Environmental Assessment of the Alaskan Continental Shelf

Annual Reports of Principal Investigators for the year ending March 1978

Volume VIII. Contaminant Baselines

U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration

U.S. DEPARTMENT OF INTERIOR
Bureau of Land Management

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Outer Continental Shelf Environmental Assessment Program
Boulder, Colorado

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U.S. DEPARTMENT OF COMMERCE
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DISCLAIMER

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CONTAMINANT BASELINES

Contents

ANNUAL REPORT

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QUALITY ASSURANCE PROGRAM FOR TRACE HYDROCARBON ANALYSIS

Research Unit #43

Reporting Period

April 1, 1977 - March 31, 1978

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April 1, 1978

I. Task Objectives and Conclusions

The task reported herein relates to serving as a quality assurance laboratory for hydrocarbon analyses of marine waters, sediments and tissues. Results to date have shown that there is an urgent need for a strong quality assurance program within the Outer Continental Shelf plan. This need has been illustrated by the results of the sediment and tissue intercomparisons conducted by the National Bureau of Standards (NBS) during the past year.

II. Introduction

A. Scope of Study

This program is being undertaken to insure the analytical integrity of hydrocarbon analyses performed by NOAA laboratories and NOAA contractors.

B. Specific Objectives

This objective is being met by: (1) conducting an interlaboratory comparison study on samples of *Mytilus* homogenized by NBS; (2) acting as a consultant laboratory to other NOAA P.I.'s involved in hydrocarbon analysis.

C. Relevance to Problems of Petroleum Development

The chemical data reported to NOAA originates from several different laboratories. It is imperative that these data be uniform in quality so that there is a basis for intercomparibility of the data produced by different laboratories. Until such a time as certified Standard Reference Materials are available, a quality assurance (control) function is essential to maintain data integrity as described above.

The program at NBS impacts upon the following NOAA tasks:

A-33 -- Determination of total content and chemical species of hydrocarbons in the water column, in selected marine organisms, in sea ice and in the sea ice-water interface.

B-8 -- Examine the processes which determine the fate of hydrocarbons introduced into the environment.

B-14 -- Develop means to predict possible interactions between ice and oil and other contaminant discharges.

III. Current State of Knowledge

Due to the lack of readily available Standard Reference Materials and intercalibration samples, a concerted laboratory intercomparison program must be maintained. This year's program at NBS showed that different laboratories analyzing the same Alaskan sediment yielded results differing in some instances by more than a factor of 10.

IV. Study Areas

N/A

V. Source Methods and Rationale of Data Collection

N/A

VI. Results and Conclusions

A. Results of the Second Sediment Intercomparison

The experimental results of the study are summarized in Tables I and II. The methods used by each laboratory are summarized in Table III.

Statistical analysis of the second intercomparison sample gave the same results as the first intercomparison sample: the values do not belong to the same population. The ranges reported for various parameters indicate that values differing by as much as a factor of 10 (1000%) did occur in this intercomparison study. This observation is alarming since the sediment sample used in this study has a hydrocarbon burden many times higher than samples normally analyzed by the laboratories participating in Outer Continental Shelf baseline studies.

A more complete discussion of these results is contained in the July - September 1977 Quarterly Report.

B. *Mytilus* Intercomparison Study

Progress on the *Mytilus* intercomparison study is summarized in the quarterly report for the period of January - March 1978.

IX. Needs for Future Study

It is obvious from the discussion of the intercalibration exercise that a quality assurance program must continue to be an integral part of the NOAA hydrocarbon program, even if only to continue demonstrating at what level of difference chemical results generated by different laboratories can be considered environmentally significant. This program must evolve to a point where hydrocarbon Standard Reference Materials will be developed and released to analytical laboratories. These SRM's will allow hydrocarbon analyses to be put on an absolute basis. Until this is possible, NOAA laboratories and contractors need to strongly commit themselves to the quality assurance program.

X. Summary of 4th Quarter Activities

See 4th quarter report, previously submitted to NOAA.

XI. Revised Milestones Chart

A. Completion of Mytilus study and final report (9/78) to NOAA.

XII. Auxiliary Materials

Attached are reprints of relevant articles published in the last year. These publications deal with, or are related to, NOAA-funded research.

The following publications were submitted as part of this report:

Christensen, R.G., and W.E. May (1978). "Detectors for Liquid Chromatographic Analysis for Polynuclear Aromatic Hydrocarbons", J. of Liq. Chromatography, 1(3), pp. 385-399.

Chesler, S.N., B.H. Gump, H.S. Hertz, W.E. May, and S.A. Wise (1978). "Determination of Trace Level Hydrocarbons in Marine Biota", Analytical Chemistry, Vol. 50, No. 6, pp. 805-810.

Hilpert, L.R., W.E. May, S.A. Wise, S.N. Chesler, and H.S. Hertz (1978). "Interlaboratory Comparison of Determinations of Trace Level Petroleum Hydrocarbons in Marine Sediments", Analytical Chemistry, Vol. 50, pp. 458-463.

Wise, S.A., S.N. Chesler, H.S. Hertz, L.R. Hilpert, and W. E. May (1978). "Methods for Polynuclear Aromatic Hydrocarbon Analysis in the Marine Environment", Carcinogenesis, Vol. 3: Polynuclear Aromatic Hydrocarbons, pp. 175-182.

Wise, S.A., S.N. Chesler, H.S. Hertz, L.R. Hilpert, and W.E. May (1977). "Chemically-Bonded Aminosilane Stationary Phase for the High-Performance Liquid Chromatographic Separation of Polynuclear Aromatic Compounds", Analytical Chemistry, Vol. 49, No. 14, pp. 2306-2310.

Hertz, W.E. May, S.A. Wise, and S.N. Chesler (1978). "Trace Organic Analysis", Analytical Chemistry, In press.

Table I. Results of Santa Barbara Sediment Intercomparison Study

Laboratory Code	Hydrocarbons in GC Range (μg/g) Aliphatic	Aromatic	Total	Total Extractables (μg/g)	Pristane/Phytane ratio	Water Content (%H_2O)
NBS	-	-	630±60	2124	1.13±.07	58.55±.04
1	98.8	216.5	315.3	4160	1.6	85.5
2	290	29	319	1329	1.33	-
3	-	-	2280±500	2100±100	.99±.10	53.8±2.5
4	-	-	-	-	4.0	-
5	488±154	51±32	539±186	-	1.95	60.08
6	-	-	-	1700	1.76	60
7:Method 1	305	138	443	4500	1.7	59
7:Method 2	262±25	60±9	322±36	4000	1.8±0.1	58
8	1200	1100	2300	-	1.38	-
9	74	34	108	2200	1.84	60
10	-	-	-	3253	1.74	-
11	905	700	1605	3365	2.0	55.8
Range	74-1200	29-1100	108-2300	1329-4500	.99-4.0	55.8-85.5
Ave	453±400	291±400	866±844	2831±1180	1.79±.73	61±9

Table II. Compound Specific Intercomparison Results*

Laboratory Code	Most Abundant Hydrocarbons (μg/g) Alphatic	Most Abundant Hydrocarbons (μg/g) Aromatic	PAHs >4 Rings	DDE Content (μg/g)
NBS	C_{13}-25±5 C_{10}-24±5 C_{14}-20±4	C_1-Naph-9±1 C_2-Naph-9±1 C_2-Naph-9±1	23±10	3.9±.2
1	C_{15}-8.6 C_{14}-8.4 C_{13}-7.5	C_2-Naph-27 C_2-Naph-16 2-Me-Naph-15	no PAHs	37
2	C_{20}-11.5 C_{21}-10.7 C_{22}-10.3	C_2-Naph-0.62 C_3-Naph-0.33 C_2-Phen-0.32	---	1.75
3	C_{16}-10.8±5.2 C_{19}- 9.4±2.9 C_{17}- 7.2±2.7	--- --- ---	---	---
4	C_{17}-8.3 C_{18}-7.2 C_{15}-6.8	--- --- ---	---	Most Abundant
5	C_{20}-16.8 C_{19}-16.7 C_{16}-15.9	--- --- ---	---	---
6	C_{15}-17.4 C_{14}-16.8 C_{17}-15.6	2-me-Naph-1.69 1-me-Naph-1.10 C_2-Naph-1.10	1.3	---

Table II (cont.)

Laboratory Code	Most Abundant Hydrocarbons (μg/g)		PAHs >4 Rings	DDE Content (μg/g)
	Aliphatic	Aromatic		
7:Method 1	C_{16}-20.1 C_{15}-19.9 C_{17}-18.9	C_2-Naph-17 2-me-Naph-5.2 1-me-Naph-3.3	--	--
7:Method 2	C_{16}-17.5±1.9 C_{17}-17.0±1.6 C_{15}-16.4±1.8	C_2-Naph-11±1.5 2-me-Naph-2.8±.6 1-me-Naph-1.3±.2	--	--
8	C_{15}-46 C_{16}-43 C_{14}-37	--- --- ---	--	--
9	C_{16}-6.23 C_{15}-6.20 C_{14}-5.53	C_2-Naph-11.53 2-me-Naph-3.35 1-me-Naph-2.35	--	--
10	C_{15}-20.0 C_{16}-16.3 Pristane-15.2	---	--	--
11	C_{15}-27.7 C_{16}-26.3 C_{14}-24.9	C_2-Naph-2.25 C_2-Naph-0.91 C_2-Naph-0.81	--	2.0

* Abbreviations used: me = methyl, Naph = naphthalene, Phen = phenanthrene

Table III. Methods Used by Participating Laboratories

Laboratory Code	Method	Method Calibration
NBS	Dynamic headspace sampling for volatiles, hexane extraction for non-volatiles; capillary column GC.	Aliphatic and aromatic internal standard added prior to sample work-up at start of analysis. Southern Louisiana crude was used as external standard for total extractable hydrocarbons.
1	Freeze dry sediment; reflux with hexane and then benzene; silica gel fractionation and capillary column GC.	n-C_{14} used as an external standard for GC analysis.
2	Freeze dry sediment; reflux with toluene:methanol; saponify with 15N KOH; silica gel fractionation; capillary column GC.	Pyrene internal standard
3	Essentially same as Laboratory 2.	Cholestane and phenanthrene internal standard added prior to GC analysis.
4	Reflux wet sample with methanol; saponify; silica gel fractionation; GC.	No correction based on internal or external standard recoveries.
5	Four methods employed; results calculated from results of all methods.	Quantitation relative to an external standard.
6	Dry sediment with methanol; roll overnight with methanol: methylene chloride; rinse sediment; silica gel fractionation; capillary column GC.	Hexamethylbenzene used as GC internal standard; triphenylmethane internal standard added prior to extraction.

Table III. (cont.)

