

AN ABSTRACT OF THE THESIS OF

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(Name) (Degree)

in OCEANOGRAPHY presented on 29 March 1972  
(Major) (Date)

Title: EARLY SPRING NUTRIENT CONDITIONS IN SOUTHEASTERN  
ALASKA'S INSIDE PASSAGE

Abstract approved: Redacted for Privacy

Observations were made of salinity, temperature, nitrate + nitrite, phosphate, silicate, total available nitrogen, and chlorophyll a in nine areas of the Alaskan Inside Passage during April of 1971. In general all properties indicated the water to be well mixed throughout this area. The conservative properties were particularly uniform. The greatest range in temperature from the surface to 200m was only  $1.1^{\circ}$  C. The largest salinity range over the same depth was 2.0 o/oo

Spring phytoplankton blooms were just beginning to appear. Clarence Strait, in the southern part, presented the most evidence of biological activity. Values of chlorophyll a in this area were the highest observed ( $7.25 \text{ mg chl } \underline{a} / \text{m}^3$ ) outside of Auke Bay. This area also had the most density structure, probably due to stabilization brought on by warming. N : Si : P ratios for Clarence Strait indicate that silicate could become limiting in this area.

The only other area, outside of Auke Bay, that had evidence (high chlorophyll a) of biological activity was Taku Inlet. The N : Si : P ratios for this area indicate that nitrate will probably be the limiting nutrient.

Low oxygen values (2 ml/l) from the bottom of several deep basins indicate the possibility of anaerobic conditions developing as the water column stabilizes.

Flow within the Inside Passage seems to be controlled by freshwater and saltwater inputs. Several major sources of both types of water are found. Tides and winds contribute to the circulation of the area but the mixing of saltwater and freshwater seems to be the predominant force.

Local effects such as land runoff, glacial melt, input from hot springs and bottom topography are important in determining water conditions.

Total available nitrogen may be a better indicator of photosynthesis than nitrate. TAN : P ratios tend to remain higher during photosynthesis than nitrate : P ratios.

Early Spring Nutrient Conditions of Southeastern  
Alaska's Inside Passage

by

David Douglas Coughenower

A THESIS

submitted to

Oregon State University

in partial fulfillment of  
the requirements for the  
degree of

Master of Science

June 1972

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Date thesis is presented 29 March 1972

Typed by Susie Kozlik for David Douglas Coughenower

To Linda, who was more help than anyone

## ACKNOWLEDGEMENTS

I would like to express my deepest appreciation to Professor Herbert Curl Jr. First of all for giving me the opportunity to undertake this thesis and secondly for his help and guidance in its preparation. A good major professor is half of the battle and I have one of the best.

I owe a very special debt of gratitude to Louis I. Gordon. His suggestions and consultation concerning the TAN analytical method were invaluable. Just as important has been his friendship and the example of research excellence that he follows.

The data acquisition system was made possible through the work of Chuck Samuelson and Peter Becker. Without this system and their help during the cruise much of the data for this thesis would not have been possible. A sincere thanks to Debbie Kirk and Cheryl Alber for their help during the cruise. Cheryl is also to be thanked for analysis of the chlorophyll samples after the cruise. Since the cruise Debbie has contributed many helpful suggestions and much support during the data reduction.

It is impossible to detail all of the support my colleagues have given while this thesis was being prepared. However, the following people have contributed in one way or another: Elliot Atlas, Saul Alvarez-Borrego, John Callaway, Mark Halsey and Rich Tomlinson.

I would like to acknowledge the following grants and contracts for the support they provided: Sea Grant Project 061, NOAA 2-35187; U. S. Department of Interior, Water Quality Trainee Program contract no. 5T1WP-111-05; ONR contract no. N00014-67-A-0369-007; and NSF grant 6A-12113.

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# EARLY SPRING NUTRIENT CONDITIONS OF SOUTHEASTERN ALASKA'S INSIDE PASSAGE

## INTRODUCTION

As a fishing ground and natural water way, the Inside Passage is an extremely important part of Alaska (Figure 1). For example, in 1968 this area recorded 70 million kilograms of fish and shellfish caught compared to 204 million kilograms for the entire state (State of Alaska, 1968). For the oceanographer this area presents some rather unique hydrographic features and conditions found nowhere else in North America. The combination of these factors would seem to be sufficient reason for extensive studies of this area. However, the literature contains very little published data on the Inside Passage.

The most significant work in this area is a survey of its physical characteristics by Pickard (1967). A few individual features have been well studied. Phytoplankton ecology by Bruce (1969), Iverson (1971), and Schell (1971), and physical features by McLain (1968) and Powers (1963) but a comprehensive look at its nutrients would seem desirable.

The investigation described in this paper is presented only as a beginning, to what is hoped will become a more complete description of nutrient distribution and cycling in the Inside Passage. The data presented here was gathered during a single cruise from 10 to 21

April, 1971, through selected portions of the Inside Passage. Data obtained in Auke Bay during the cruise and the summer of 1971 are discussed by Kirk (1972). Additional observations at different times of the year for several years will be needed to complete the nutrient picture.

The cruise sampling plan was designed with biological features in mind. Consequently the samples are concentrated in the upper 50m with only a few deeper samples at each station.

The nutrients surveyed are silicate, phosphate, nitrate + nitrite, and total available nitrogen (TAN). Temperature, salinity and sigma-t data are presented along with the nutrients. A few oxygen values are reported for some of the deeper areas of the Passage. Chlorophyll a data are presented as an indicator of primary production.

Total available nitrogen refers to the total of all forms of nitrogen in seawater that can be utilized as a nutrient source by phytoplankton. This includes nitrate, nitrite, ammonia and most amine containing compounds (i.e. dissolved amino acids and urea). TAN is a biologically meaningful measurement since phytoplankton can use all of these sources equally well, although they do show a thermodynamically directed preference (Harvey 1940).

## METHODS AND MATERIALS

### Cruise Tracks

Nine areas of the Inside Passage were surveyed during this cruise. The cruise tracks and station numbers are given in Figure 1. Throughout this paper the different tracks are referred to at times by letter designation and at times by their common name. The stations are numbered sequentially from the beginning of the cruise to the end.

### Sampling Methods

Salinity, temperature and depth data were acquired using a Bisset-Berman Model 6040 STDS sensor. The STD system includes a pump that provides a water sample from the same depth as the sensor (Becker and Curl, 1971). Nutrient samples were collected in 60 ml plastic bottles. At some stations duplicate samples were taken, one set being analyzed at sea for nitrate + nitrite and total available nitrogen (TAN), the other set frozen. For all stations at least one set of samples was frozen and returned to Corvallis for phosphate, silicate, nitrate and TAN analysis.

The maximum pumping depth was 200m. At a few stations (6, 49, 59, 61, 63) bottle casts were made to obtain salinity, temperature, nutrient and oxygen samples from greater than 200m.

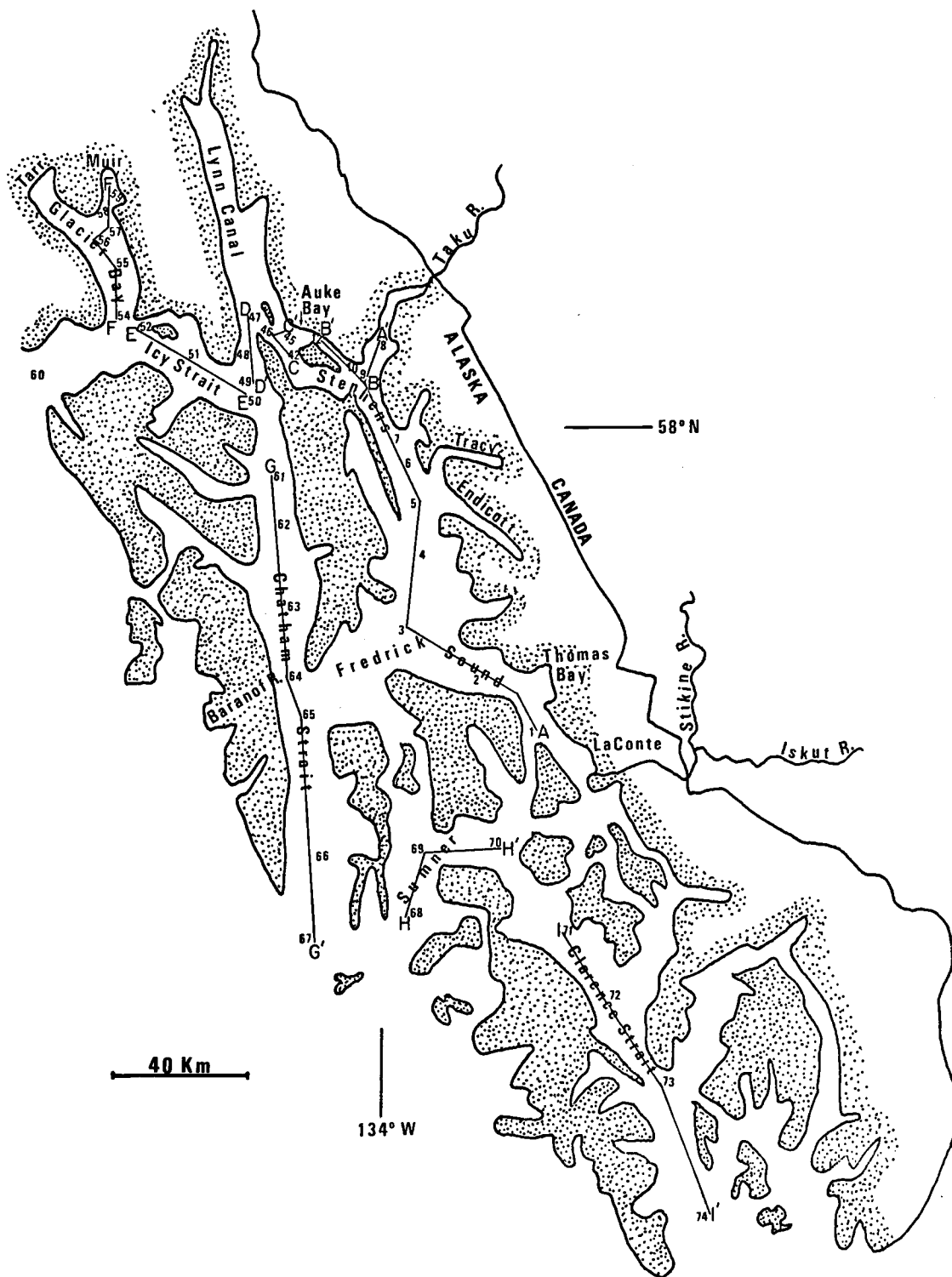


Figure 1. Southeastern Alaska's Inside Passage.



### Nutrient Methods

All the silicate, phosphate, and most of the nitrate and TAN analyses were done in the Corvallis laboratory using a three-channel Technicon® AutoAnalyzer® system. The silicate method is basically that of Armstrong, Stearns and Strickland (1967) as modified by Hager, Gordon and Park (1968). The phosphate analysis is that of Bernhart and Wilhelms (1967) with several modifications by Atlas et al. (1971). The nitrate + nitrite is that of Wood, Armstrong, and Richards (1967) with modifications for automated analysis by Hager et al. (1968). TAN was determined using the photo-oxidation method of Armstrong, Strickland and Williams (1966) as modified for automated analysis by Coughenower (See Appendix I).

The reagents for the Winkler oxygen determinations were those of Carpenter (1965). Salinity samples from the bottle casts were analyzed in Corvallis using a Bisset-Berman Model 630 inductive salinometer.

In most cases two liters of water were filtered to obtain chlorophyll a samples. These samples were analyzed using the spectrophotometric method of Richards and Thompson (1952).

## RESULTS I

### Sections

The nine areas surveyed are designated by transect lines on the chart of the Inside Passage (Figure 1). The hydrographic and nutrient data, for each of these transects, are contoured in Figures 2 - 10. The contour intervals used in these figures are temperature,  $0.5^{\circ}\text{C}$ ; salinity, 0.2 o/oo; sigma-t, 0.1 units; phosphate,  $0.2\ \mu\text{M}$ ; silicate,  $5\ \mu\text{M}$ ; nitrate + nitrite,  $5\ \mu\text{M}$ ; TAN,  $5\ \mu\text{M}$ ; chlorophyll a,  $1\ \text{mg chl a/m}^3$ . The dashed line at 200m that appears on some of the figures is used to indicate a depth scale change.

