration of $\text{CO}_3^{=}$ to a negligible amount; his equilibrium pH's ranged from 6.02 - 6.42. The equation for the thermodynamic solubility product

$$K_{sp}(\text{CaCO}_3) = [\text{Ca}^{++}] [\text{CO}_3^{=}] \quad \text{Equation (a)}$$

can be arranged to give the following apparent solubility product in terms of easily measured quantities

$$\begin{aligned} K'_{sp} \text{CaCO}_3 &= \frac{(\text{Ca}^{++})(\text{HCO}_3^-)}{[\text{H}^+]} \times K'_2(\text{H}_2\text{CO}_3) \quad (\text{b}) \\ &= C' \times K'_2(\text{H}_2\text{CO}_3) \end{aligned}$$

Wattenburg determined (HCO_3^-) by titration and measured $[\text{H}^+]$ using a quinhydrone electrode. Since the analytical procedures available for determining calcium was difficult in 1932, he estimated the (Ca^{++}) from the following relation

which holds for normal seawater at pH's less than 7.1.

$$(\text{Ca}^{++}) = \text{Ca}_0^{++} + \frac{(\text{HCO}_3^-)}{2} \quad \text{Equation (c)}$$

$$= 0.000477 \text{ Cl } \% + \frac{(\text{HCO}_3^-)}{2} \quad \text{(d)}$$

Since Wattenburg used the Sorenson Scale of pH, the table of $\log C'$ values included here on page 73 are corrected for the difference between the modern and Sorenson pH scales

$$\text{pH} = \text{pH}_s + 0.04 \quad \text{(e)}$$

Using these values of $\log C'$ and pK'_2 for carbonic acid, the apparent solubility product for seawater of varying chlorinities and temperatures can be calculated. Modern values of $\text{pK}'_2(\text{H}_2\text{CO}_3)$ are listed on page 74 (Lyman 1957).

In determining the ion product of calcium carbonate in the anoxic basins the concentration of calcium ion was estimated by Wattenburg's method for normal seawater, equation (d) above. The concentration of carbonate ion was determined from the relation given in Harvey (1955), where

$$(\text{CO}_3^{--}) = \text{carbonate alkalinity} \times \frac{K'_2(\text{H}_2\text{CO}_3)}{[\text{H}'] + 2 K'_2(\text{H}_2\text{CO}_3)} \quad \text{(f)}$$

TABLE A

WATTENBURG'S LOG C' VALUES CORRECTED FOR CHANGE TO THE
MODERN pH SCALE. THEY ARE GIVEN FOR 0 - 20 ‰ Cl
AND 4 - 20°C.

Cl ‰	T°C				
	4°	8°	12°	16°	20°
0	2.36	2.29	2.21	2.13	2.05
1	2.70	2.63	2.55	2.47	2.39
2	2.79	2.72	2.64	2.56	2.48
4	2.90	2.83	2.75	2.67	2.59
6	2.99	2.92	2.84	2.76	2.68
8	3.04	2.97	2.89	2.81	2.73
10	3.08	3.01	2.93	2.85	2.77
12	3.10	3.03	2.95	2.87	2.79
14	3.12	3.05	2.97	2.89	2.81
16	3.14	3.07	2.99	2.91	2.83
18	3.15	3.09	3.00	2.92	2.84
20	3.15	3.09	3.00	2.92	2.84

TABLE B

K_2' (H_2CO_3) FOR 0 - 17‰ IN CHLORINITY AND 0 - 16°C.
FROM LYMAN (1957) BUFFER MECHANISM OF SEAWATER.

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Cl/‰ T°C	T°C			
	4°	8°	12°	16°
0	10.56	10.51	10.47	10.42
	INTERPOLATION NOT PRACTICAL BETWEEN 0 AND 1‰ Cl/‰			
1	10.00	9.95	9.91	9.86
2	9.91	9.86	9.82	9.77
3	9.82	9.78	9.74	9.69
4	9.73	9.69	9.65	9.60
5	9.70	9.66	9.62	9.57
6	9.67	9.63	9.59	9.54
7	9.65	9.60	9.56	9.51
8	9.62	9.58	9.53	9.48
9	9.59	9.54	9.49	9.45
10	9.56	9.51	9.47	9.42
11	9.54	9.49	9.45	9.40
12	9.51	9.46	9.42	9.37
13	9.49	9.44	9.40	9.35
14	9.46	9.42	9.37	9.32
15	9.44	9.40	9.35	9.30
16	9.41	9.37	9.33	9.28
17	9.39	9.34	9.30	9.26