Laboratory Code	Method	Method Calibration
7 Method 1	Soxhlet wet sediment with benzene:methanol; silica gel fractionation; GC	C_{19}-cyclohexane internal standard added prior to GC analysis
Method 2	Essentially same as Laboratory 2.	
8	Soxhlet wet sediment with benzene:methanol; silica gel fractionation; capillary column GC.	Quantitation relative to an external standard composed of $\underline{n}$-C_{14}, $\underline{n}$-C_{18}, $\underline{n}$-C_{22}, $\underline{n}$-C_{32} and anthracene.
9	Shake wet sediment with anhydrous Na_2SO_4 and hexane overnight; silica gel fractionation; GC.	Internal standard added prior to GC analysis.
10	Freeze dry sediment, Soxhlet with methanol:toluene; TLC fractionation; capillary column GC.	Series of $\underline{n}$-alkanes used as external standard for GC analysis.
11	Saponify and reflux sediment in methanolic KOH:toluene; Extract methanolic layer with toluene:petroleum ether; Cu-alumina clean-up; TLC fractionation; GC.	Androstane, $\underline{n}$-C_{20}, and hexamethylbenzene added at time of extraction.

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TRANSPORT MECHANISMS AND HYDROCARBON ADSORPTION PROPERTIES OF SUSPENDED MATTER IN LOWER COOK INLET

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I. Summary

The seasonal distributions and elemental composition of suspended particulate matter in Lower Cook Inlet were studied and compared with current patterns and bottom sediment distributions. In general, the suspended matter distributions appear to follow the pattern of circulation in Lower Cook Inlet and Shelikof Strait. The inflowing relatively clear (~0.5 mg/ℓ suspended load) saline Gulf of Alaska water, which is enriched in biogenic particles and depleted in particulate trace elements, flows northward along the eastern side of Lower Cook Inlet until it reaches the region near Cape Ninilchik where it mixes with the outflowing brackish water. The outflowing turbid (>5.0 mg/ℓ suspended load) water, which contains terrigenous particles derived from the Susitna, Matanuska and Knik Rivers, moves seaward along the western side of the Inlet past Augustine Island and Cape Douglas into Shelikof Strait where it mixes with the oceanic water and is dispersed. Comparisons of physical characteristics of suspended matter and sediments from the central basin indicates that net sedimentation of the fine grained suspended particles is minimal. However, sedimentation may be occurring in the numerous embayments along the coast. Chemical analysis of the particulate matter reveals that fine grained aluminosilicate minerals comprise about 80-95% of the suspended matter with biogenic material making up the rest. Analysis of seasonal variations of the C:N ratio of the particulate organic matter indicates that organic matter of marine origin is dominant in summer whereas terrestrially derived organic material predominates in winter when productivity is low.

Laboratory experiments involving the interactions between Cook Inlet crude oil and suspended matter from Lower Cook Inlet show that the accommodation capacity of suspended matter for crude oil increases with the concentration of added oil. Important parameters in the accommodation process include: the

chemical nature and viscosity of the oil; the mineralogical and size characteristics of the particulate matter; temperature; and degree of mixing.

II. Introduction

The development of petroleum and natural gas resources on the Alaskan outer continental shelf will undoubtedly result in an increased potential for crude oil contamination of its coastal waters. Of particular concern are the major accidents which cause massive oil spills, such as the ARGO MERCHANT oil spill on Fishing Rip near Nantucket (NOAA Special Report, 1977). However, chronic release of oil through minor spills and localized transfer operations may be more important over the long term.

Oil spilled onto the surface of the ocean is acted upon by several physical processes, including evaporation, solution, emulsification, and injection into the atmosphere (Kreider, 1971; McAuliffe, 1966, 1969; Baier, 1970). With respect to the oceanic environment, only the solution and emulsificaiton processes represent important mechanisms by which spilled oil becomes entrained in the water column, thus increasing its potential for impacting marine organisms.

Since crude oil is sparingly soluble in sea water, it tends to form emulsions when introduced into sea water, especially under intense wave action. The emulsions have high affinity for particles and tend to be adsorbed rapidly. Recent studies of oil spills in coastal waters containing high suspended loads have indicated rapid dispersal and removal of the oil by adsorption onto suspended matter (Forrester, 1971; Farrington and Quinn, 1973).

There is very little published information about the processes by which oil is transported in association with suspended particles or the quantities of oil that can be adsorbed onto the particles. Early investigators have shown that flocculation of oil bears an inverse relationship to salinity (Chapman, and Galtsoff, 1979; Hartung and Klinger, 1968).

Later investigations indicate that sedimentation of oil involves a two-step process (Bassin and Ichiye, 1977; Huang and Elliott, 1977). This process begins with the adsorption of oil onto the suspended particles and is followed by the flocculation of these oil-sediment emulsions by electrostatic interactions. The amount of oil that can be accommodated by a specific quantity of suspended matter appears to be dependent upon the physical and chemical nature of the suspended particles as well as the amount of naturally occurring organic matter that is associated with the particles (Poirier and Thiel, 1941; Meyers and Quinn, 1973).

Once oil is adsorbed by suspended particles, it can easily be injested marine organisms, particularly by detrital feeders. Following the spill of the ARGO MERCHANT, oil particles were observed in some species of zooplankton and on the surfaces of Pollock eggs (NOAA Special Report, 1977). After the breakup of the oil tanker ARROW in Chedabueto Bay, Conover (1971) determined that zooplankton could assimilate up to 20 percent of the oil particles less than 1 mm in diameter and sediment them as fecal matter. Since fecal matter is an important food source for other marine organisms, oil tansmitted to the sea floor in this form becomes an important mechanism by which benthic detrital feeders may be impacted by oil. Many of these species, including shrimp, clams, oysters, and crabs, are economically important renewable resources in Lower Cook Inlet.

After oil is sedimented on the bottom, it is usually degraded by microbial activity. However, in many cases this process is very slow and depending upon the bottom circulation oil contaminated sediments may persist for a considerable amount of time. For example, Blumer and Sass (1972) have documented benthic changes that have resulted from the Buzzards

Bay oil spill in 1969. They show that fuel oil was retained in the sediments for at least 2 years and seriously retarded the recruitment rate of organisms into the infected area.

In more active bottom environments oil contaminated sediments may be resuspended into the water column by the actions of waves and storm surges and may reinfect the water column. For example, the preliminary report of the ARGO MERCHANT oil spill indicates that oil contaminated sediments southwest of the grounding point were probably the result of resuspension and transportation of contaminated sediments by the area's southwesterly bottom currents (NOAA Special Report, 1977). Thus, the persistence of oil in the sediments and its resuspension into the overlying water column may seriously affect not only the recruitment rate of organisms into an infected area, but also the feeding and reproductive behavior of planktonic organisms (Wilson, 1975).

For the past 12 months we have been conducting integrated studies of the distribution, composition, transport and adsorptive properties of suspended matter from Lower Cook Inlet. The major objective of the particulate matter program in Lower Cook Inlet is to determine the seasonal variations in the distribution, composition and transport of suspended matter. Other objectives include: (1) an investigation of the high frequency (hourly) variability in the distribution of suspended matter; and (2) a study of the adsorptive characteristics of suspended matter from Cook Inlet for crude oil.

III. Current State of Knowledge

There is little published information about the distribution and composition of suspended particulate matter in Lower Cook Inlet.

Sharma et al. (1974) studied the distribution of suspended matter in Lower Cook Inlet during several cruises in 1972 and 1973. Suspended matter concentrations ranged from 100 mg/ℓ near the Forelands to 1-2 mg/ℓ near the entrance to the Inlet. Large temporal variations were observed which were related to tidal variations in water circulation and seasonal variations in river runoff.

Suspended matter from Lower Cook Inlet consists largely of mechanically abraded rock debris transported by glacial streams. The clay fraction of the suspended matter consists primarily of illite (Sharma and Burrell, 1970).

IV. The Study Area

Cook Inlet is a large tidal estuary in south central Alaska. It lies on a northeast-southwest axis and is about 150 nautical miles long and 50 nautical miles wide at the mouth. Physiographically, the Inlet is divided into three sections. At the head of the Inlet, it separates into Knik and Turnagain Arms, which are 45 and 43 nautical miles long, respectively. Near the middle, Upper Cook Inlet is separated from Lower Cook Inlet by two geographic constrictions, the East and West Forelands. The Inlet receives freshwater from four major rivers: the Matanuska and Knik Rivers at the head of Knik Arm and the Susitna and Beluga Rivers to the northwest. These rivers supply about 70 to 80 percent of the freshwater input to the Inlet (Rosenberg and Hood, 1967). In addition, there are numerous streams containing large concentrations of glacial flour which drain into the Inlet from both sides.

Water circulation in Lower Cook Inlet is characterized by a net inward movement of oceanic water up the eastern shore and a net outward movement of runoff water along the western shore. In the vicinity of the Forelands, the water masses are vertically mixed due to the turbulent action of tidal currents. However, lateral separation of the water masses is apparent, resulting in a shear zone between the incoming saline water on the east-side and the outgoing less saline waters on the west.

The sediments of Lower Cook Inlet are primarily comprised of medium to fine grain sands; however, occasionally silt and clay-sized sediments have been observed (Bouma and Hampton, 1976).

V. Sources, Methods and Rationale of Data Collection

In order to obtain information about the seasonal variations of the distribution and composition of suspended matter, we have completed two surveys in Lower Cook Inlet (Cruise RP-4-Di-77A-IV, 4-16 April 1977 and Cruise Acona-245, 28 June - 12 July 1977). The field studies have been integrated with the physical program so that concomitant information about circulation and watermass structure has been obtained.

In addition to the seasonal distributions, we have conducted a number of high frequency (hourly) time series studies at selected locations in the Inlet. This has provided valuable information about the variability of the distribution of suspended matter that may be due to tides and the "patchiness" of primary productivity in surface waters and resuspension of sediments in near bottom waters.

A second aspect of the suspended matter program was concerned with the role of suspended matter in transporting accommodated oil through the water column. To this end, suspended material from the region near Kalgin Island was collected and stored for subsequent interaction studies with Cook Inlet crude oil. The interaction studies were conducted in 250 and 1000 mℓ separatory funnels at 5 and 10°C, simulating the environmental conditions present in Lower Cook Inlet. These experiments have been designed to determine the capacity of suspended matter for accommodating crude oil and to illucidate critical parameters involved in the accommodation process.