### Fredrick Sound to Taku Inlet

Transect A-A' (Figure 2) takes in the area Fredrick Sound to Taku Inlet. It has a mean depth of about 200m, and is strongly influenced at its northern end by the Taku River (average mean flow,  $260\ \text{m}^3/\text{sec}$ ). The southern end comes under the influence of Fredrick Sound and in between are a variety of inputs from streams, rivers and glaciers (Pickard, 1967). The slight decrease in temperature around station 5 is an example of the input of colder water from Tracy and Endicott arms which are glacier fed. Stations 5, 6 and 7 all show the slight temperature inversions discussed later. The most prominent feature in this area is the cold, low nutrient area between stations

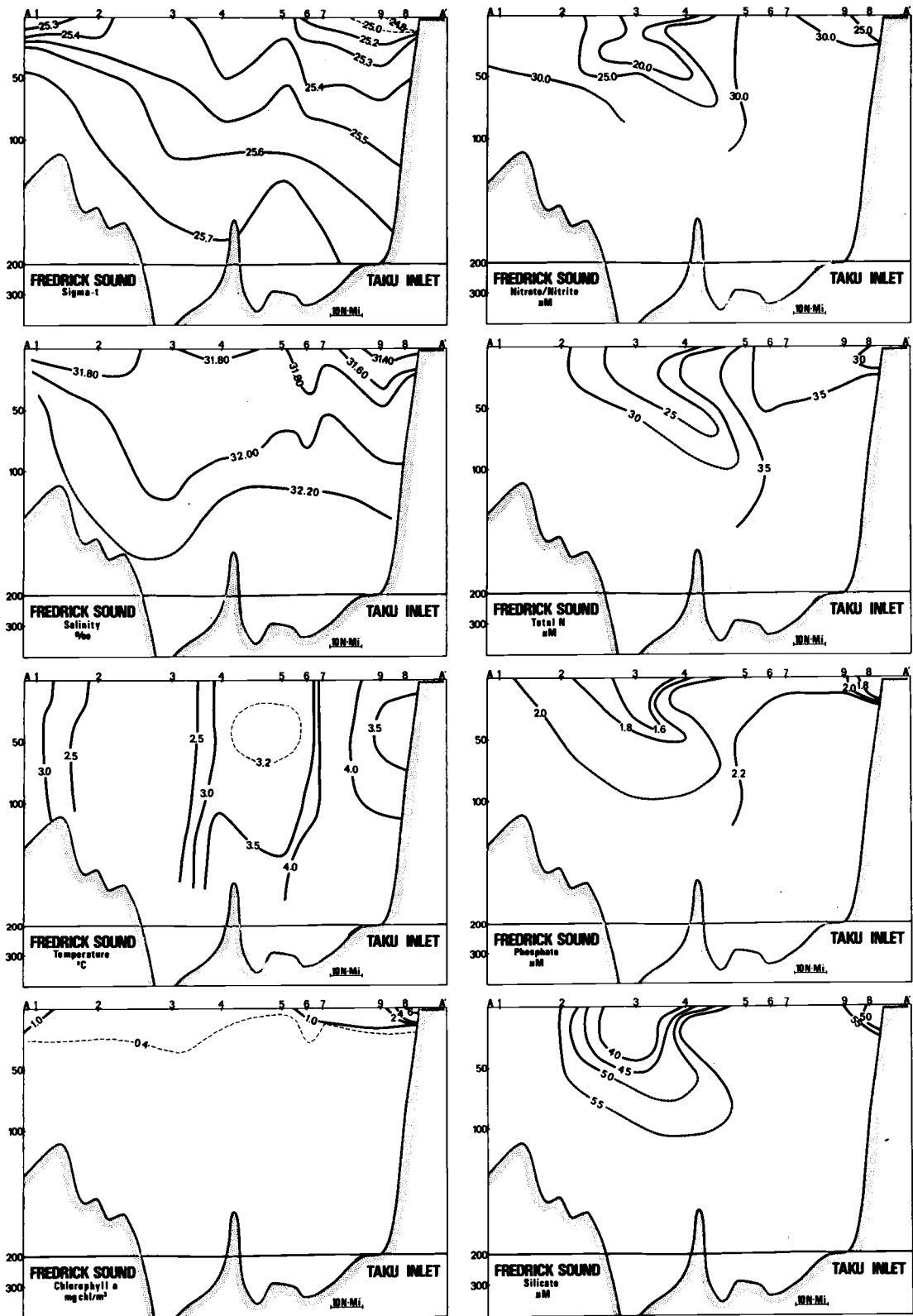


Figure 2. Contours of nutrient, hydrographic and chlorophyll *a* data for transect A-A', Fredrick Sound to Taku Inlet.

2-4. This is probably due to cold water coming from LeConte glacier and Thomas Bay, then flowing North. This water tends to stay to the East side of Fredrick Sound.

### Chatham Strait

Transect G-G' (Figure 3) is the area known as Chatham strait. It also runs North-South with an average depth of 600m. Station 67 is representative of open ocean water and its influence in the strait can be seen on all parameters. The reduced sigma-t value around station 66 is probably due to input from a stream, Deer Creek, directly opposite this station.

The influence of colder, less saline (plus higher nutrients) water from Glacier Bay and Lynn Cannal on the northern end of Chatham Strait is evident in the sigma-t, temperature and nutrient contours. This is an interesting effect with a wedge of colder less saline water poking its way into warmer, saltier ocean water. This effect's similar to, but not the same as the classic estuary system.

The unusual temperature structure occurring around station 64 and moving south seems to be related to fresh water input of the Baranof River ( $13 \text{ m}^3/\text{sec.}$ , Pickard, 1967), located near this station. This river is fed partly by a hot spring, whose volume and temperature are  $0.3 \text{ m}^3/\text{sec.}$  and  $16-50^\circ\text{C}$  (Waring, 1965).

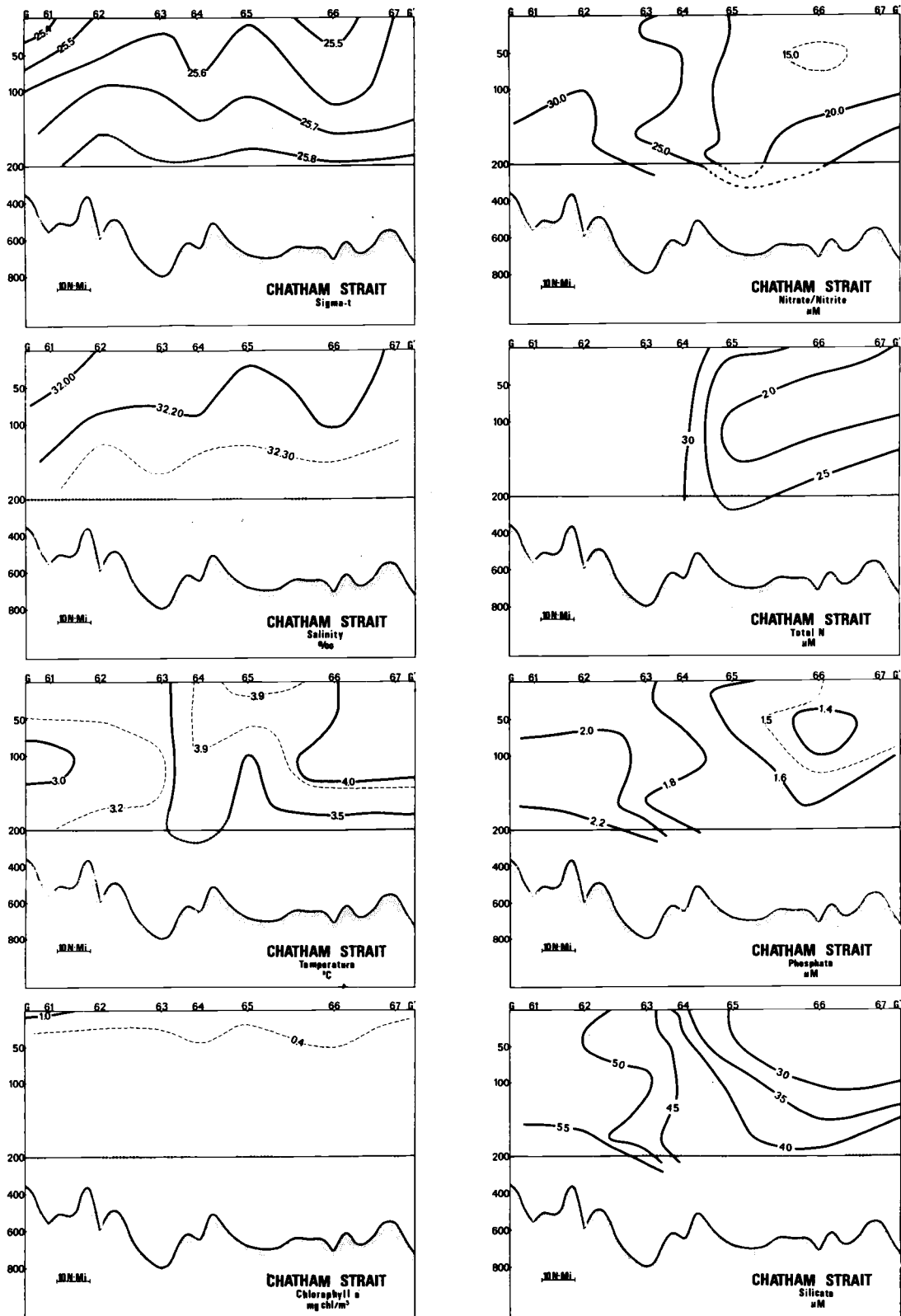


Figure 3. Contours of nutrient, hydrographic and chlorophyll *a* data for transect G-G', Chatham Strait.

About 12 hours elapsed between station 64 and 65 due to a storm that blew north up Chatham Strait with 40+ knot winds. Because of this the joining of the contour lines in this area may not be justified.

The slight decrease in temperature at the surface of station 65 is probably due to water coming out of Fredrick Sound.

I have just pointed out several places in Chatham Strait where local influences have quite an effect on water conditions. The Inside Passage is a very dynamic area with high tidal ranges and frequent winds. The importance of local effects cannot be overlooked.

#### Clarence Strait

Clarence Strait (Figure 4) is another of the larger areas surveyed. Also running North-South, it has an average depth of 400m. This area is open to the ocean at its southern end and again we see the estuary effect, that was observed in Chatham Strait, evident here in the temperature and nitrate contours.

The sigma-t contours have more stratification than any other area surveyed. This is probably due to stabilization brought on by warming. The temperatures here are about two degrees warmer than any other area. This warming may result from this area being further south, but I think the primary effect is from the input of warmer ocean water.

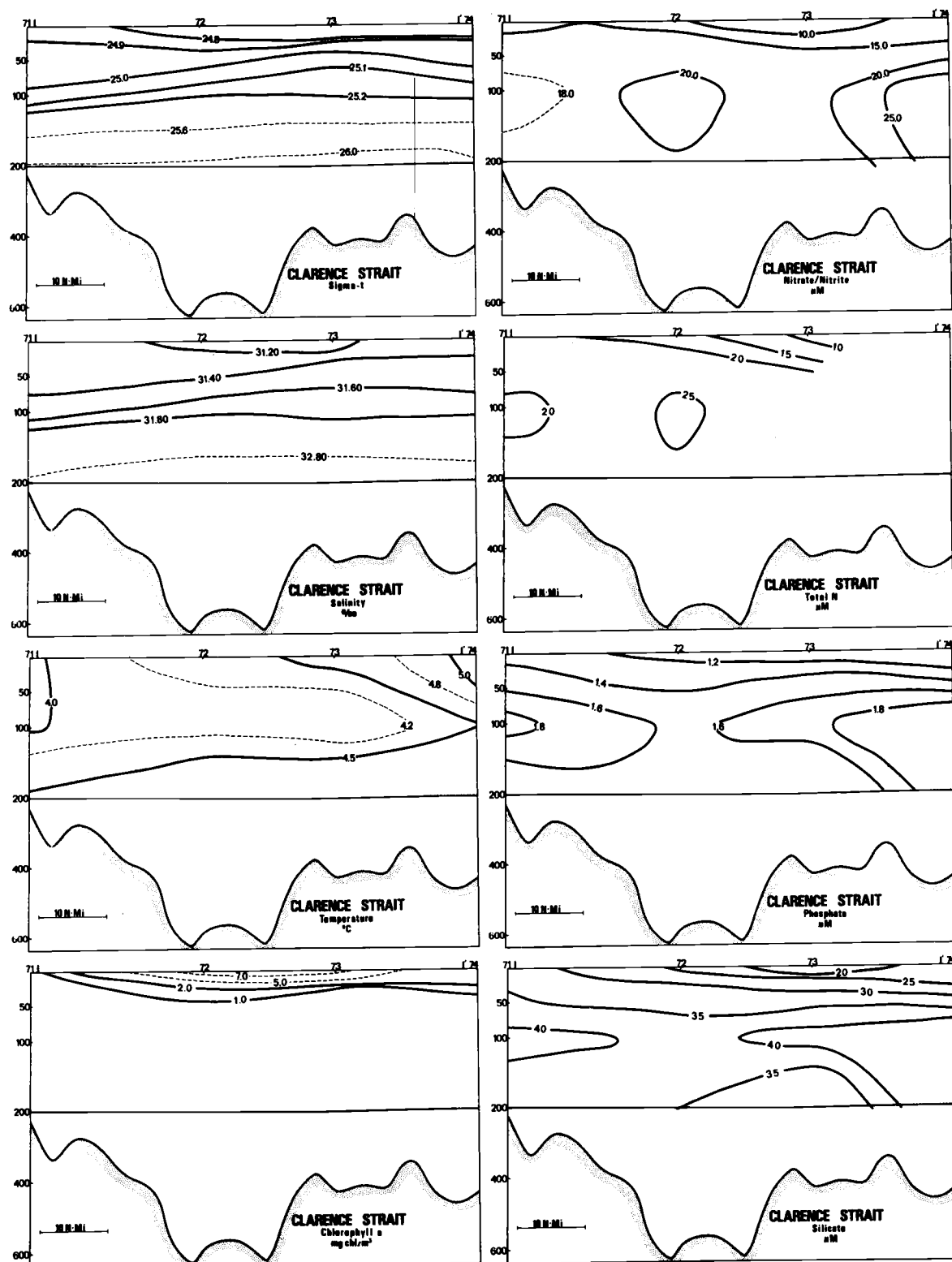


Figure 4. Contours of nutrient, hydrographic and chlorophyll *a* data for transect I-I', Clarence Strait.