A. Sampling Methods

Sample collection has occurred concurrently with CTD hydrocasts so that the particulate matter distributions can be related to the hydrography. Water samples were collected in 10-liter PVC Model 1070 Top-Drop Niskin® bottles from preselected depths. Nominally these depths included: surface, 10 m, 20 m, 40 m, 60 m, 80 m and 5 meters above the bottom. Aliquots were drawn within one-half hour after collection from each sample and vacuum filtered through preweighed 0.4 μm pore diameter Nuclepore® polycarbonate filters for total suspended matter concentration determinations and multielement particulate composition analyses. Samples were also filtered through 0.45 μm pore diameter Selas® silver filters for particulate carbon and nitrogen analyses. All samples were rinsed with three 10 mℓ aliquots of deionized and membrane filtered water, placed in individual polystyrene petri dishes with lids slightly ajar for a 24-hour desiccation period over sodium hydroxide and then sealed and stored (silver filters frozen) for subsequent laboratory analysis.

B. Analytical Methods

1. Gravimetry

Total suspended matter concentrations were determined gravimetrically. Volumetric total suspended matter samples were collected on 47 mm, 0.4 μm pore diameter Nuclepore® filters which were weighed on a Cahn® Model 4700 Electrobalance before and after filtration. The suspended matter loadings were then determined by difference. The weighing precision ($2\sigma = \pm .011$ mg) and volume reading error (± 10 mℓ) yield a combined coefficient of variation in suspended matter concentration (mg/ℓ) at mean sample loading and volume (2.057 mg and 2 ℓ, respectively) of approximately 1%. However, preliminary investigations of sampling precision (coef. of var.: 25%) suggest that the actual variability in the particulate matter concentrations of these waters is much greater than the above analytical precision.

2. Gas Chromatography

Analysis of total particulate carbon and nitrogen in suspended matter was performed with a Hewlett Packard Model 185B C-H-N analyzer. In this procedure, particulate carbon and nitrogen compounds are combusted to CO_2 and N_2 (micro Dumas method), chromatographed on Poropak® Q, and detected sequentially with a thermal conductivity detector. NBS acetanilide is used for standardization. Analyses of replicate surface samples yield coefficients of variation ranging from 2 to 10% for carbon and 7 to 14% for nitrogen.

3. X-Ray Secondary Emission Spectrometry

The major (Mg, Al, Si, K, Ca, Ti, and Fe) and trace (Cr, Mn, Ni, Cu, Zn, and Pb) element chemistry of the suspended particulate matter samples was determined by x-ray secondary emission (fluorescence) spectrometry utilizing a Kevex® Model 0810A-5100 x-ray energy spectrometer and the thin-film technique (Baker and Piper, 1976). The inherent broad band of radiation from a Ag x-ray tube was used to obtain a series of characteristic emission lines from a single element secondary target which then more efficiently excited the thin-film sample. Se and Zr secondary targets were used to analyze the samples for both major and trace elements. Standards were used to analyze the samples for both major and trace elements. Standards were prepared by passing suspensions of finely ground USGS standard rocks (W-1, G-2, GSP-1, AGV-1, BCR-1, PCC-1) and NBS trace element standards through a 37 μm mesh polyethylene screen followed by collection of the size fractionated suspensates on Nuclepore® filters identical to those used for sample acquisition. The coefficient of variation for 10 replicate analyses of a largely inorganic sample of approximately mean mass was less than 3% for the major constituents and as high as 5% for the trace elements. However, when sampling precision is considered, the coefficients of variation increase, averaging 12 and 24% for major and trace elements, respectively.

4. Hydrocarbon-Suspended Matter Interaction Studies

The preliminary objective of the sediment/oil interaction study was to establish the loading characteristics of Cook Inlet suspended matter relative to a typical Cook Inlet crude oil. The particular approach used was designed to evaluate the quantity of petroleum that might be adsorbed to indigenious particles, assuming that particles and oil would achieve rapid equilibrium with each other. Experiments were conducted in sea water near 32°/oo and 10°C. Equilibration times were set for one hour in these preliminary observations.

Suspended matter was recovered from near Kalgin Island (station 4) with a Sorvall SS-3 continuous flow centrifuge. Previous testing of this recovery technique has shown that more than 95% of all particles greater than 0.4 μm are sedimented as computed from mass differences between the source water the centrifuge effluent (Baker et al., 1978).

Small organic particles are not efficiently retained because of the relatively low density. In upper Cook Inlet, the relatively low abundance of organic matter (this report) would negate any significant compositional fractionation occurring as the result of the centrifugation process.

After recovery, the sediment was transferred to a clean jar, fitted with an aluminum foil top, frozen, and returned to the laboratory. Water was removed from the sediment by freeze drying, resulting in a fine dry powder which was subsequently used in the agglutinization study.

The loading characteristics of Cook Inlet suspended matter was investigated under controlled laboratory conditions. Approximately 50 mg suspended sediment (dry weight) was added to 800 mℓ of filtered Cook Inlet seawater (S ≈ 32°/oo) in a 1-liter separatory funnel. To this was added varing quantities of crude oil, resulting in initial loading factors (mg oil/mg sediment) ranging from 0.17 to 1.7. Prior to the addition of the oil, the water temperature was decreased to the desired experimental value. The mixture was shaken gently for 1 hour to simulate natural mixing conditions, but not severe enough to generate frothing or air bubbles on the solution. After one hour, the separatory funnels were allowed to stand vertically in the water bath for 1-3 hours to promote settling of the oil/sediment flocs. These were removed carefully with a small bore pipette and transferred to a 25 mm filtration apparatus. The oil was separated from the sediment particles by dissolving in methylene chloride and retaining the inorganic material on 0.4 μm Selas® silver filter. The preweighed filters were dried at 110°C and the residual weight determined. Excess water was removed via pipette and sodium sulfate and the volume of methylene chloride reduced to 2 mℓ in a concentrator tube.

The remaining mixture in the separatory funnel is made up of emulsified oil, surface slick (in some instances), oil adsorbed to the walls of the separatory funnel, and oil adsorbed to suspended particles that did not settle. This mixture was extracted with 20% ethyl ether/methylene chloride solution to recover the remaining oil. A total of 3-20 mℓ aliquots of the solvent mixture was used to effect the extraction. This fraction (referred to as the water accommodated oil) and the previous fraction, both were reduced to a 2 mℓ volume in a concentrator tube and a 25 μℓ aliquot taken for gravimetry. Both extracts were saved for future GC analyses.

Prior to actual experimentation, oil recovery efficiencies were conducted. It was determined that approximately 15% of the total oil was lost during concentration step (presumably volatiles). Extraction of approximately 20 mg Cook Inlet crude oil from 800 mℓ of seawater was effectively carried out with the previous solvent mixture with total recoveries better than 95% after correction for evaporative losses. When sediment is added to oil-water mixture, the extraction efficiency decreases in proportion to the amount of oil present. This experimental artifact will be discussed below.

Because both the seawater and sediment contain extractable organics, separate tests were made to determine the amount of organics that would be included in the lipid fraction. We assumed that no partitioning of the organics occurred in the mixture and simply corrected the final oil recoveries based on sediment and water recoveries in each fraction. In actuality, the distribution of the natural organics is affected by the addition of petroleum to the system, but no serious consequences arise since the concentration of oil was usually much greater than the combined amounts of extractable organics from the water and sediment. The exception is the case where only 8.4 mg of oil was added.

In order to compare particle size distributions of Cook Inlet suspended matter with the oil-suspended matter aggregates, samples of each were subjected to microscopic analysis utilizing a scanning electron microscope for the particulate samples and a light microscope for the oil-suspended matter aggregates and the techniques outlined by Feely (1976). For the particulate samples small volumes of sea water (250-500 mℓ) were filtered through 0.4 μm Nuclepore filters, washed with three 10 mℓ portions of deionized filtered water and stored in plastic petri dishes. In the laboratory the filters were cut into 5 mm squares and mounted onto aluminum stubs. The stubs were placed into a sputter coater and coated with Au. Five stubs were prepared from each filter. The stubs were placed into a ISI Super Mini Sem II scanning electron microscope and were observed at a manification of 1000X.

For the oil-suspended matter aggregates, aliquots of samples from the interaction studies were placed onto a microscope slide and observed with an AO Model 3025TU Epi-LUME microscope at a magnification of 150X. Photo micrographs were made from the microscope images. Approximately 20 micrographs from each sample were used for particle counting and sizing.

VI and VII. Results and Discussion

[illegible] date we have completed both cruises in Lower Cook Inlet scheduled for FY77. The first cruise was conducted during early spring (4-16 April) of 1977. The second cruise was conducted in the summer (28 June - 12 July). The station locations for the two cruises are shown in figures 1 and 2. Suspended matter samples were collected from the surface and 5 meters above the bottom at each of the stations. Also, vertical profiles were obtained at stations 24 through 29, between Kachemak Bay and Kamishak Bay. In addition to the above data, vertical profiles of suspended matter distributions

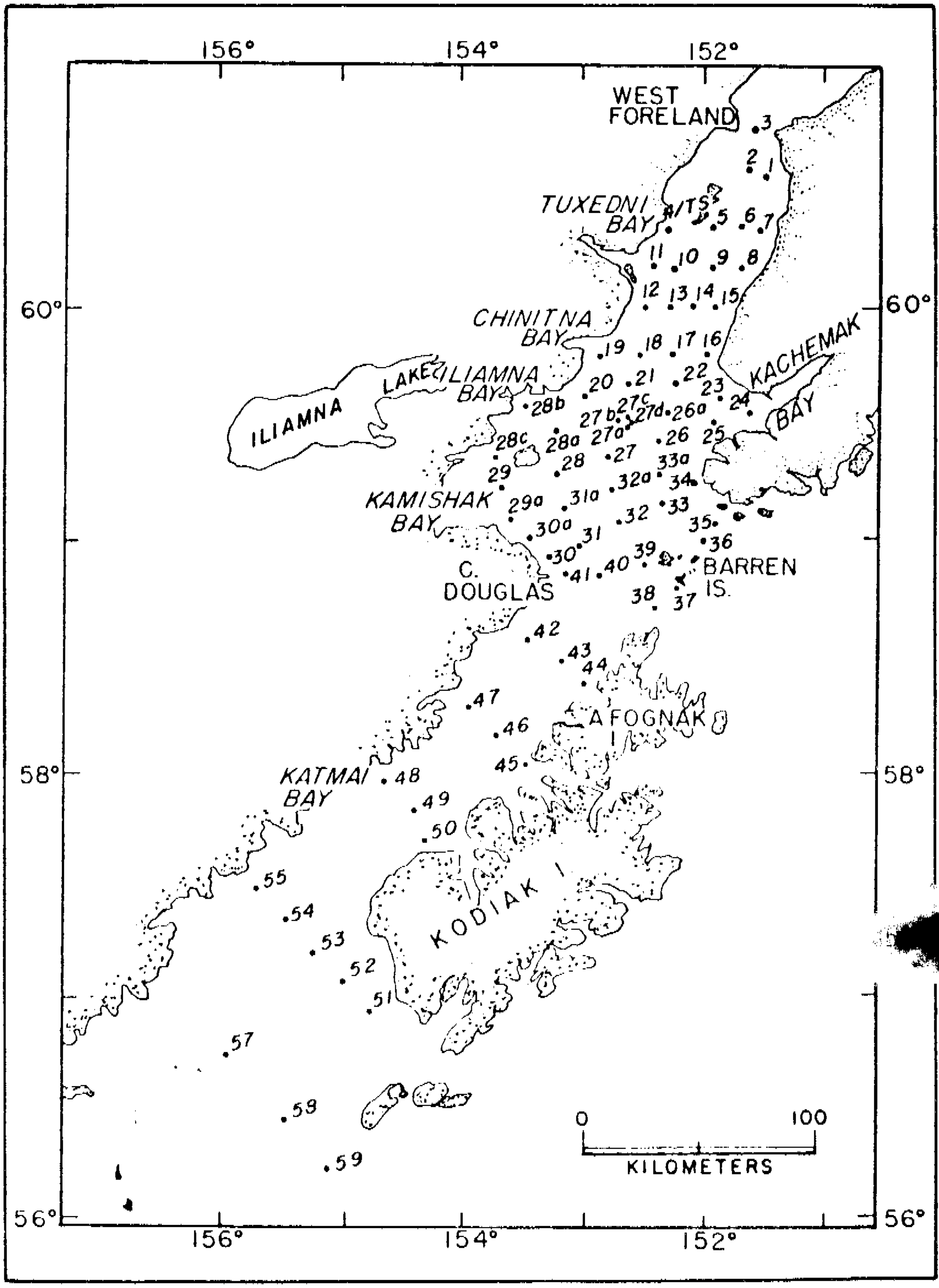

Figure 1. Locations of suspended matter stations in Lower Cook Inlet and Shelikof Strait (Cruise RP-4-Di-77A-IV, 4-16 April 1977).

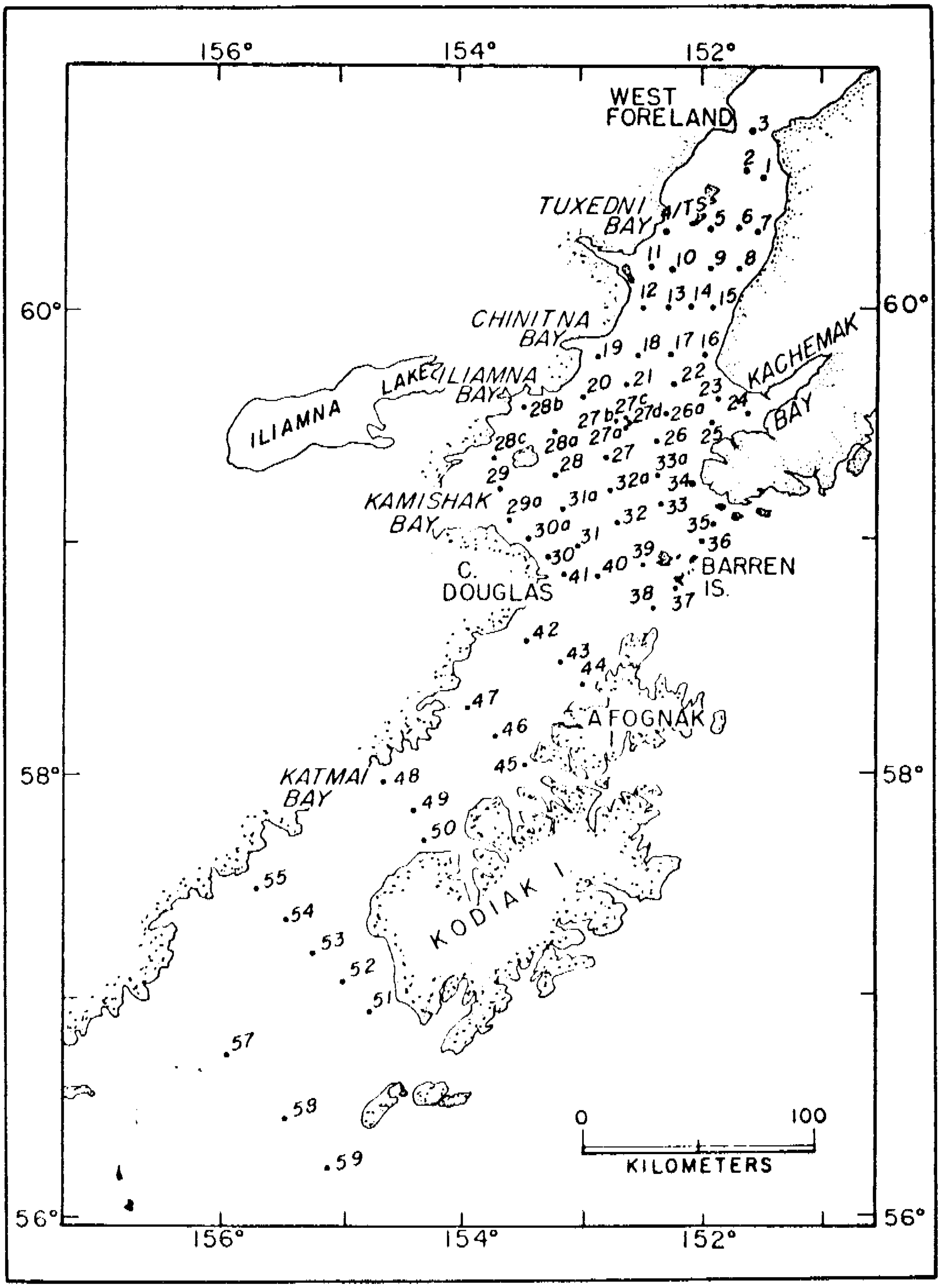

Figure 2. Locations of suspended matter stations in Lower Cook Inlet and Shelikof Strait (Acona-245, 28 June - 12 July 1977).

and hydrographic data were obtained for the fall (3-12 October) during a current meter-sediment trap deployment cruise. These data provide the basis for the following discussions of the distributions, transport and chemical composition of suspended matter in Lower Cook Inlet. The results of the time series experiments and hydrocarbon accommodation studies will also be discussed below.

A. Particulate Matter Distributions and Transport

Figures 3 through 6 show the distributions of salinity, temperature sigma-t and particulate matter at the surface and 5 m above the bottom for the April and July cruises in Lower Cook Inlet and Shelikof Strait. As shown in figures 3 and 5, the surface particulate matter distributions are characterized by unusually high horizontal gradients. On the eastern side particulate concentrations were relatively low, ranging from 0.5 mg/ℓ near Cape Elizabeth to about 5.0 mg/ℓ near Cape Ninilchik. On the western side suspended loads increased rapidly from concentrations around 5.0 mg/ℓ in Kamishak Bay to concentrations greater than 100 mg/ℓ north of Tuxedni Bay. The salinity and temperature data (figs. 3 and 5) for these cruises show very similar horizontal distribution patterns, illustrating the predominance of the inflowing relatively clear saline Gulf of Alaska water on the eastern side and the outflowing turbid low salinity water from Upper Cook Inlet on the western side. The outflowing turbid water is transported to the southwest past Augustine Island and Cape Douglas into Shelikof Strait where it mixes with the oceanic water and the suspended matter is dispersed.

The near bottom suspended matter distributions (figs. 4 and 6) are very similar to the surface distributions, suggesting that cross-channel gradients in the suspended matter distributions exist throughout the water column. In apparent agreement with this, the vertical cross-sections of the distribution

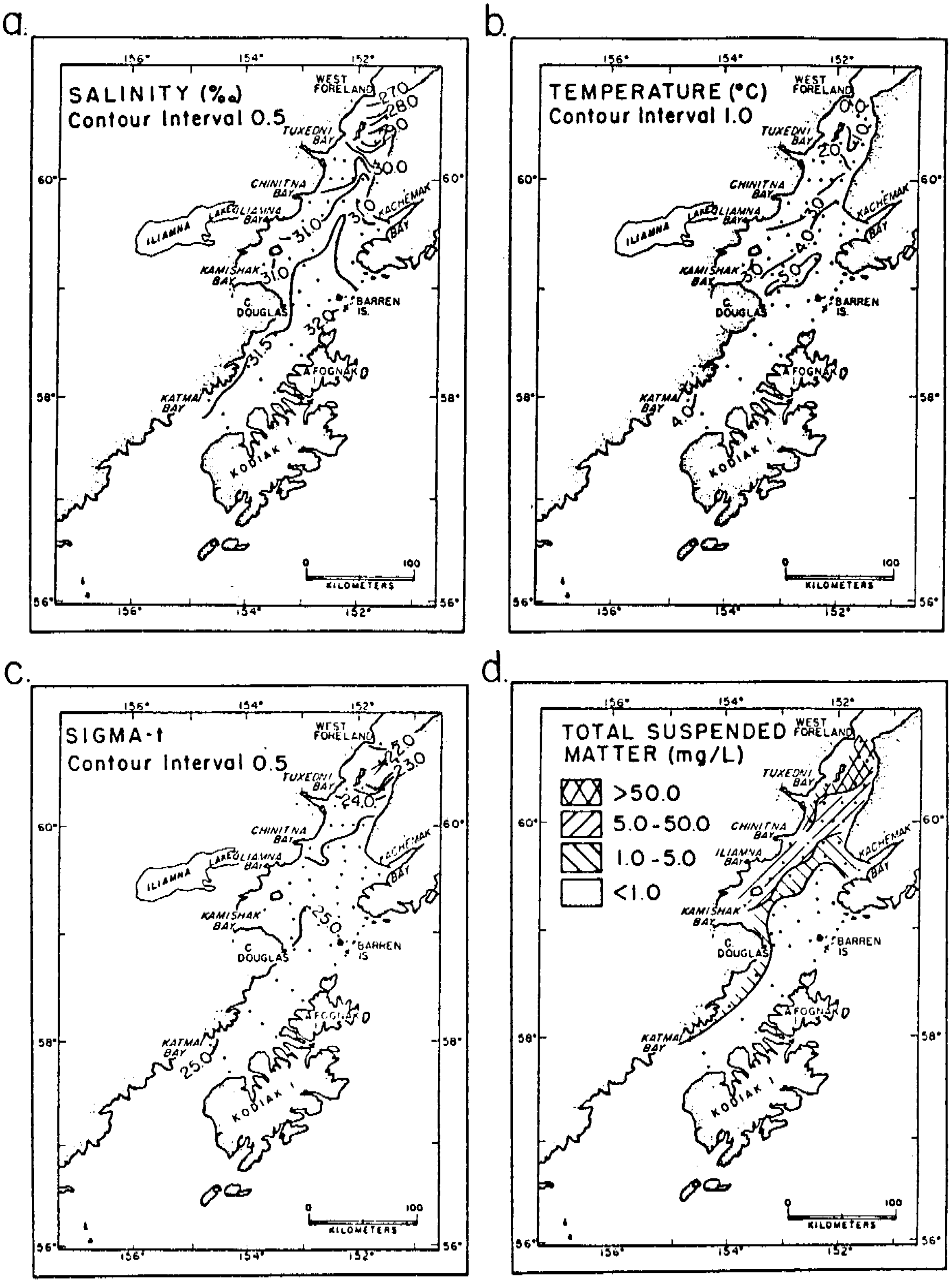

Figure 3. Distribution of: a. salinity; b. temperature; c. sigma-t; and d. total suspended matter at the surface (Cruise RP-4-Di-77A-IV, 4-16 April 1977).