A result of this warming and stabilization is the appearance of biological activity at stations 72 and 73. This is evident on both the nutrient and chlorophyll a contours. This was the most biologically active area, outside of Auke Bay.

### Glacier Bay

With an outer sill depth of about 60m the bay is restricted in its mixing with adjacent areas. As its name implies, Glacier Bay was formed by a complex of glaciers, presently receding; consequently its bottom profile is very irregular. It has a mean mid-inlet depth of 370m (Pickard, 1967). The bay is basically glacier fed and the temperatures observed here were cold and uniform. Salinity and sigma-t (Figure 5) indicate that the cold glacial melt remains near the surface while the deep water is well mixed.

### Icy Strait

Transect E-E', known as Icy Strait, has a mean depth of 240m and is open to the ocean at its western end. The sill depth is 66m so that any exchange between Icy Strait and the ocean takes place near the surface. Depending on the winds and tide Icy Strait acts as a channel for water coming out of Glacier Bay, down Lynn Canal or in from the ocean. These combined waters then flow into the northern end of



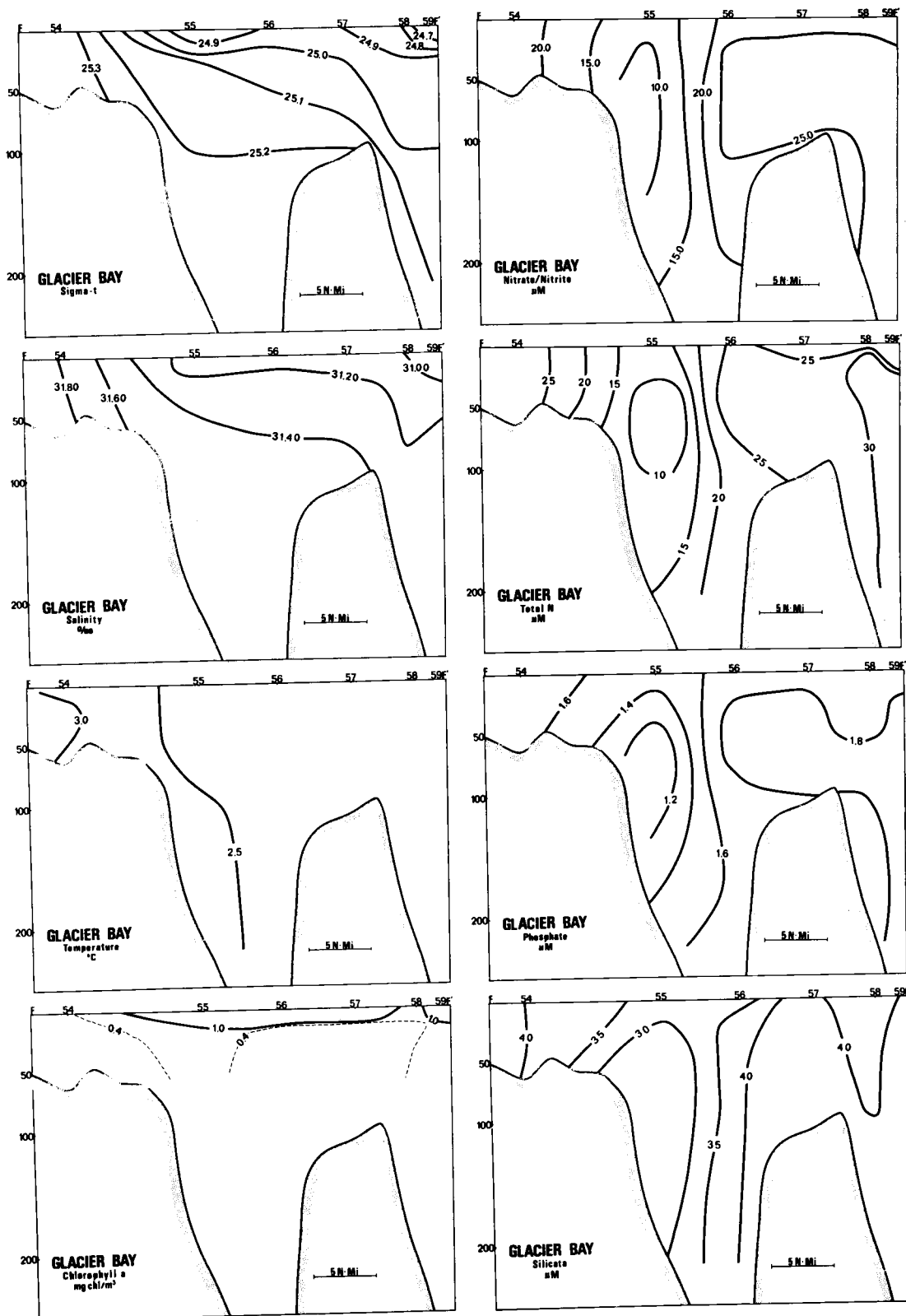


Figure 5. Contours of nutrient, hydrographic and chlorophyll a data for transect F-F', Glacier Bay.

Chatham Strait. The high nutrients and low chlorophyll a (Figure 6) mark this region as one of low productivity.

At the time this area was surveyed there was a layer of lower salinity water, probably from Glacier Bay, lying at the surface and some colder, saltier water moving west near 100m.

### Lynn Canal

Transect D-D' is only the southern end of Lynn Canal. The portion surveyed has a mean depth of 500m. Lynn Canal merges with Icy Strait and then Chatham Strait. The presence of water from Lynn Canal is apparent in Chatham Strait (Figure 7).

It is conceivable that water conditions at the northern end of D-D' are influenced by water coming out of West Stephens Passage (C-C'). A comparison of stations 46 and 47 for all properties (Figures 7 and 8) would seem to support this idea. However, no data is available for the area North of station 47.

No salinity, temperature or sigma-t data are available for station 48 and joining the contour lines between stations 47 and 49 may be questionable. There are reduced nutrient concentrations down to 100m at station 48 but the chlorophyll a data are not above average. The absence of temperature and salinity data makes this feature difficult to explain.

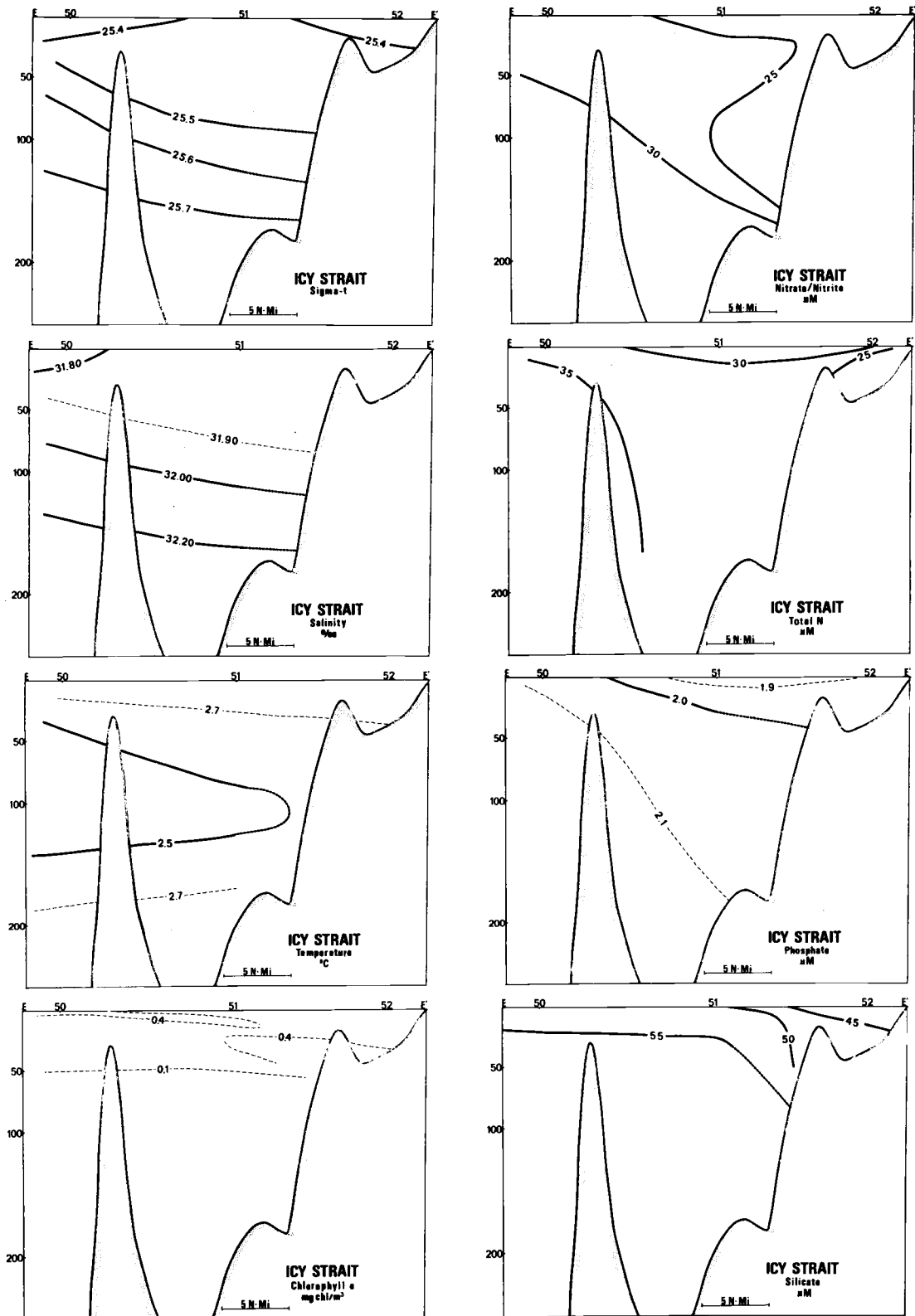


Figure 6. Contours of nutrient, hydrographic and chlorophyll *a* data for transect E-E', Icy Strait.

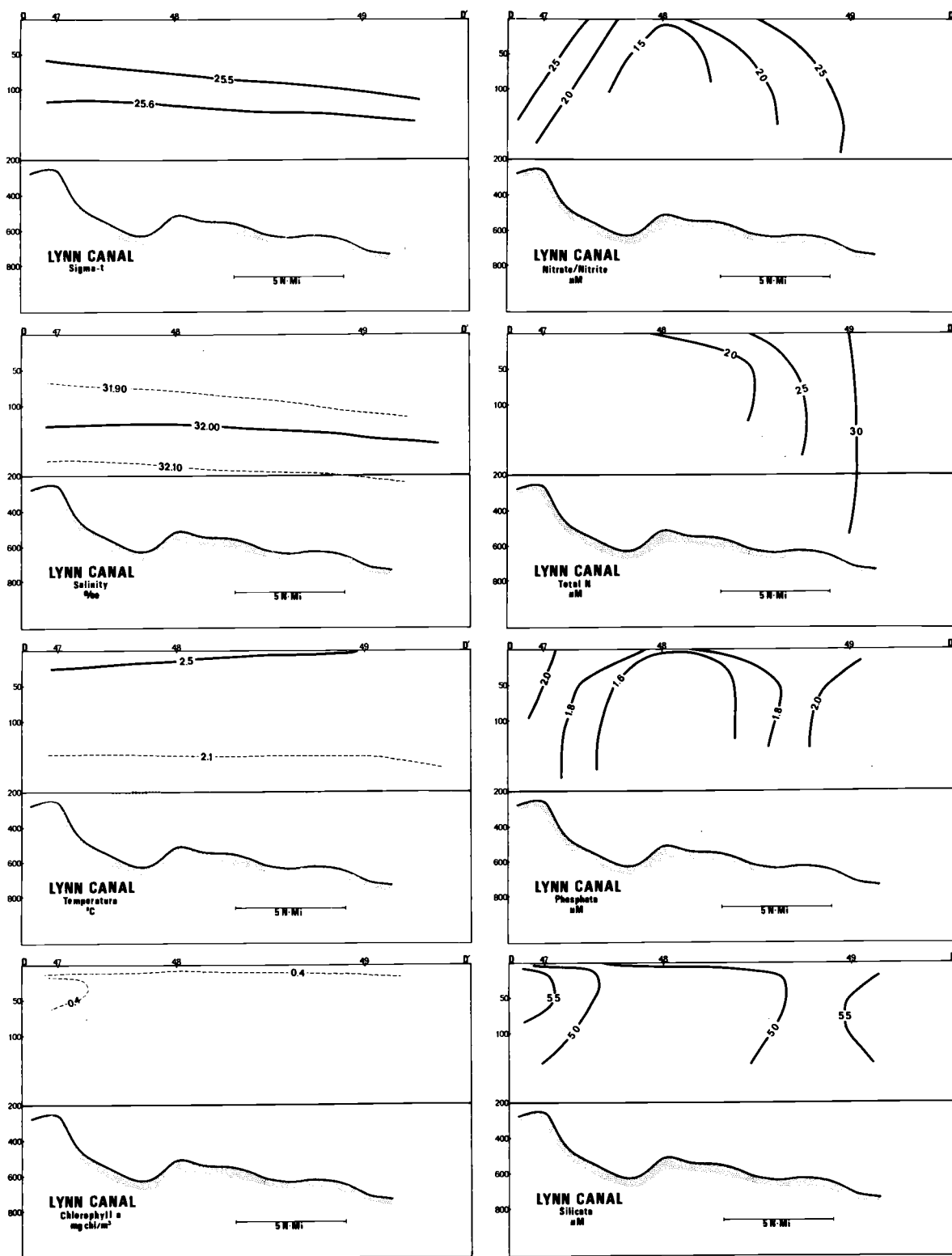


Figure 7. Contours of nutrient, hydrographic and chlorophyll a data for transect D-D', Lynn Canal.