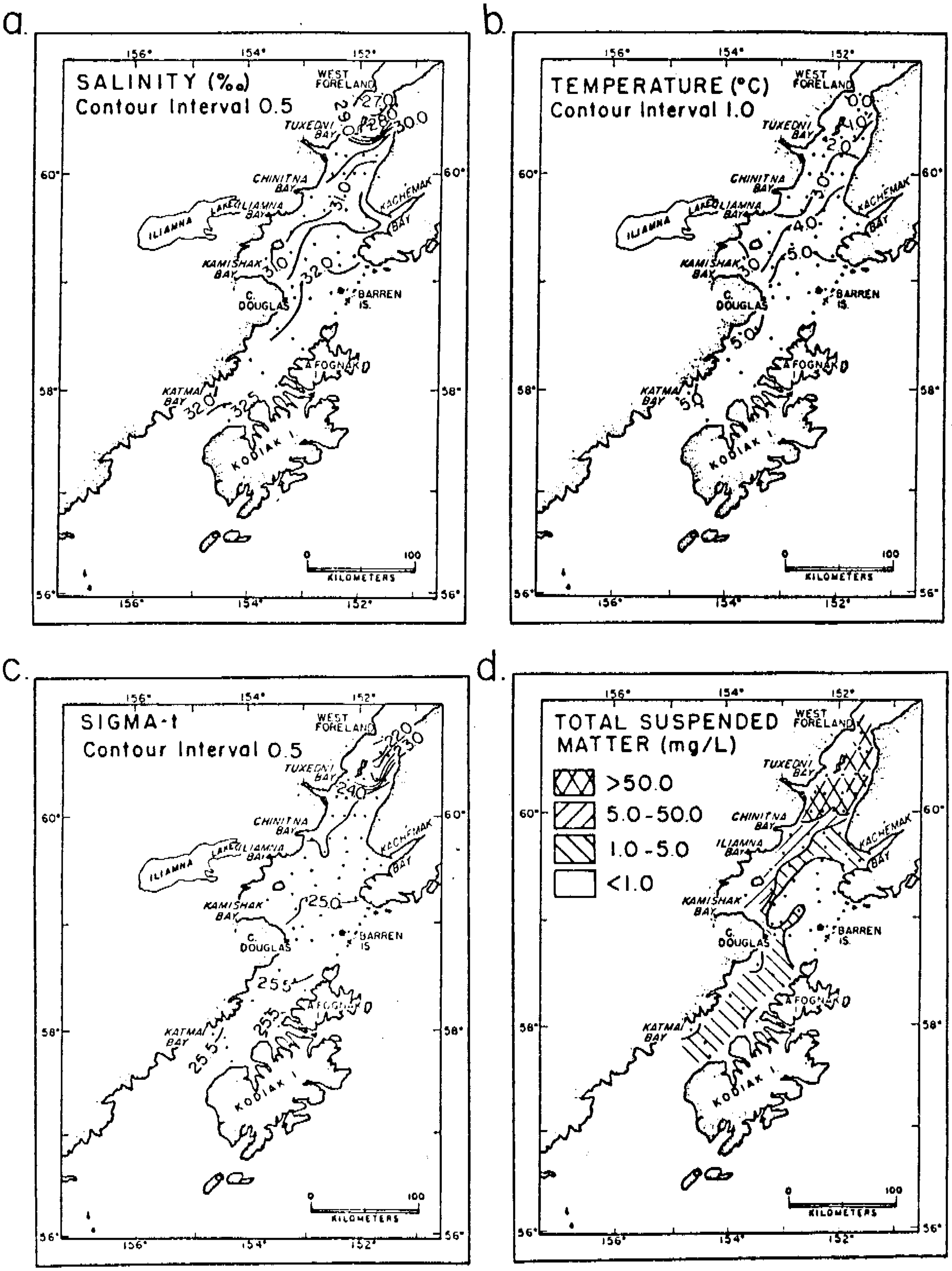

Figure 4. Distribution of: a. salinity; b. temperature; c. sigma-t; and d. total suspended matter 5 m above the bottom (Cruise RP-4-Di-77A-IV, 4-16 April 1977).

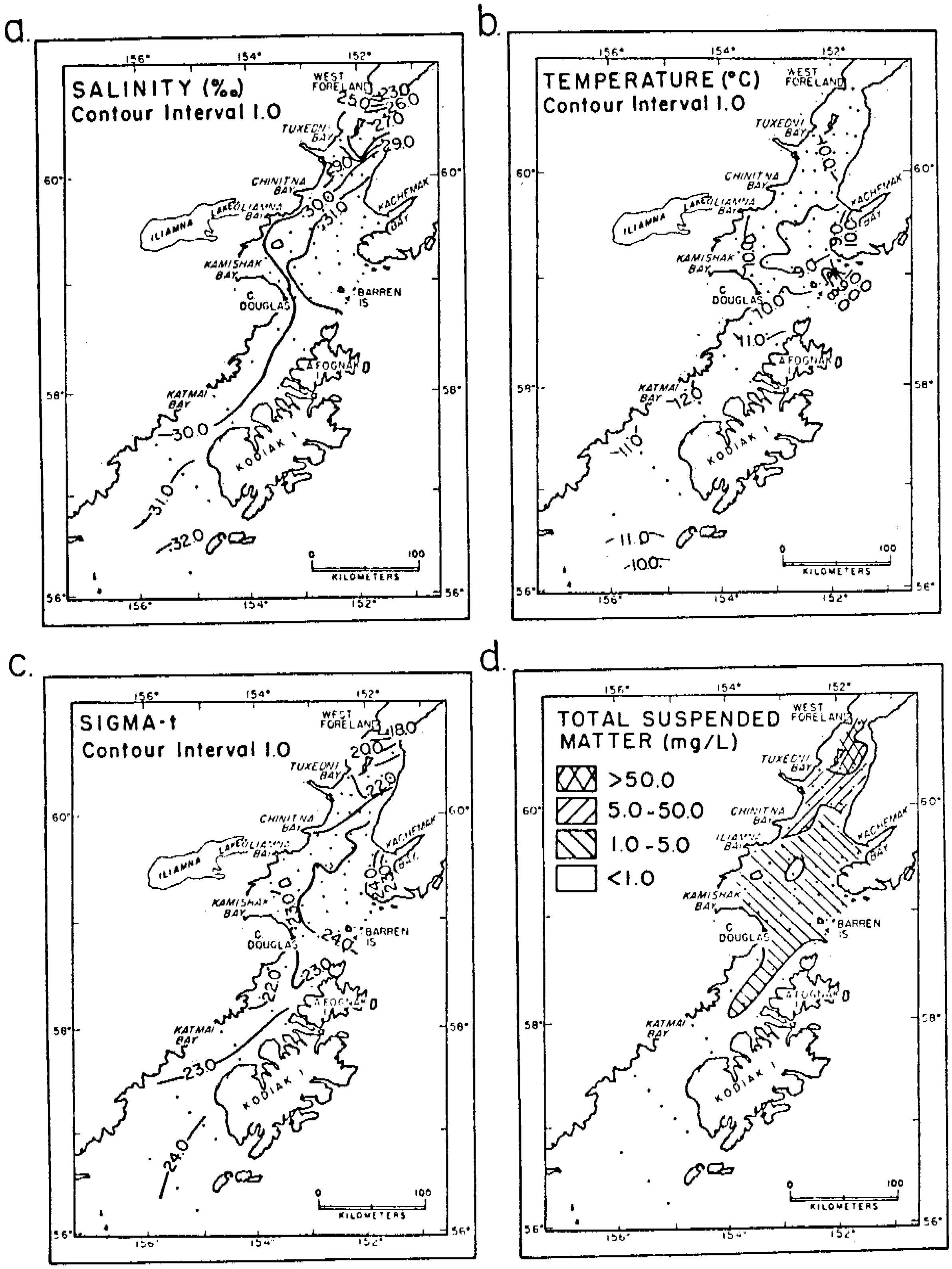

Figure 5. Distribution of: a. salinity; b. temperature; c. sigma-t; and d. total suspended matter at the surface (Cruise Acona-245, 28 June - 12 July 1977).

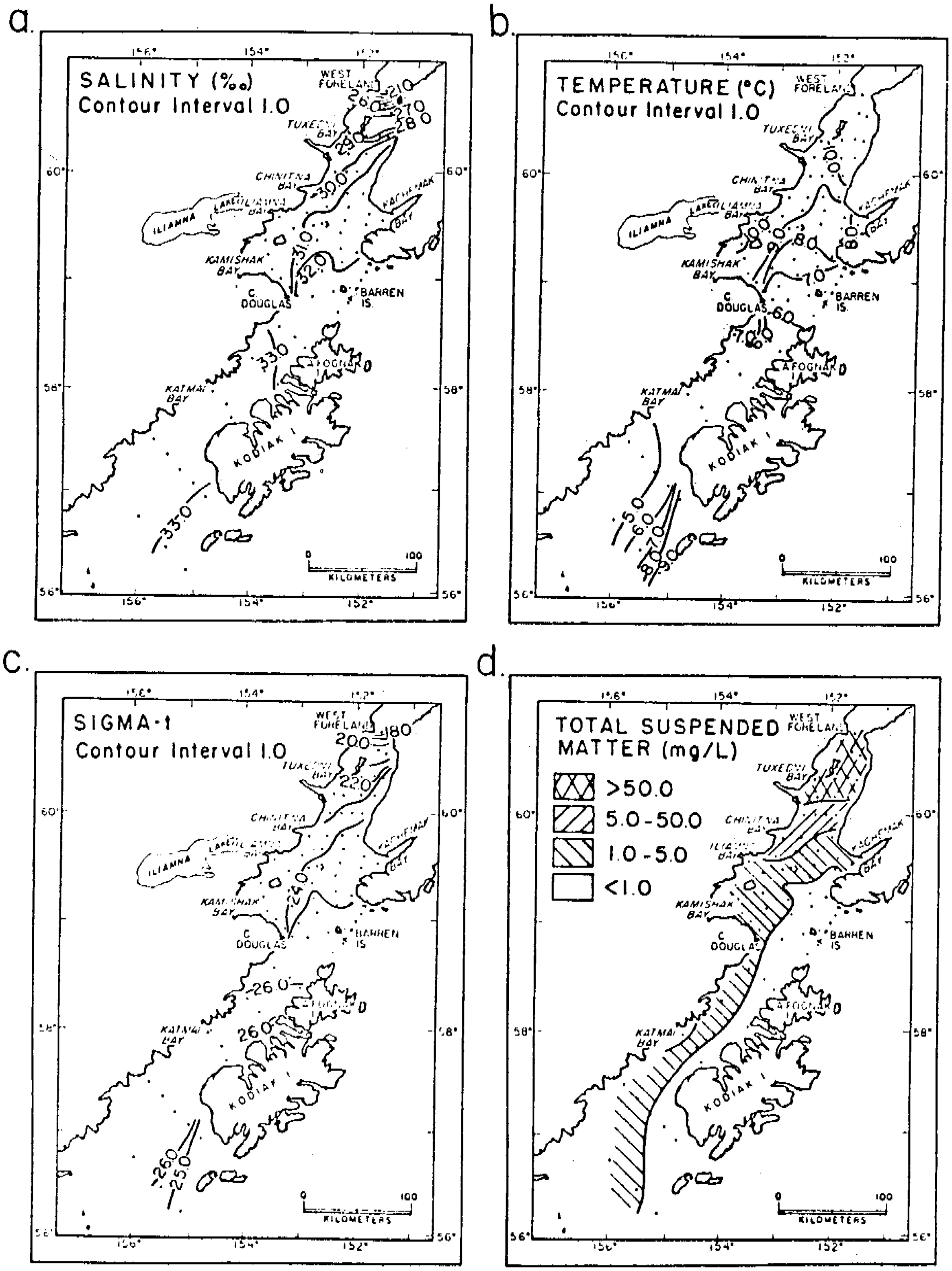

Figure 6. Distribution of: a. salinity; b. temperature; c. sigma-t; and d. total suspended matter 5 m above the bottom (Cruise Acona-245, 28 June - 12 July 1977).

of suspended matter from Kachemak Bay to Kamishak Bay (figs. 7 through 9) show large cross-channel variations. For example, in April (fig. 7) suspended matter concentrations range from <1.0 mg/ℓ near Kachemak Bay to >8.0 mg/ℓ near Kamishak Bay. The salinity and temperature data (fig. 7a and 7b) also showed striking cross-channel gradients, indicating the presence of the two distinctly different water masses. Similar cross-channel gradients can be observed in the July and October data although they are not quite as pronounced. The horizontal gradients averaged about 2.0 mg/ℓ/100 km in July and 1.0 mg/ℓ/100 km in October. The decrease in the horizontal gradients from early spring to late summer and fall were probably due to a combination of factors including: (1) variations in suspended matter inputs from local streams; (2) increased water column stability and lateral mixing in the summer and fall; and (3) increased productivity on the eastern side of the Inlet in the summer (e.g. Larrance, 1977).

Since suspended matter may play an important role in scavenging and transporting contaminants from the study region, the question of where the large amounts of suspended materials that passes into Lower Cook Inlet ultimately reside becomes important. The dramatic decrease in suspended loads from >100 mg/ℓ near the Forelands to <1.0 mg/ℓ near the Inlet's mouth may by an indication of particulate settling. However, recent studies of major sediment types in Lower Cook Inlet indicate that the sediments in the central part of the Inlet consist primarily of unconsolidated coarse-grained sands deposited during the retreat of the Pleistocene glaciers (Bouma and Hampton, 1976). Another possibility is that the suspended matter gradients are the results of dilution of the brackish water by the less turbid oceanic water. Figure 10 shows a scatter plot of the relationship between total suspended matter and salinity for the surface samples from the

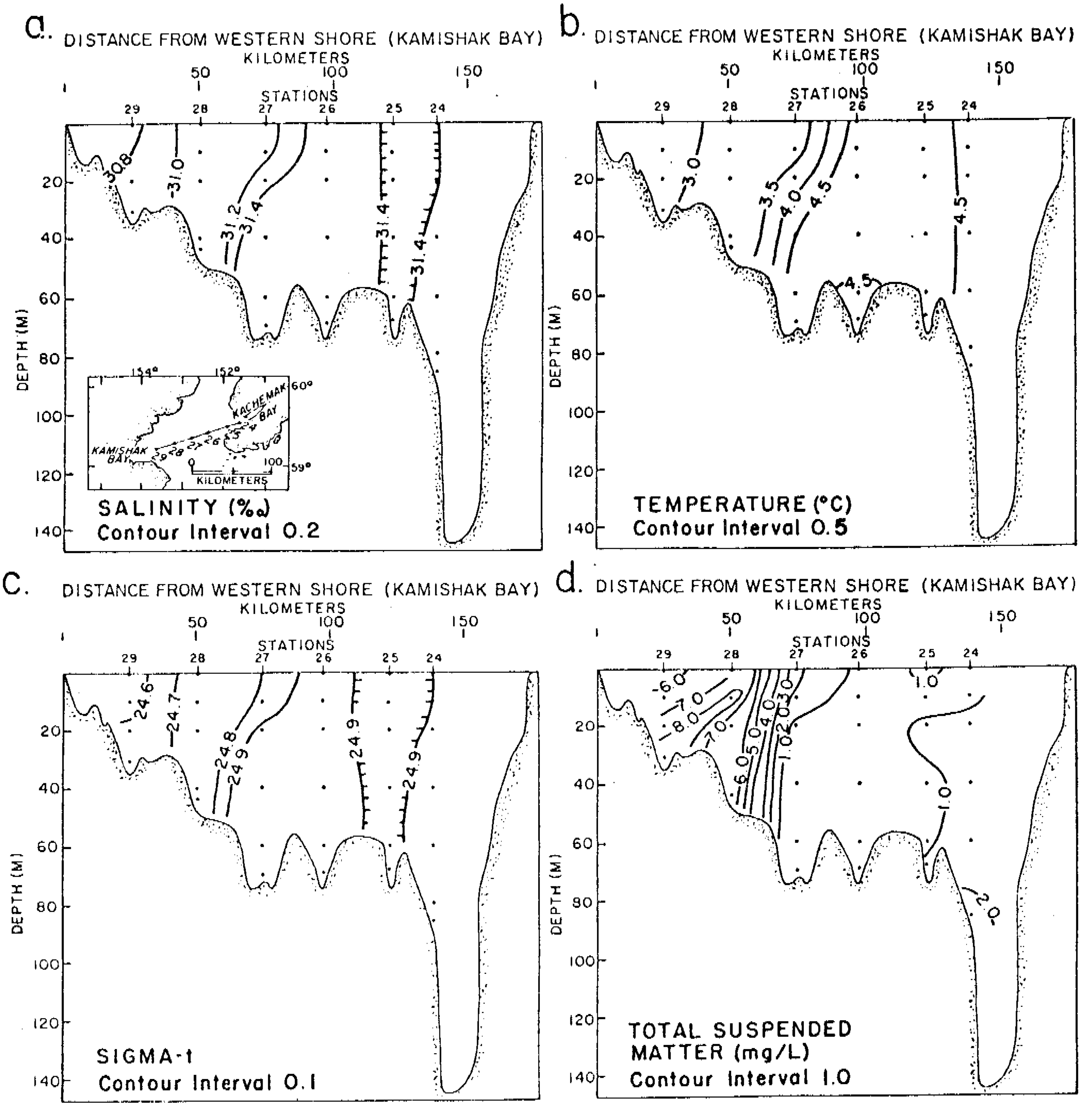

Figure 7. Vertical cross sections of the distributions of: a. salinity: b. temperature; c. sigma-t; and d. total suspended matter for stations 25 thru 29 in Lower Cook Inlet (RP-4-Di-77A-IV, 4-16 April 1977).

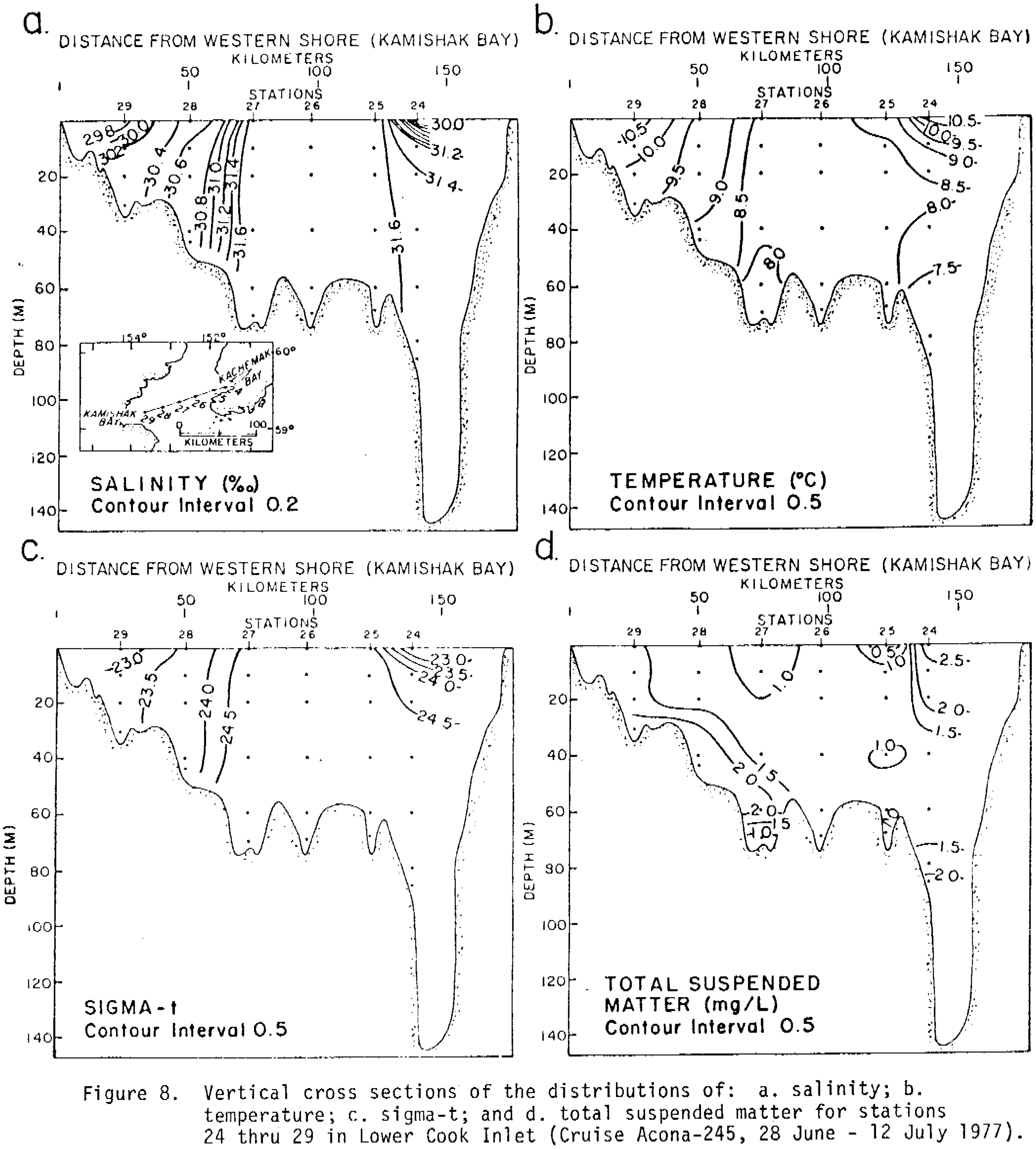

Figure 8. Vertical cross sections of the distributions of: a. salinity; b. temperature; c. sigma-t; and d. total suspended matter for stations 24 thru 29 in Lower Cook Inlet (Cruise Acona-245, 28 June - 12 July 1977).