### West Stephens Passage

Transect C-C' (Figure 8) is actually the northern end of Stephens Passage. This area has a mean depth of about 90m. A small area of topographically upwelled water is located around stations 44 and 46. This is evident in salinity, temperature, and sigma-t contours, and less evident in the nutrient contours. Station 45 and perhaps Auke Bay is the source of some low nutrient water below 10m.

### Gastineau Channel

Gastineau Channel (Figure 9) is a short, shallow stretch of water that branches NW off of Stephens Passage. It has a mean depth of less than 40m and drops off at its mouth to over 200m. Gastineau channel is closed at its northern end by mud flats during most of a tidal cycle. Juneau harbor, is located near its northern end (station 12), is probably one of the prime nutrient sources for this area.

### Sumner Strait

Sumner Strait, transect H-H' (Figure 10), has a mean depth of 240m and a maximum depth of 450m. Sumner is open to the ocean at its western end and the effect of ocean water can be seen in the increasing salinity and temperature at station 68. The saltier and slightly warmer ocean water moves into the strait below 50m and the fresher water

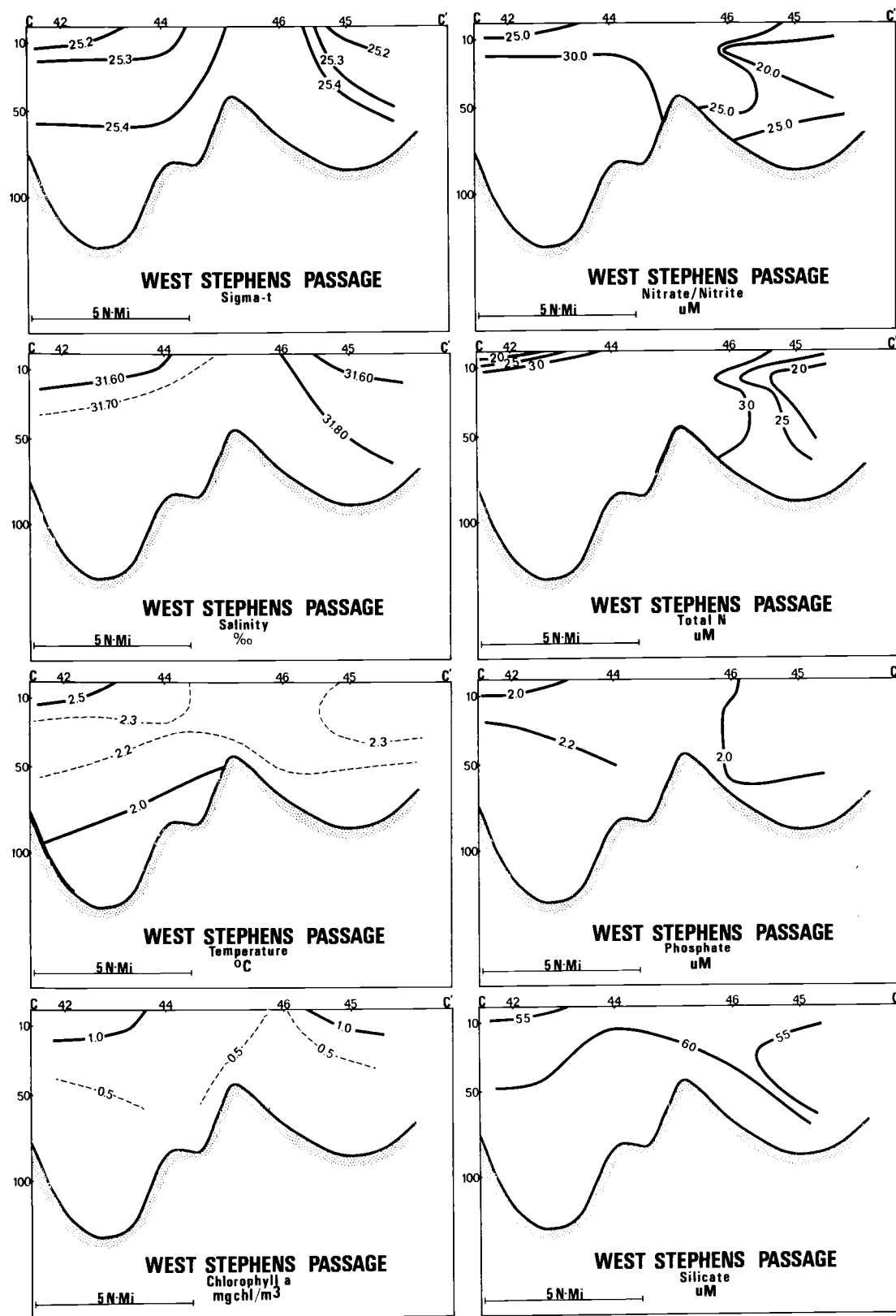


Figure 8. Contours of nutrient, hydrographic and chlorophyll *a* data for transect C-C', West Stephens Passage.

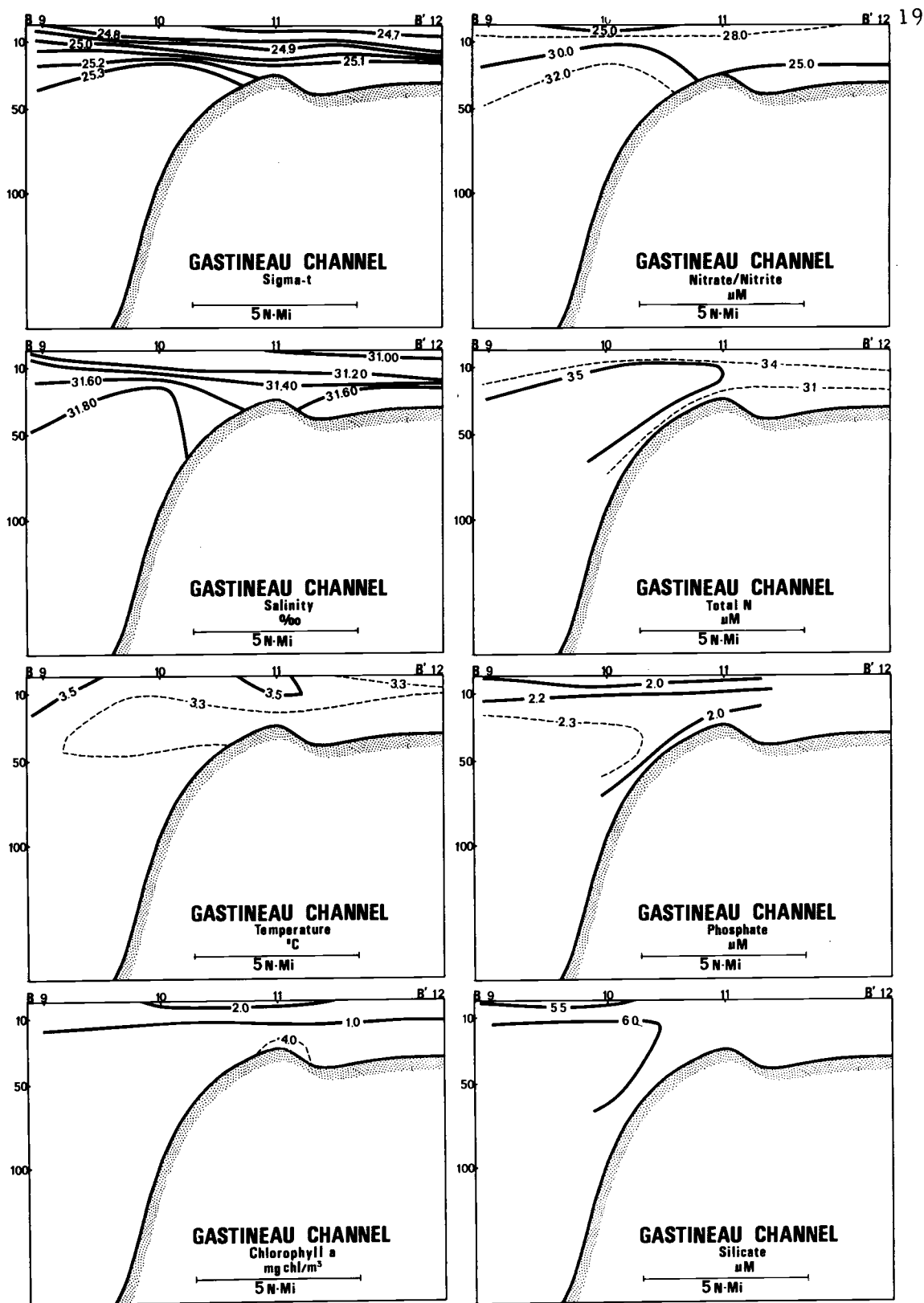


Figure 9. Contours of nutrient, hydrographic and chlorophyll a data for transect B-B', Gastineau Channel.

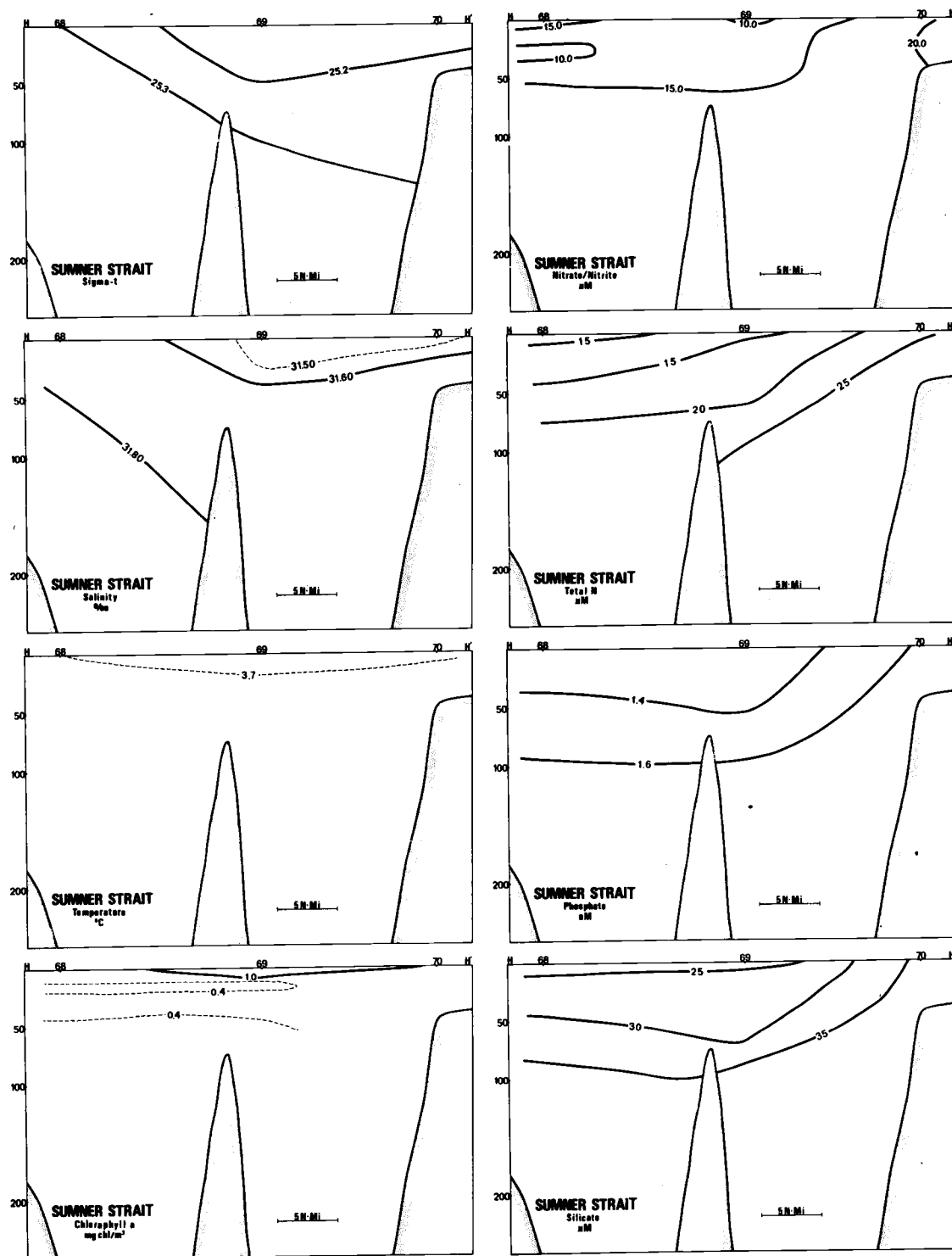


Figure 10. Contours of nutrient, hydrographic and chlorophyll a data for transect H-H', Sumner Strait.



moves out above 50m. This area is well mixed with an increase in salinity of only 0.3 o/oo down to 200m.

The nutrient contours follow a pattern similar to that of salinity and temperature. Nutrient concentrations are higher below 50m. The deeper concentrations are similar to those found at station 67.

Chlorophyll a data from Sumner Strait reveals only average amounts of biological activity.

## RESULTS II

### Properties

Generally what we observed during the cruise were initial oceanographic conditions as the spring bloom was beginning. The Inside Passage system was well mixed hydrographically, and the vertical differences observed in all parameters were small, except in Auke Bay (Kirk, 1972).

### Temperature

The winter conditions that still existed throughout most of the Inside Passage were reflected in the water temperatures. The maximum surface temperature (Table 1) was  $5.1^{\circ}\text{C}$  at station 74, while the minimum was  $2.1^{\circ}\text{C}$  at station 46. The greatest range in temperature, from the surface to 200m, was only  $1.1^{\circ}\text{C}$  at station 67.

Slight temperature inversions were observed in parts of Stephens Passage, Glacier Bay, Sumner Strait and Clarence Strait. Cold glacial runoff flowing over slightly warmer bottom water is the most likely explanation of these inversions. However, in the case of Clarence Strait it is also due to the influence of open ocean water.

Table 1. Maximum and minimum salinity and temperature values at surface for each transect. Also maximum range, surface to 200m. The enclosed number is the station where value was observed.

	SALINITY o/oo			TEMPERATURE °C		
	Max	Min	Range	Max	Min	Range
A-A'	31.86(5)	30.13(8)	1.71(8)	4.6(7)	2.4(2)	+1.6(6) *
B-B'	31.11(10)	30.90(12)	---	3.5(11)	2.4(12)	---
C-C'	31.81(46)	31.40(42)	---	2.6(42)	2.1(46)	---
D-D'	31.85(47)	31.79(49)	0.30(49)	2.5(47)	2.4(47)	-0.4(49)
E-E'	31.83(51)	31.79(50)	0.57(51)	3.0(52)	2.8(50)	-0.3(52)
F-F'	31.81(54)	30.59(59)	0.79(59)	3.0(54)	2.2(59)	+0.4(55)
G-G'	32.25(67)	31.83(61)	0.38(66)	4.4(67)	3.2(61)	-1.1(67)
H-H'	31.73(68)	31.47(69)	0.33(69)	3.7(68)	3.6(69)	+0.2(68)
I-I'	31.27(71)	31.17(72)	1.97(73)	5.1(74)	4.0(71)	+0.6(72)

\* + range indicates increasing temperature with depth.

### Salinity

Surface salinity values confirm that this was a time of minimum run off (Pickard, 1967) for most of the rivers. A minimum surface salinity (Table 1) of 30.13 o/oo was recorded at station 8, near the mouth of the Taku river. The maximum surface salinity, 32.25 o/oo, was observed at station 67.

### Sigma-t

Sigma-t values at the surface (Table 1) reached a maximum of 25.6 at station 65 and a minimum of 23.9 at station 8. The greatest range of sigma-t, between the surface and 200m, was 1.6 units at station 73. The minimum range over the same depth was 0.1 units at stations 63 and 68. Under the conditions of temperature (2-5°C) and salinity (30-32 o/oo) observed in the Inside Passage sigma-t values are most strongly influenced by changes in salinity.

### Oxygen

Only a few oxygen samples were taken, by bottle cast, from several deep, isolated basins (Table 2). The depth of these basins ranged from 325m to 785m and the oxygen values at these depths averaged 2.3 ml/L. The surface values at these same stations were 7.1 - 7.7 ml/L. The age of the water and the ventilation rate are unknown

but these areas could conceivably become anoxic (if water column stability continued or increased).

Table 2. Dissolved oxygen data from several deep basins.

Station	Depth (m)	O <sub>2</sub> (ml/L)
6	0	7.7
	50	6.6
	200	4.0
	325	2.3
49	690	2.1
59	112	6.9
	200	7.1
	287	7.0
63	200	7.1
	300	5.0
	600	2.5
	785	2.4

### Nutrients

For the non-conservative nutrients it would not be meaningful to report maximum and minimum surface values or ranges. They often passed through several maximums in the upper 100m. The contour maps (Figures 2 - 10) give a much better picture of nutrient distributions. Some general trends in the nutrients will be mentioned here. Slightly higher nutrient concentrations were observed in the eastern most transect (A-A') compared to another major transect, G-G'. This could be due to A-A' receiving a more thorough mixing because it is

shallower. Also conditions in G-G' are partly determined by open ocean water.

### Total Available Nitrogen

Throughout the areas surveyed the difference between TAN and nitrate + nitrite ranged from 2-13  $\mu$ M with the average closer to 4  $\mu$ M. By definition this difference includes ammonia, urea and dissolved amino acids. The 13  $\mu$ M difference was observed at the surface of station 8. Chlorophyll data from this station does confirm some biological activity in the upper 10m. However, the TAN, nitrate difference at stations 72 and 73 (also biologically active) was not significantly greater than average. Possibly this indicates that the bloom in the latter area was just getting started, with fewer dissolved organic compounds in the water.

### Chlorophyll a

Chlorophyll a data is presented as an indicator of primary biological activity. Samples were taken to 50m but in most cases this will encompass the photic zone and be an accurate indicator of primary production. The maximum surface value for chlorophyll a was 7.25 mg chl a/m<sup>3</sup> (station 72) while the minimum was 0.23 mg chl a/m<sup>3</sup> (stations 51, 52). The maximum in Auke Bay was 15 mg chl a/m<sup>3</sup>

(Kirk, 1972). During the summer of 1971 chlorophyll a averaged 25 mg/m<sup>3</sup> (Zakar, 1972). The overall average was very close to 1 mg chl a/m<sup>3</sup>. This is evidence that the productivity of the Inside Passage was not very great at the time of this cruise and that the spring bloom was just beginning.

## DISCUSSION

The word that best describes the Alaskan Inside Passage is dynamic. High tidal ranges, frequent winds, heavy land runoff and high precipitation characterize some of the events that influence water conditions in this area. A rugged topography carved by receding glaciers makes its presence felt on the physical character of the land. Even during the time of this cruise, a time when water conditions were mostly uniform, there were enough differences to make things interesting.

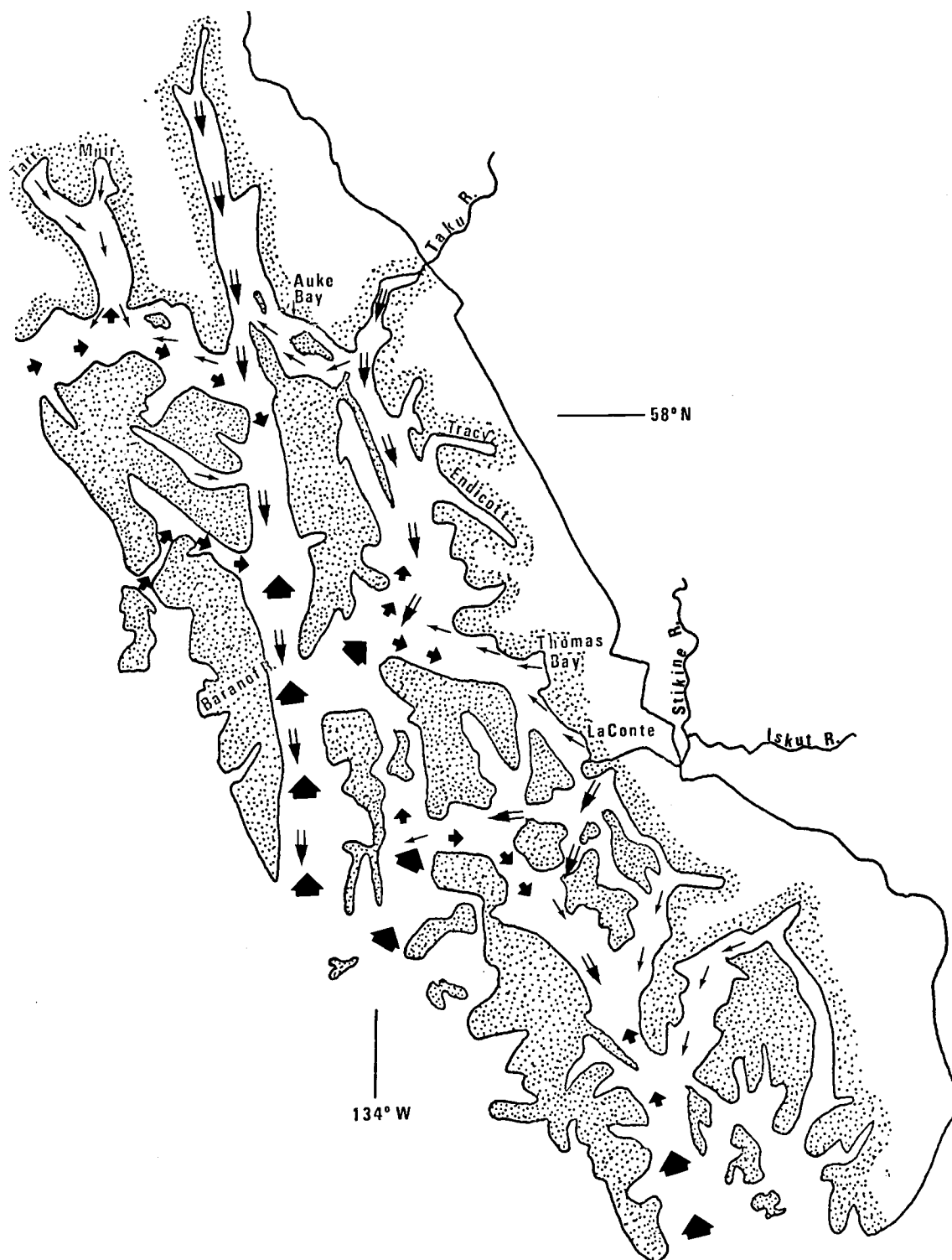
### Hydrography and Circulation

#### Circulation Control

Surface salinity data from this cruise and salinity information from Pickard (1967) were used to plot the influx of saltwater and the out flow of freshwater in the Inside Passage (Figure 11). This diagram is not intended to be a quantitative representation of transport. Its purpose is to present an easily read, semi-quantitative picture of the predominant fresh and saltwater sources and the most probable route these inputs take through the Inside Passage. The large solid arrows indicate major saltwater sources and the smaller solid arrows the minor saltwater sources. The major freshwater sources are indicated by the hollow arrows and the minor sources by the thin arrows.



Figure 11. Dominant patterns of flow in the Inside Passage due to saltwater and freshwater inputs. The large, solid arrows represent major sources of high salinity water; the small, solid arrows are minor sources of saltwater. Major freshwater inputs are marked by the hollow arrows and minor sources by the thin arrows.



As an input weakens, away from the source, major sources become minor sources.

The intrusion of saltwater up Chatham Strait is surprisingly strong. Freshwater coming out of Taku Inlet seems to split going into Stephens Passage and its influence is seen as far west as Lynn Canal. According to Pickard (1967), most of the freshwater coming out of the Stikine-Iskut rivers flows south. These surface flows are subject to the influence of winds, tidal currents, and increased runoff but the pattern shown is probably the predominant one.

### Major Areas

Fredrick Sound to Taku Inlet, Chatham Strait and Clarence Strait are the three areas that seem to dominate the Inside Passage, both in size and in their influence on water conditions. The first of these is one of the main channels for freshwater into the system and the other two are main sources of saltwater. The other areas surveyed are smaller, with interesting and in some cases unique features that contribute to the three major areas.

### Features of Specific Areas

#### Gastineau Channel

The sigma-t and salinity contours are well structured in the upper 40m (Figure 9) with a layer of fresher water at the surface,

probably the result of runoff. During a tidal cycle an exchange of water between Gastineau Channel and Taku Inlet can be expected. This exchange seems to take place below 10m. The chlorophyll data around station 10 and 11 are slightly higher than average at the surface. The lower nutrient and higher chlorophyll a values near the bottom of the channel may be the result of primary production.

Circulation patterns for the summer in Gastineau Channel have been described in a study done by the FWPCA (1966) in August of 1965. They suggest that the observed freshwater layer at the surface probably comes from Stephens Passage because there are so few local sources in Gastineau Channel. The exchange of water between Gastineau Channel and Stephens Passage is described as slow with input at the surface and output below 10m. For winter conditions they predict a reversal of this trend with a slight output at the surface and input at depth. The data in Figure 9 tends to support their prediction of an input below 10m during winter conditions.

### Glacier Bay

Pickard (1967) noted some distinctive conditions in the inlets with icebergs. He found low temperature and high salinity at the head of the inlet. A small range of sigma-t indicated less stability and more vertical mixing. He reported high O<sub>2</sub> at depth due to vertical mixing and low biological activity in the upper layers leading to low

oxygen demand from detrital material. Many of these same conditions were observed by us in Glacier Bay with the exception of higher salinities at the head. However, we noted very little ice during this cruise.

In general nutrients are somewhat lower in Glacier Bay (Figure 5) than in other parts of the Inside Passage. I think it is to be expected that glacial waters would be a poorer source of nutrients than land runoff. Muir Inlet is slightly higher in nutrients than that coming out of Tarr Inlet. The chlorophyll a data for stations 55-59 are slightly higher than average. A decrease in nutrients for these same stations may indicate a small amount of biological activity.

Once the water leaves Glacier Bay it can move in two directions depending on the tide and winds. An outgoing tide would take it west toward the ocean and an incoming tide would take it east into Icy and Chatham Straits. An incoming tide can also influence water conditions near the mouth of Glacier Bay, bringing water from Icy Strait into the bay. Station 54 was taken on an incoming tide.

### Distribution of Nutrient Properties

#### Nitrate

A comparison was made between deep nitrate + nitrite values within the Inside Passage and deep values from the stations nearest

the open ocean (Figure 12). There seems to be very little deep exchange of nitrate between station 60 and the inner stations. This is understandable because of the sill depth (60m).