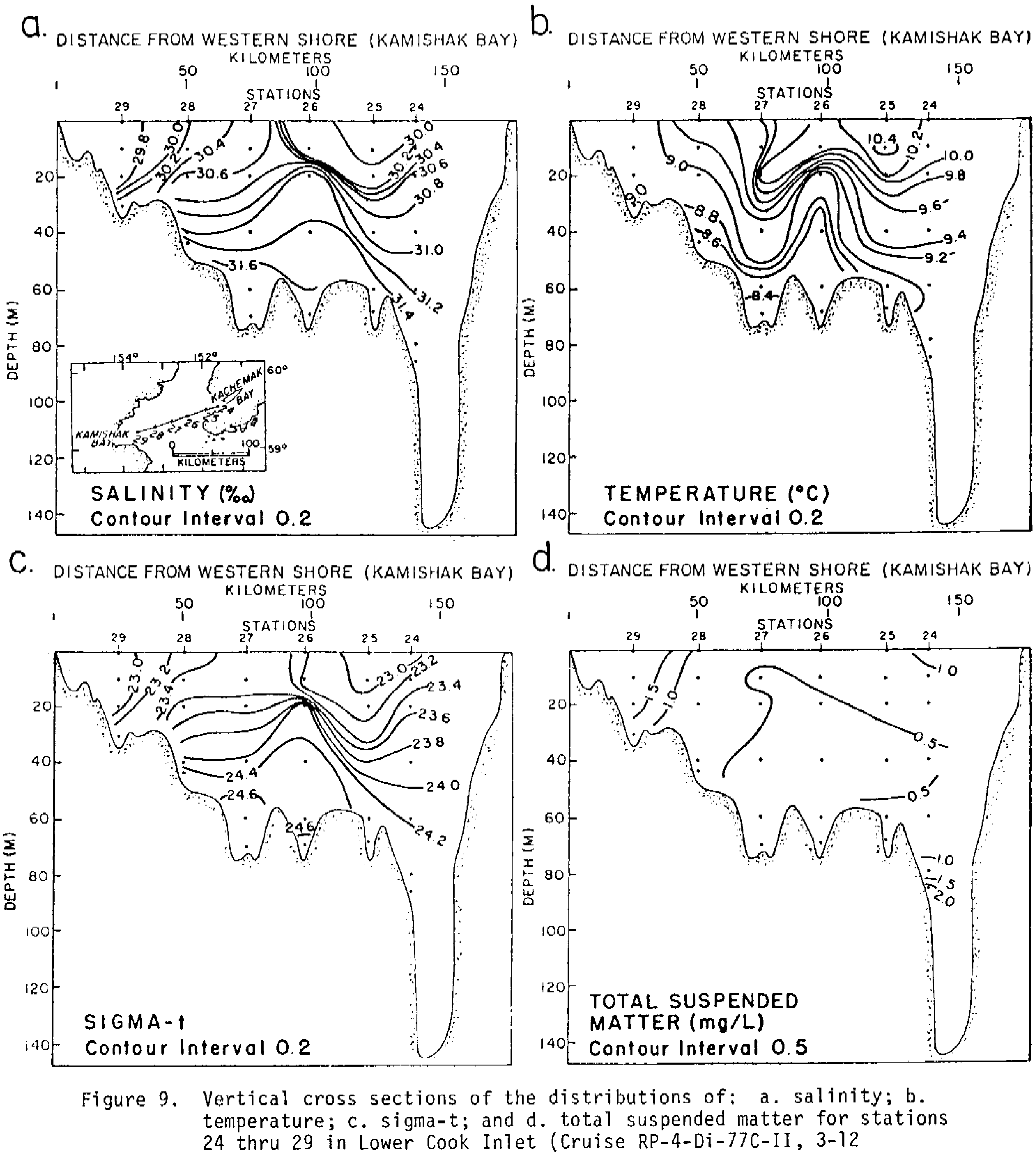

Figure 9. Vertical cross sections of the distributions of: a. salinity; b. temperature; c. sigma-t; and d. total suspended matter for stations 24 thru 29 in Lower Cook Inlet (Cruise RP-4-Di-77C-II, 3-12 October 1977).

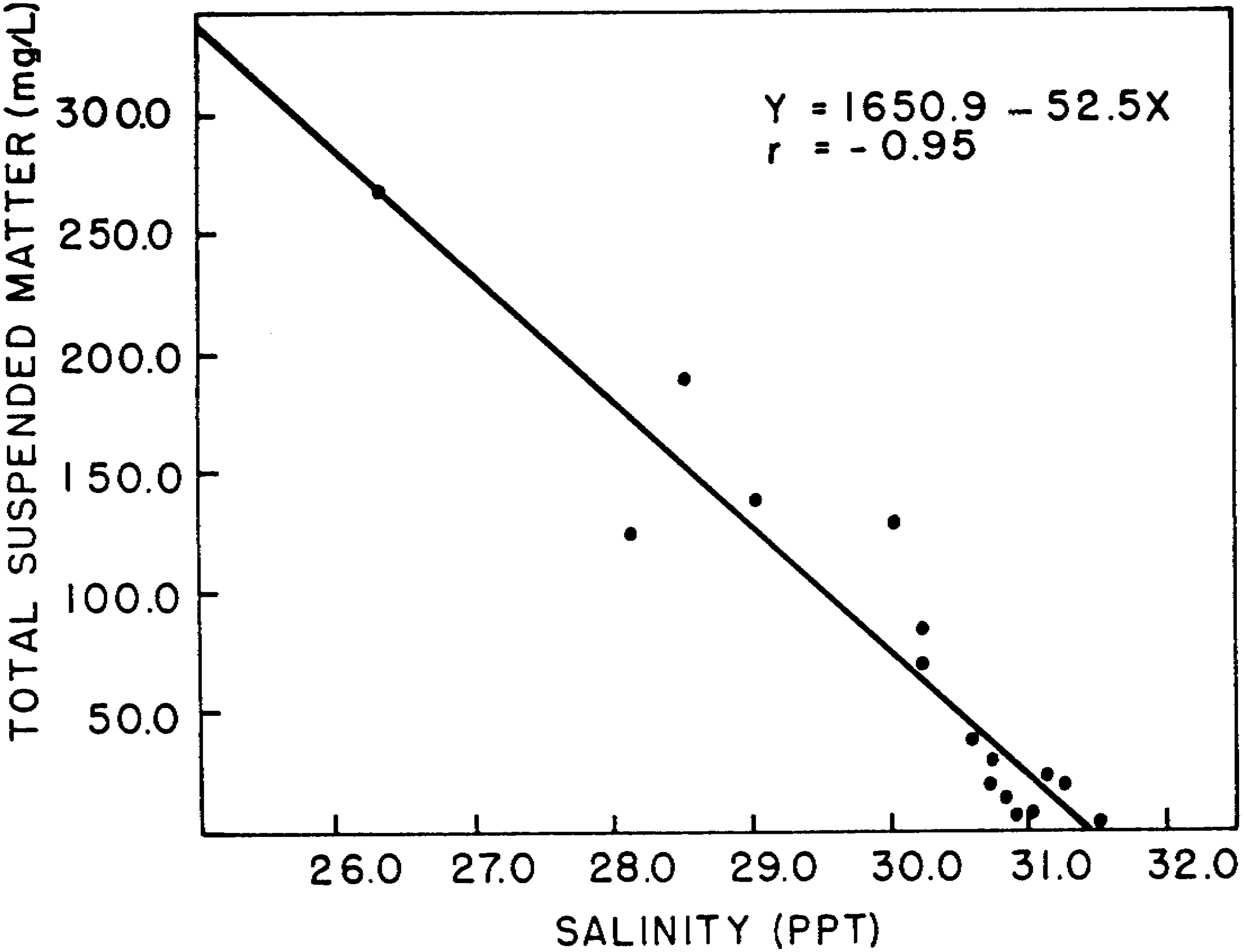

Figure 10. Scatter plot of the relationship between total suspended matter and salinity for surface samples from Lower Cook Inlet (Cruise RP-4-Di-77A-IV, 4-16 April 1977).

central region of Lower Cook Inlet, where the cross-channel gradients are highest. The data, which was from the April cruise show that the suspended loads are linearly correlated with salinity, indicating that dilution is the major process-controling suspended matter concentrations in the central portion of Lower Cook Inlet. A scatter plot for the July cruise shows similar results. These results suggest that the central part of Lower Cook Inlet acts like a conduit, allowing large amounts of suspended material to pass through the system with little net sedimentation. Sedimentation of suspended matter may be occurring in the numerous small embayments along the coast. It will be necessary to determine the vertical fluxes of suspended materials in the embayments if their role in the sedimentation of suspended matter and associated contaminants is to be properly evaluated.