Nitrate exchange between station 67 and stations within the Straits (66 and 68) seems to take place around 100m. Station 74 is not as typical of open ocean water as 67 because of its location. The only nitrate influence of station 74 on station 73 seems to be at 50m.

The stations as they are plotted in Figure 12 are oriented essentially North to South. The higher numbered stations being further south. Discounting a good deal of noise in going from station to station there seems to be, at all three depths, a tendency toward higher nitrate + nitrite values as one moves further north. If station 60 is omitted as not being a part of the Inside Passage the trend is even stronger. The northerly increase in nitrate is also evident in Figure 13, a contour of nitrate data. The strongest increase is noted north of station 65.

Nitrate + Nitrite and salinity values for all stations and all depth were regressed against each other to see if they might be correlated in some way. The resulting correlation coefficient (0.24) indicates that there is no statistical relationship between the two properties.

#### Preformed Nutrients

Calculation of preformed N and P in deep water (greater than

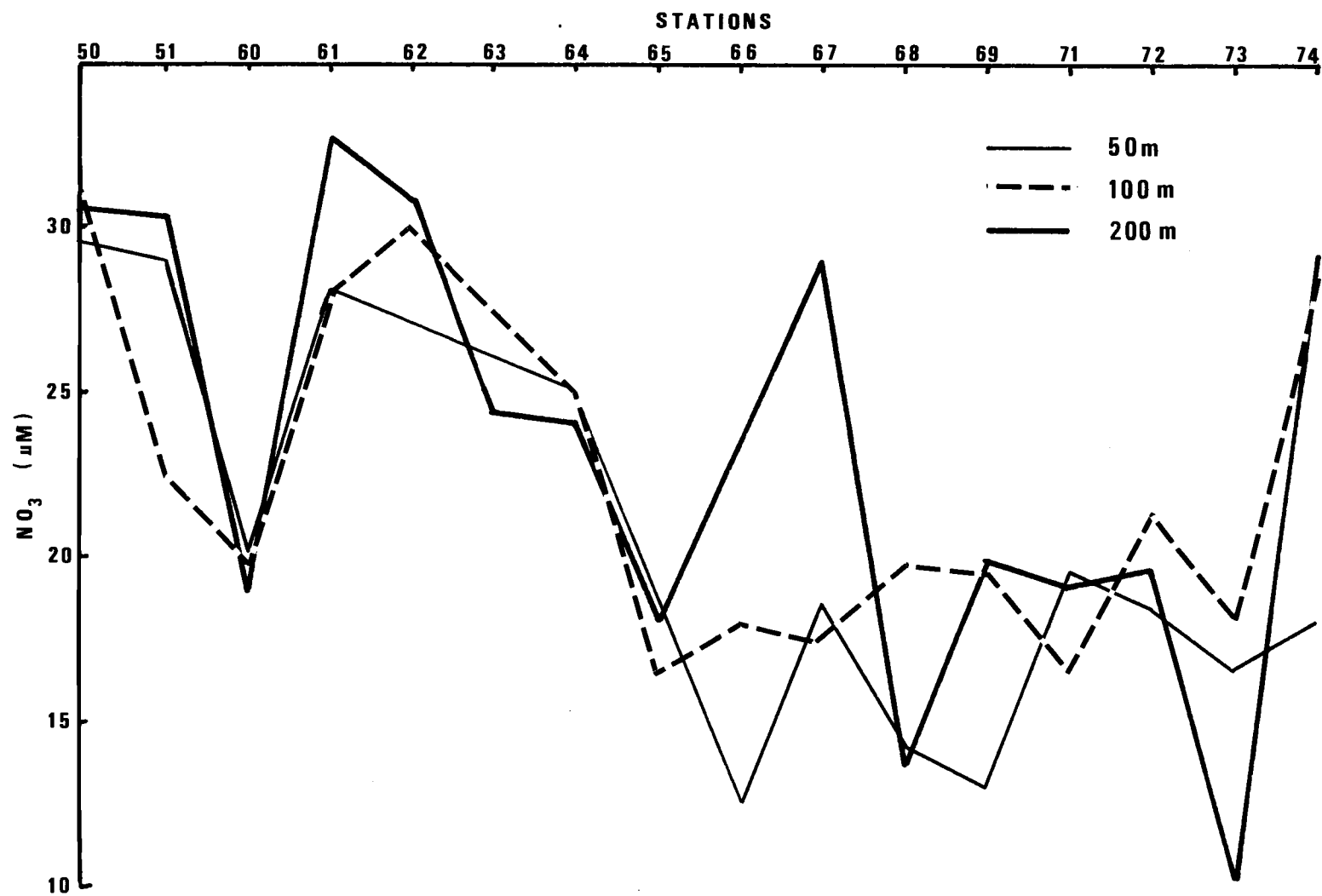


Figure 12. Comparison of deep nitrate + nitrite values from inside the Passage with open ocean water.

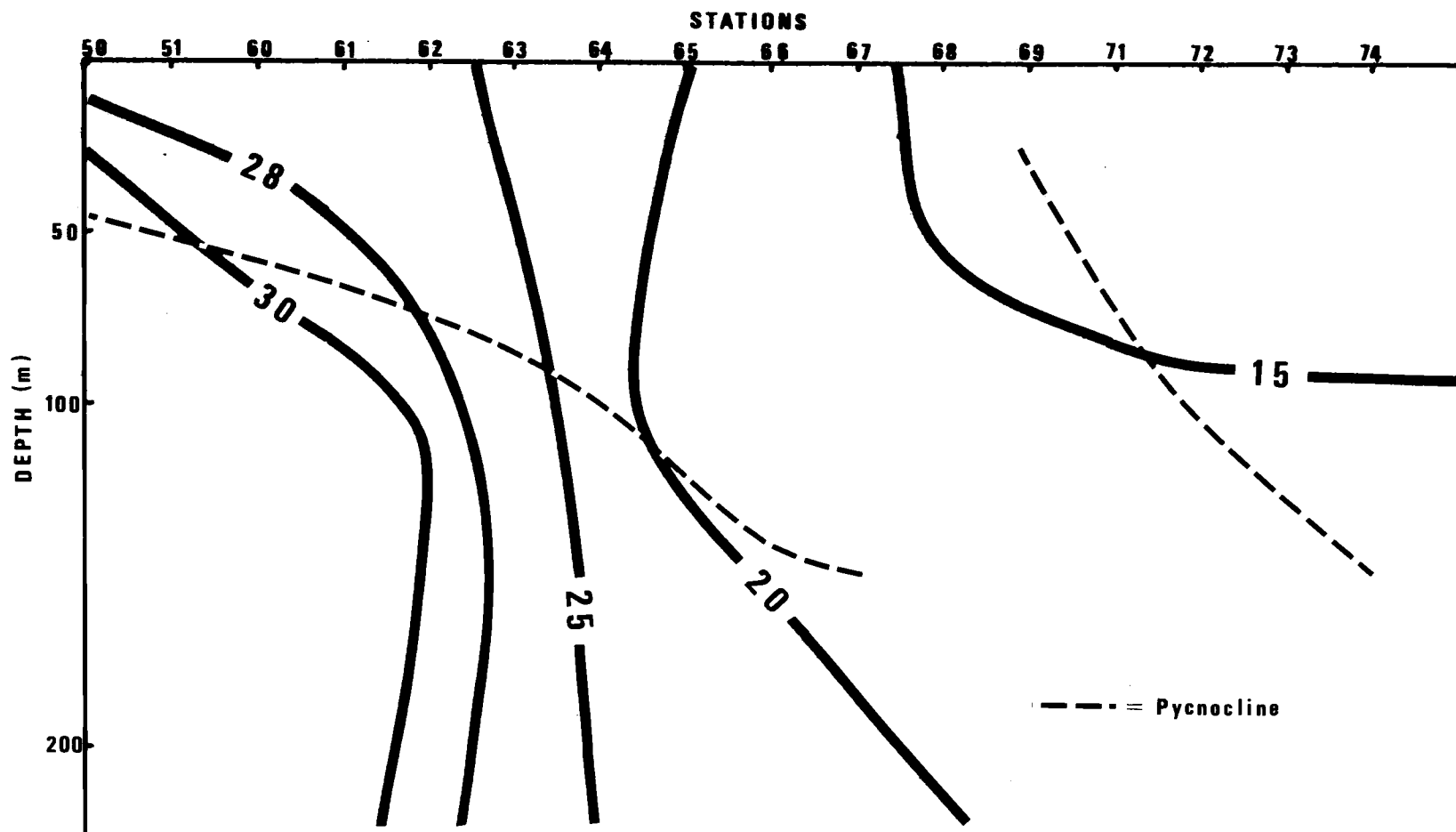


Figure 13. Contour of nitrate + nitrite data illustrating the northerly increase.



300m) averaged  $11.8 \mu\text{M}$  for N and  $1.06 \mu\text{M}$  for P. The largest concentration of preformed N and P was found at 200m at several places in the Inside Passage (Table 3). Below 200m the preformed nutrients decreased rapidly until at 600m the preformed N and P were 10.8 and  $0.91 \mu\text{M}$  respectively, or about 30% of the total N and P.

In several places the preformed nutrient concentrations above 200m were much greater than the oxidized nutrients. One possible explanation for this is that during the winter months preformed nutrients are supplied to the surface waters by land runoff. If the Inside Passage were mixed down to 200m this would account for the high preformed nutrients above 200m. Below 200m oxidized nutrient concentrations become much greater than preformed. This could be due to organic matter raining out of the upper layer and decomposing below 200m. Low oxygen values below 200m tend to support this idea. Additional data will be necessary to clear up this point.

#### Biologically Related Features

The N : P ratios for some of the deeper stations, as determined from nitrate + nitrite and phosphate have an average of 14 : 1 (Table 3). This is slightly less than the widely accepted value of 16 : 1 (Redfield, Ketchum and Richards, 1963), but quite similar to the 11.9 to 13.9 : 1 found in the San Juan channel by Phifer and Thompson (1937).

Table 3. Nitrogen, TAN, Silicon and Phosphorus ratios for surface and deep water at selected stations throughout the Inside Passage. Also preformed N and P for those stations where O<sub>2</sub> data was available.

Sta.	Depth (m)	N	:	TAN	:	Si	:	P	N <sub>p</sub> μM	P <sub>p</sub> μM
6	0	14		15		26		1		
	200	14		14		26		1	17.2	1.46
	325	13		13		27		1	11.4	1.26
8	0	12		20		32		1		
46	0	15		17		28		1		
56	0	13		14		18		1		
	200	12		14		24		1	18.3	1.55
59	0	12		15		25		1		
	200	13		14		23		1	23.2	1.82
61	0	14		--		27		1		
	540	15		--		28		1	13.1	1.01
63	0	14		--		26		1		
	160	14		--		25		1	21.9	1.64
	600	15		--		27		1	10.8	0.91
72	0	11		16		22		1		
	200	14		17		25		1		
73	0	6		10		17		1		
	200	8		15		21		1		

It seems reasonable that Redfield's ratios would not hold completely in areas where local conditions such as the proximity of land, the inflow of rivers, and local flora and fauna may change the picture. It is interesting to note however, that if the N : P calculations are made using TAN and phosphate an average of 15 : 1 is obtained.

In areas showing some biological activity (station 72 and 73) the N : P ratios from nitrate and phosphate decrease, indicating that nitrate could become limiting. However, the ratios obtained from TAN and phosphate remain quite high (Table 3).

Silicate is not a universal requirement of living matter, however, it is present in large quantities in the tests of diatoms, which dominate the phytoplankton in cooler waters. Richards (1958) found a linear relationship in the changes in the concentration of silicate and phosphate in the Western Atlantic. He obtained an Si : P ratio of 15 : 1 or about the same as nitrogen. The two biologically active areas observed during this cruise had quite different Si : P ratios. At station 8 the ratio was 32 : 1 (Table 3) at the surface. This high ratio could reflect a large concentration of silicate being dumped into the area by the Taku river. This area had the highest silicate values observed. Station 73, the other biologically active area, had Si : P ratios of 17:1 at the surface. This approaches Richards value and indicates that silicate could reach a limiting concentration.

From the Si : TAN : P ratios discussed above it would appear that at station 8 nitrogen will eventually become the limiting nutrient. At station 73, however, silicate will probably be limiting.

### TAN vs. Nitrate

The measurement of TAN rather than nitrate seems to have distinct advantages in regard to the photosynthetic potential of an area. When measuring initial conditions TAN values give a more accurate N : P ratio and a better estimate of the nitrogen pool. This permits assessment of the limiting nutrient, if any, and the potential fertility of an area. Measurement of TAN during a bloom gives a more accurate picture of the nitrogen available to the phytoplankton. N : P ratios using nitrate may decrease during a bloom while ratios calculated from TAN may remain quite high (Table 3).

### Phytoplankton Bloom Areas

Two areas outside of Auke Bay gave evidence that spring phytoplankton blooms were in progress. Those two areas, Taku Inlet and Clarence Strait, seem to suggest that blooms were initiated by stabilization of the water column, in accordance with the critical depth concept of Sverdrup (1953). In the case of Clarence Strait stabilization brought on by warming produced the mixed depth necessary to initiate the bloom. In Taku Inlet density differences due to freshwater input could have established the mixed depth and triggered the bloom.

### Potential Fertility

Harvey (1947) suggested that the potential fertility of natural waters may be determined from the total phosphorus or total combined nitrogen.

The potential fertility was defined by Redfield, Ketchum and Richards (1963) as the quantity of organic matter which could be produced by photosynthesis from a unit volume of seawater if it was brought from depth to the surface and illuminated there until the limiting nutrients were exhausted.

Station 46 was selected to make a calculation of the potential fertility of the Inside Passage. This station is of a reasonable depth that might allow all the nutrients to reach the photic zone. Nitrate was assumed to be limiting and by using Redfield's ratios an average parcel of water was found to be capable of producing  $2.18 \text{ g C/m}^3$ . This compares favorably with the theoretical value of  $2.74 \text{ g C/m}^3$  calculated by Redfield et al. (1963). Carrying the calculation one step further we can determine that the potential fertility of the entire water column is  $386 \text{ g C/m}^2$ . Ryther (1960) has estimated that the phytoplankton of the oceans as a whole contain  $3 \text{ g C/m}^2$ . The estimate of potential fertility serves only to indicate the maximum production that could occur in the photic zone during the year.

This estimate is made assuming no recycling of the available nutrients. If recycling were considered this estimate might be increased several fold. Other factors that tend to decrease this theoretical estimate are losses due to grazing, respiration and sinking from the water column. The actual production for this area can be expected to be much less than this theoretical estimate.

## SUMMARY

1. During the time of this cruise the Inside Passage was well mixed to at least 200m. Spring phytoplankton blooms were just beginning in a few areas.

2. Of the nine areas surveyed three stand out as being most important in setting the nutrient conditions in the Inside Passage. The three areas are Fredrick Sound to Taku Inlet, Chatham Strait and Clarence Strait. Perhaps because of their size these three areas tend to dominate the circulation in the Inside Passage. The other areas are smaller with particular features that contribute to the three major areas.

3. The importance of localized effects in determining water conditions in the Inside Passage should not be overlooked. Some of the local effects found to be important are: land runoff, glacial melt, input from hot springs, bottom topography, tides and winds.

4. The most important of the local influences seems to be input of open ocean water. The input of saltwater up Chatham Strait is surprisingly strong. The circulation of the Inside Passage seems to be controlled by the input of fresh and saltwater.

5. Some of the deep isolated basins in the Inside Passage may become anoxic if the water column stability increases with the onset of warmer weather.

6. Phytoplankton blooms in the Inside Passage are probably initiated by stabilization brought on by warming. The southern areas are most likely to warm up first and therefore should be the first areas to have blooms.

7. Nitrate is probably the limiting nutrient in most areas of the Inside Passage. The N : P ratios were very similar to Redfield's values (16 : 1) and the ratio decreased in the few areas that had biological activity. TAN may be a better predictor of photosynthesis than nitrate. TAN : P ratios tend to remain high during photosynthesis.

8. Slightly higher nutrient concentrations were observed in the eastern most transect (A-A') compared to the western most transect (G-G'). There was also a slight tendency for nitrate + nitrite concentrations to increase as one moved north.

9. Glacier Bay exhibited many of the same conditions that Pickard (1967) observed in his "iceberg" inlets (i. e. low temperatures, small sigma-t range and high O<sub>2</sub> at depth).

The data presented here are only the beginning to what, it is hoped, will be a more comprehensive look at nutrient properties in the Inside Passage. Additional cruises to these same areas, at other times of the year, will be necessary to enlarge the nutrient picture. Two cruises for 1972 are already in the planning stages.

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## APPENDIX

## APPENDIX I

AN AUTOMATED TECHNIQUE FOR THE ANALYSIS OF TOTAL  
AVAILABLE NITROGEN BY ULTRAVIOLET OXIDATIONIntroduction

Dissolved inorganic nitrogen compounds in seawater, such as nitrate, are often analyzed because in most marine situations these are the most abundant. However, with the increased interest being shown in organic nitrogen compounds as nutrient sources for phytoplankton (Bruce, 1969; Guillard, 1963; Griffiths, 1965) nitrate values alone do not always provide the biological oceanographer with an adequate picture. A more useful measurement would be total available nitrogen (the total of all forms of nitrogen in sea water that can be utilized as a nutrient source by phytoplankton). This should include nitrate, nitrite, ammonia and any amine or amide containing compounds (e. g. dissolved amino acids) that phytoplankton can utilize. Total available nitrogen (TAN) is a biologically meaningful measurement since phytoplankton can use all of these sources equally well, although they do show a thermodynamically directed preference (Harvey, 1940).

One means of obtaining total available nitrogen values would be to measure each form separately and sum them. This is within present methodology. However, replacing four or five methods with a single

one would mean a great savings in equipment and time. This is most important if a sea-going method capable of giving real-time data is sought.

The only method I found that seemed to satisfy the single-method criterion for TAN was the ultraviolet oxidation technique of Armstrong, Strickland and Williams (1966). High-intensity UV radiation is used to oxidize reduced forms of nitrogen compounds (ammonia, amino acids, etc.) into nitrate and nitrite. The original nitrate and nitrite content of the sample remains relatively unchanged during radiation. The result is that the total nitrogen content of a sample is in inorganic forms (nitrate and nitrite) that can be easily analyzed by colorimetric techniques (Wood, Armstrong and Richards, 1967).

There is a major drawback to the original method. The radiation time recommended by Armstrong et al. (1966) is three hours for 12 samples. This is far too slow for a method designed to provide real-time data at sea. I have worked on this method with two objectives in mind. To reduce the radiation time as much as possible and to automate the method for use with a Technicon® AutoAnalyzer®.

## METHODS AND MATERIALS

The method is basically that of Armstrong, Strickland, and Williams (1966). The one important difference is the use of a continuous coil of small diameter (2mm i.d.) quartz tubing in place of the discrete sample tubes (Figure A1). Use of the continuous coil makes the nitrate + nitrite analysis readily adaptable to the Technicon® AutoAnalyzer® (Figure A2). After oxidation of the ammonia (and most amine containing compounds) to nitrate and nitrite, samples were analyzed according to the method of Wood, Armstrong, and Richards (1967) as adapted to the AutoAnalyzer® by Atlas et al. (1971).

The ultraviolet source is a 1200 watt lamp (189A, Hanovia Lamps) utilizing a 550 VAC power source (supplied by Hanovia). The UV system is cooled by a 100 cfm blower and the lamp is shielded with a quartz tube to prevent over-cooling, as suggested by Armstrong et al. (1966).

Sampling is at the rate of 0.42 cc/min for seven minutes. The initial standard is usually run for eight minutes and the final ASW blank about 10 minutes (i. e. when large differences in concentrations are expected sampling time is increased). This sampling rate permits 7-8 samples per hour with standards being run every 10 samples and blanks every 20 samples. Prior to entering the UV system samples are filtered through glass fiber paper and three percent hydrogen peroxide is added (0.015 cc/min.), as an oxygen source.

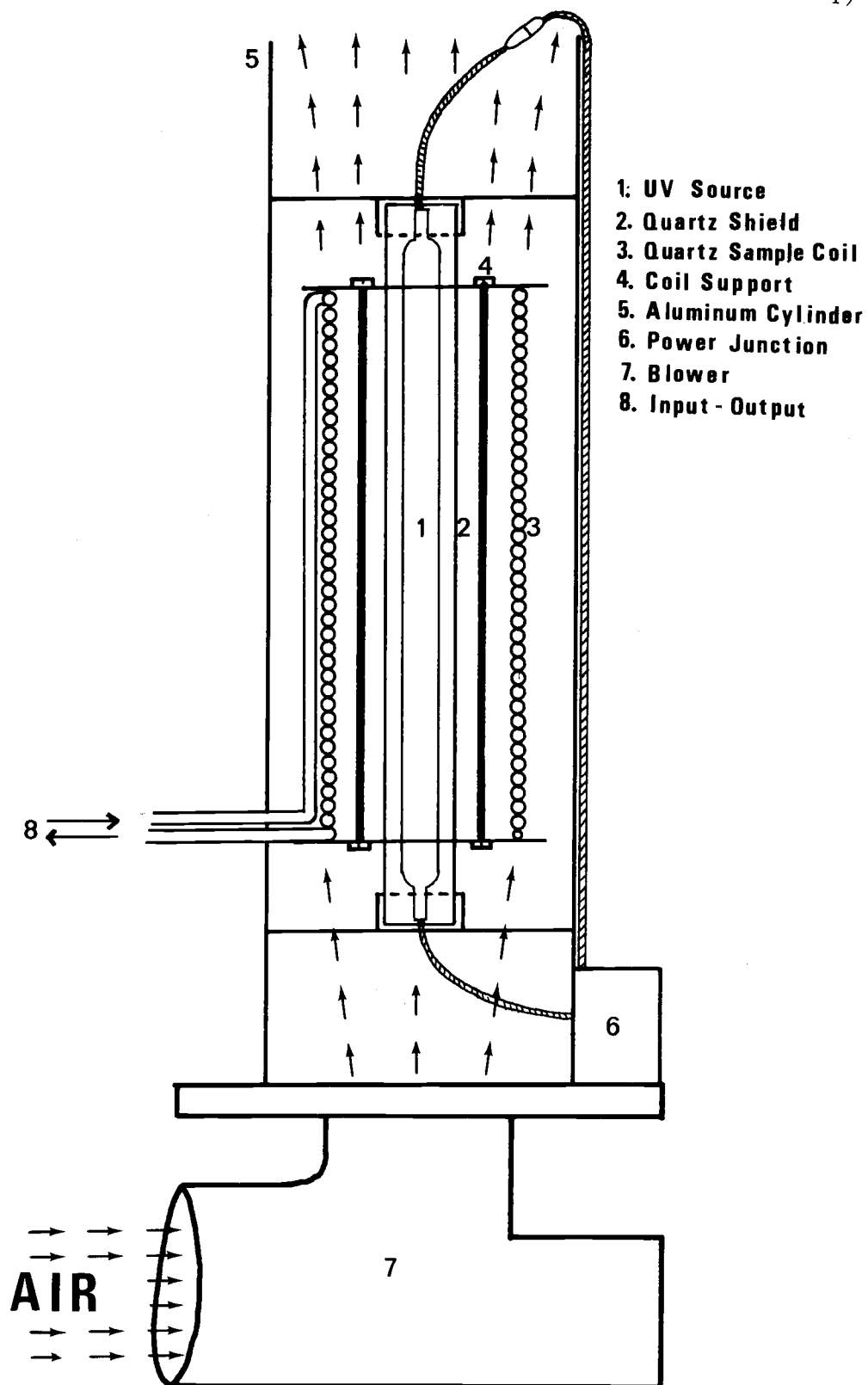


Figure A1. Physical layout of continuous UV system.

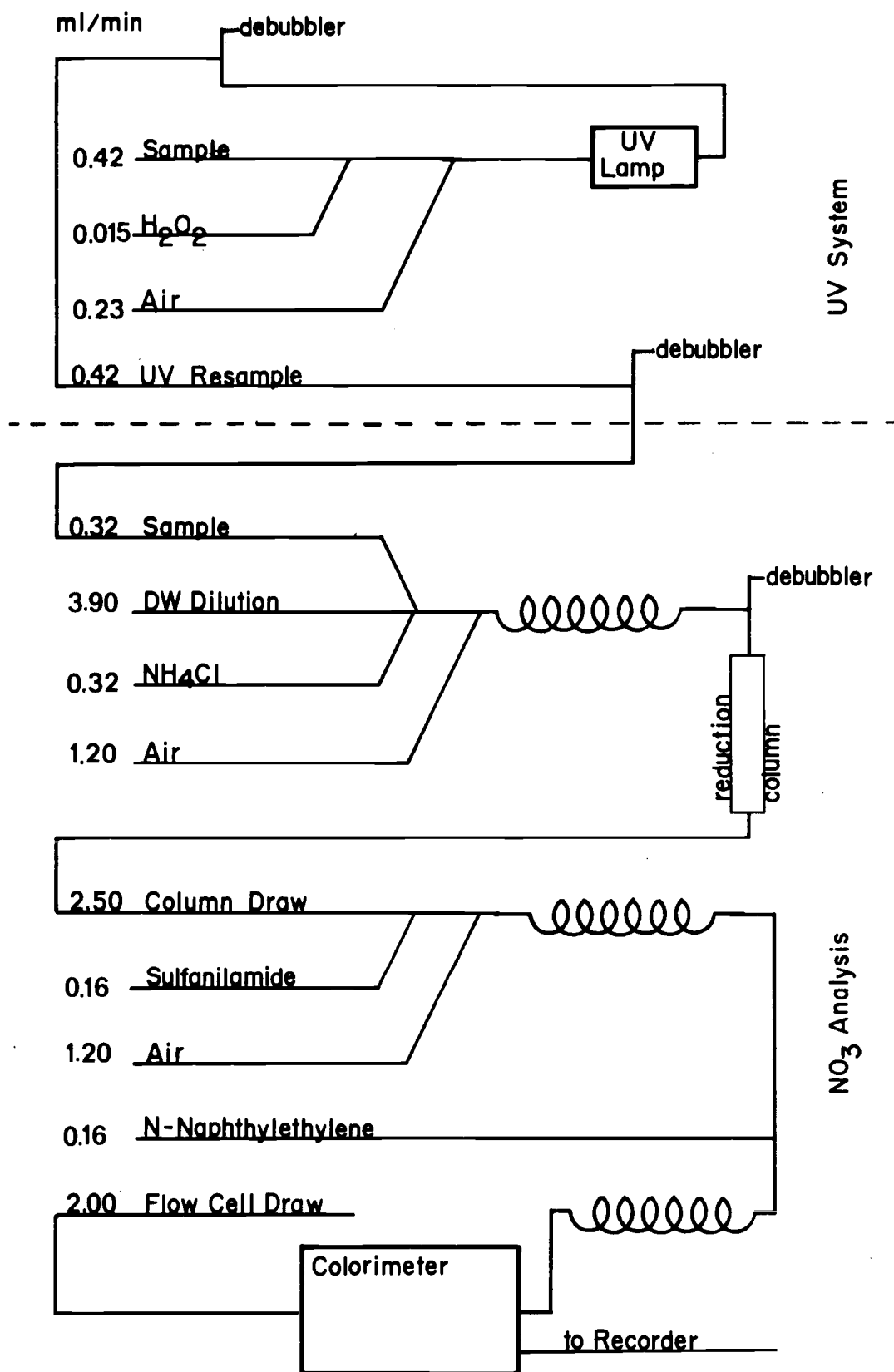


Figure A2. Interfacing of UV system with automated nitrate analysis.



## RESULTS

A wide range of AutoAnalyzer® pump tubes are available (0.015 cc/min. to 3.90 cc/min.) (i.e. a wide range of residence times). However, the volume requirements of the nitrate + nitrite analysis dictate some limitations on the pumping rates that can be used in the UV system. The volume of sample coming out of the UV system cannot be less than the sampling tube going into the nitrate + nitrite analysis. Three different pumping rates were tried in the UV system (Table A1). The resulting residence times were 60, 80 and 110 minutes. The recovery of the different standards was about 3% better for the 80 minute residence time than for 60 minutes. The concentrations in Table A1 are calculated using an F-factor determined from a nitrate standard as suggested by Strickland and Parsons (1968). These calculations indicate that even at 80 minutes the oxidative process is not yet complete. Manny, Miller and Wetzel (1971) have suggested that in seawater samples it is the oxidation of ammonia to nitrate and nitrite that requires the most time.

From the above results one would expect the 110 minute residence time to give an even better percent recovery. However, the recovery for this residence time was the lowest of the three. In order to obtain this residence time the nitrate + nitrite analysis had to be altered to accept a smaller volume. These changes may have altered

Table A1. Recovery of four different standards at three different residence times. A=16  $\mu\text{M}$   $\text{NO}_3$ ; B=24  $\mu\text{M}$   $(\text{NH}_4)_2\text{SO}_4$ ; C=10  $\mu\text{M}$  glycine; D=8  $\mu\text{M}$   $\text{NO}_3$  + 12  $\mu\text{M}$   $\text{NH}_3$ . Each value is an average of 3 samples.

STD.	60 Min.		80 Min.		110 Min.	
	Conc.	% Recovery	Conc.	% Recovery	Conc.	% Recovery
A	15.4*	96	15.6	97	14.7	92
B	20.6	86	21.4	89	19.4	81
C	9.3	94	10.0	100	8.0	80
D	17.9	89	18.1	91	16.8	84

\* Calculations were made using a non UV treated  $\text{NO}_3$  standard.

the linearity of the analysis. Also, the longer the residence time the more difficult it becomes to maintain sample integrity.

After determining an optimum residence time several known concentrations of different amino acids and one mixed solution were tested in the UV system. The percent recovery of all the amino acids and the mixture (Table A2) was 95-100 with the exception of arginine (86%). The structure of arginine might be expected to make it more difficult to decompose. Armstrong, Strickland, and Williams (1966) reported some difficulty in recovering urea. No similar difficulty was encountered using this UV system. Eight  $\mu\text{M}$  urea gave a 95% recovery.

There is a tendency for sample to sample boundaries to become mixed as they pass through the UV system. This leads to a somewhat poorer response time when compared to samples that pass only through the nitrate analysis. However, the system does give a linear response

Table A2. Percent recovery at 80 minutes residence time.

N Containing Compound	Concentration $\mu\text{M}$	% Recovery
$(\text{NH}_4)_2\text{SO}_4$	12	100
$(\text{NH}_4)_2\text{SO}_4$	16.5	100
$(\text{NH}_4)_2\text{SO}_4$	24	90
Glycine	12	100
Urea	8	95
Aspartic Acid	12	100
Proline	10	100
Arginine	8	86
Mixture	16*	95

\* 4  $\mu\text{M}$  Proline + 4  $\mu\text{M}$  Arginine + 4  $\mu\text{M}$  Aspartic Acid

over a suitable concentration range. A linearity test for  $(\text{NH}_4)_2\text{SO}_4$  over a concentration range of 3 to 40  $\mu\text{M}$  was performed (Figure A3) as was one for glycine over a range of 5-30  $\mu\text{M}$ .

A departure from linearity for glycine occurs at the higher concentrations (about 12% at 30  $\mu\text{M}$ ) (Figure A3). I am convinced that the reason for this departure is an insufficient supply of  $\text{O}_2$  rather than too short of an exposure to UV radiation.

One of the problems encountered was maintaining a good bubble pattern through the UV system. I finally concluded that it would be impossible to keep an integral bubble pattern in a sample that was being slowly pumped through 24.4 meters of 2mm tubing while being subjected to intense heating and gas generation. The best that could be hoped for was to keep the samples separated without using an excessive volume of sample. Although the bubble pattern emerging from the UV system was very irregular I found that a sampling time of seven minutes was sufficient to produce a good plateau on the recorder.

The residence time is largely controlled by the pump tubes used (both air and sample tubes must be considered). However, the small volume of the quartz coil (60ml) makes the residence time particularly susceptible to volume changes. For example, the expansion of the air segments as they pass through the UV system are enough to change the residence time considerably. Once the system reaches thermal equilibrium, the residence time will become constant but changes in

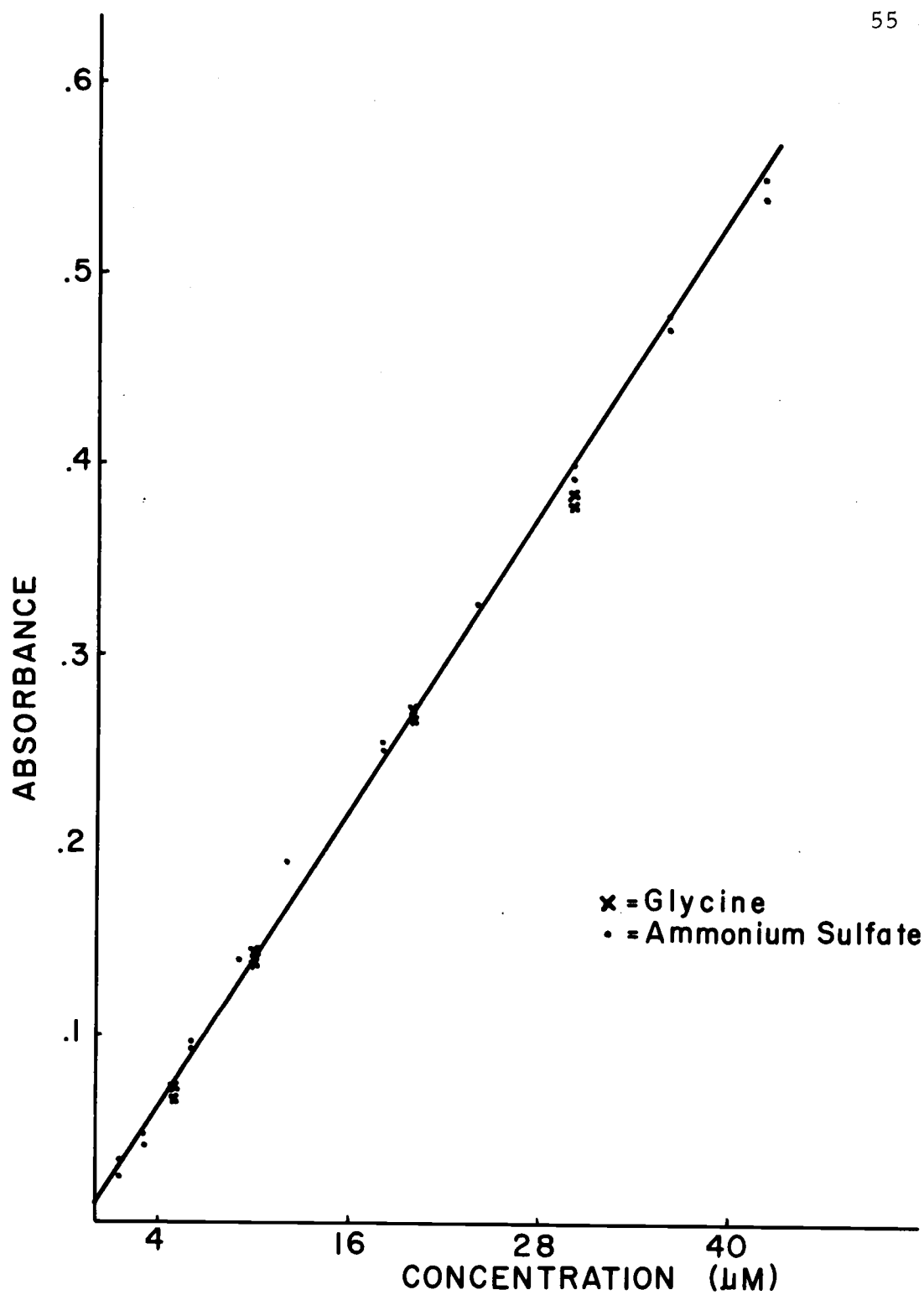


Figure A3. Linearity test for  $(\text{NH}_4)_2\text{SO}_4$  and glycine.

ambient temperature can change this equilibrium. At least a 30 minute warm up time is recommended.

The generation of gas within the UV system can also have a drastic effect on the residence time. Because of this I found it necessary to use only a 3%  $\text{H}_2\text{O}_2$  solution rather than the 30% used by Armstrong, et al. (1966).

The freshness of the  $\text{H}_2\text{O}_2$  solution also needs to be considered. Over a (long) period of time a 3% solution of  $\text{H}_2\text{O}_2$  will deteriorate. This will change both the oxidative power of the  $\text{H}_2\text{O}_2$  and the residence time of the sample.

Table A3. Percent recovery of glycine.

Conc. ( $\mu\text{M}$ )	Recovered Conc.	% Recovery
5	5.0*	100
10	9.8	98
20	18.7	93
30	26.3	88

\* Calculations based on F-factor of 5 uM glycine

## DISCUSSION

A small diameter sample circulating around and in close proximity to the UV source provides a continuous sample stream readily adaptable to automated analysis. It has the added advantage of reducing the time required for oxidation of amine and amide containing compounds. By varying the pumping rate through the quartz coil the residence time of the sample can be controlled.

Automating the photo-oxidation technique for analyzing total available nitrogen has increased the sampling rate considerably. Armstrong et al. (1966) required more than three hours to analyze 12 samples. Using the automated technique described here it is possible to analyze 24 samples plus blanks and standards in three hours. Being a continuous system this rate is constant. Although this rate does not approach the rates now possible for nitrate, phosphate and silicate (Atlas et al., 1971) it is rapid enough to be useful at sea. The system is portable and rugged enough to be safely taken to sea. The system described here was tested at sea during April of 1971 with very satisfactory results (see thesis text).

The insufficient supply of  $O_2$  noted in the glycine linearity test seems also to be the explanation of the lower recovery (90%) of  $24 \mu M$   $(NH_4)_2SO_4$  (Table A2). The glycine curve was obtained using the present UV system where 3%  $H_2O_2$  is added at 0.015 cc/min. The

recovery of the  $24 \mu\text{M } (\text{NH}_4)_2\text{SO}_4$  was determined using the same system. The  $(\text{NH}_4)_2\text{SO}_4$  linearity test (Figure A3) and the other recoveries of amino acids (Table A2) were obtained using a system in which one drop of 30%  $\text{H}_2\text{O}_2$  was added to 60 ml of sample, by hand, before introducing it into the UV system. Apparently the diluted  $\text{H}_2\text{O}_2$  does not supply sufficient  $\text{O}_2$  to oxidize the higher concentrations.

I would suggest trying oxygen gas in place of air as the segmenting agent in the UV system. The oxygen would replace the  $\text{H}_2\text{O}_2$  as the oxidizing agent. This should provide a more adequate source of  $\text{O}_2$  atoms since  $\text{H}_2\text{O}_2$  tends to be destroyed fairly rapidly by UV radiation (Manny, et al., 1971).

Although automation of this technique and reduction of radiation time have been accomplished there are several areas that I feel deserve additional research. Armstrong and Tibbets (1968) reported little success with photosensitizers. However, they tried only a few while using a lower intensity lamp. The application of the right photosensitizing compound could reduce the residence time further.

Anything that could be done to improve the efficiency of the system would be useful. Perhaps using a double layer sample coil might improve the absorption of UV radiation. Also polishing the inside of the aluminum cylinder might increase the UV radiation reflected back towards the sample coil.



The sampling rate presently being used (0.42 cc/min.) is almost too slow for the nitrate analysis system. Using a double coil might make it possible to increase the sample flow rate (giving a smoother flow through the system and better sample separation) and yet decrease the sampling time (which effectively increases the number of samples per hour).

Since total available nitrogen is a biological parameter we must know how well this method performs in "real life." All the data for the development of this technique came from ammonia salts and prepared amino acids. The next step is to use the automated TAN method in a nitrogen budget experiment with an algal culture.

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