B. Temporal Variability of Suspended Matter

In order to obtain some information about high frequency (hourly) fluctuations of particulate concentrations in Lower Cook Inlet, a 36-hour time series experiment was conducted at station 11 during the April cruise and a 26-hour experiment was conducted at station 4 during the July cruise. Water samples were collected and filtered every two hours from the surface and 5 m above the bottom. The results of these experiments are shown in figures 11 and 12. The high and low tides are represented in the figures by arrows. The reference point for the data was as indicated in the figures captions. Concentrations of suspended matter are highly variable both at the surface and near the bottom. At the surface particulate concentrations range from 40-90 mg/ℓ at station 11 and 10-115 mg/ℓ at station 4. The surface maximum have a 12-hour period and appear to reach their peak shortly after the tidal currents have come to maximum velocity. Near the bottom the suspended matter concentrations are more variable and may reach concentrations

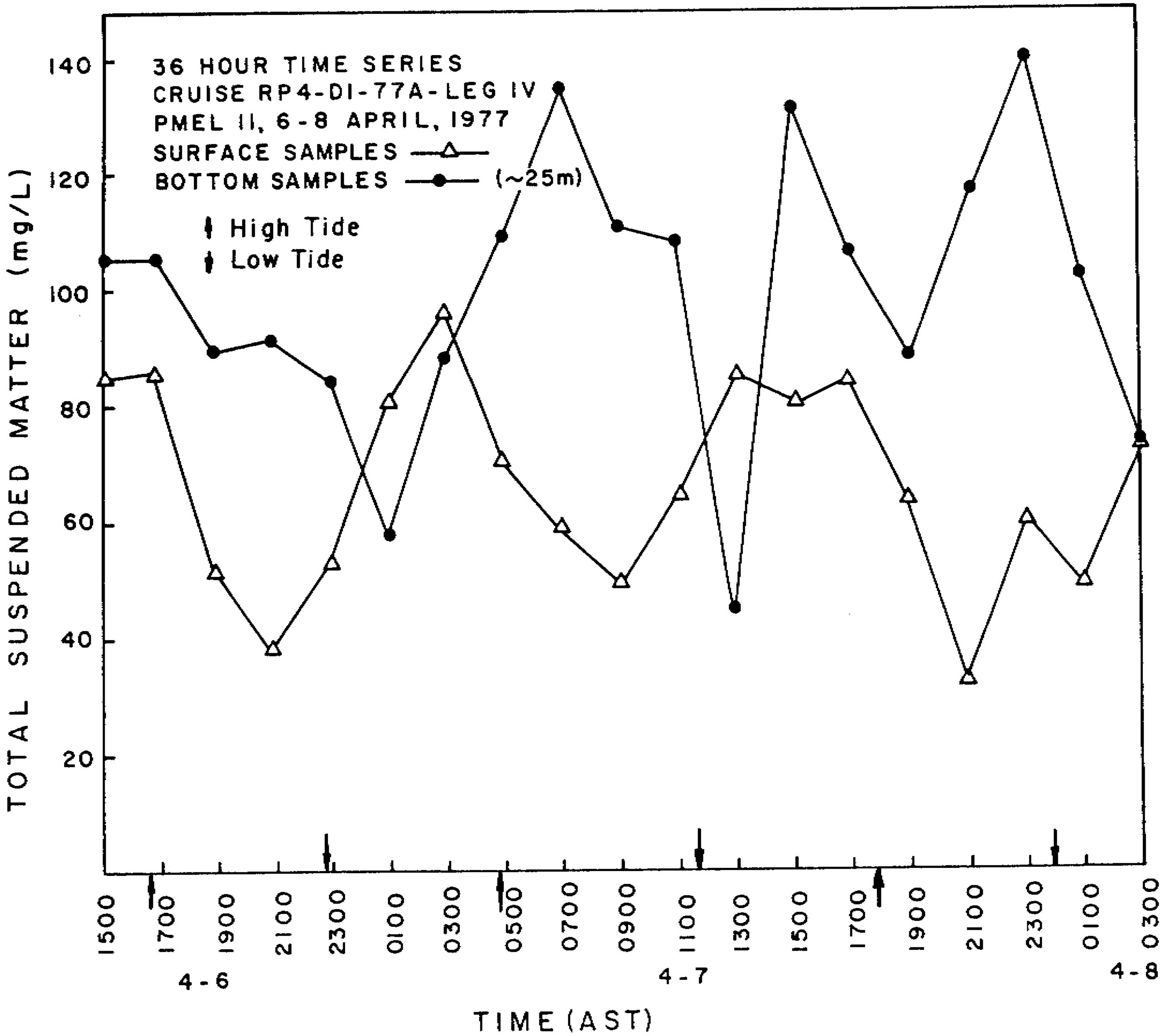

Figure 11. Temporal variability of total suspended matter at the surface and 5 m above the bottom at station 11 in Lower Cook Inlet (Cruise RP-4-Di-77A-IV, 4-16 April 1977). The reference point for the tidal data was Tuxedni Channel.

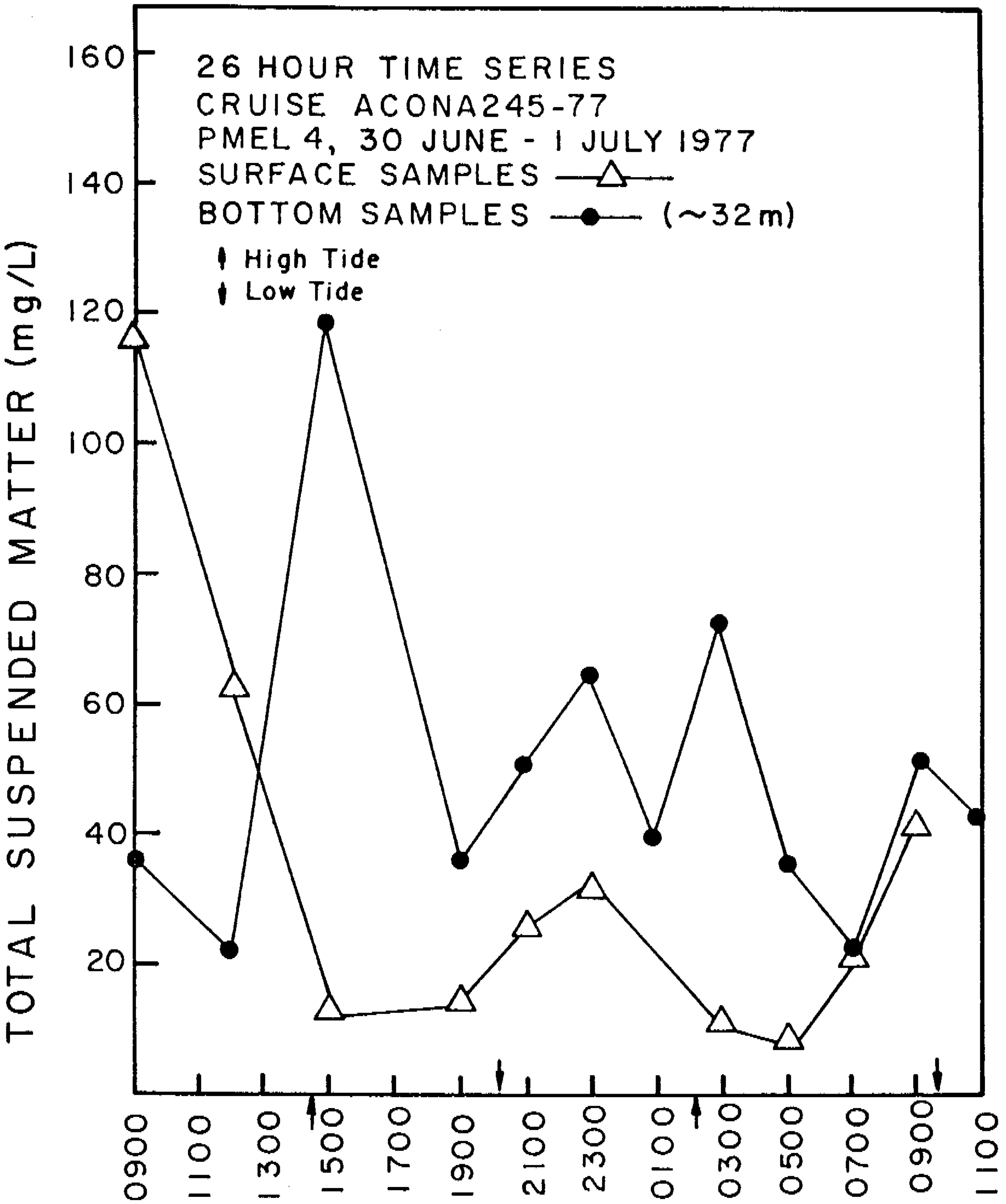

Figure 12. Temporal variability of total suspended matter at the surface and 5 m above the bottom at station 4 in Lower Cook Inlet (Cruise Acona-245, 28 June - 12 July 1977). The reference point for the tidal data was Drift River Terminal tide station.

in excess of 130 mg/ℓ. The near bottom particulate maxima do not show any consistent periodicity, and most probably, reflect local variations in the amount of material that is resuspended into the water column by bottom currents.

C. Elemental Composition of the Particulate Matter

Tables 1 through 3 compare summaries of the data on the elemental composition of suspended matter from the Susitna, Knik, and Matanuska Rivers with summaries of the surface and near bottom data for the April and July cruises in Lower Cook Inlet. Within the statistical limits of the measurements the samples from Lower Cook Inlet have very nearly the same major element composition as the samples from the rivers. This is especially true for Al, K, Ti, and Fe which have been shown to be almost exclusively associated with aluminosilicate minerals of terrestrial origin (Price and Calvert, 1973). The high concentrations of these elements in the surface and near bottom samples from Lower Cook Inlet indicate that aluminosilicate minerals are the most dominant solid phase in the particulate matter. These data indicate that approximately 80-95% of the particulate matter is aluminosilicate minerals. These results are not surprising since the Susitna, Matanuska and Knik Rivers supply about $15\text{-}20\times10^6$ tons of sediment annually to the Inlet.

Tables 2 and 3 also summarizes the elemental composition of 42 samples taken 5 meters above the bottom. In general, the major element concentrations of the near bottom samples are similar to the surface samples. This is especially true for the April cruise and in the northern part of the Inlet where the water column is well mixed. However, during the July cruise and in the southern part of the Inlet the water column was vertically strutified (fig. 8) and the elemental composition of the suspended matter showed distinct differences between the surface and 5 meters above the bottom. For

Table I.

Summary of the elemental composition of particulate matter samples from the major rivers discharging into Cook Inlet. (Surface samples were obtained with a precleaned 4-ℓ polyethylene bottle extended from a bridge 26 June 1977.)

Element	Susitna River	Matanuska River	Knik River
C(Wt. %)	1.04 ± 0.3	0.55 ± 0.04	0.75 ± 0.06
N(Wt. %)	0.06	0.03	0.05 ± 0.01
Mg(Wt. %)	3.80 ± 0.7	2.65 ± 0.2	4.19 ± 0.2
Al(Wt. %)	10.62 ± 1.4	7.55 ± 0.5	12.05 ± 0.8
Si(Wt. %)	36.52 ± 2.9	26.63 ± 1.0	33.56 ± 2.4
K(Wt. %)	2.83 ± 0.2	1.83 ± 0.1	2.89 ± 0.2
Ca(Wt. %)	2.13 ± 0.2	2.61 ± 0.05	1.28 ± 0.1
Ti(Wt. %)	0.67 ± 0.03	0.61 ± 0.01	0.68 ± 0.06
Cr(ppm)	120 ± 5	93 ± 2	115 ± 9
Mn(ppm)	1346 ± 41	1267 ± 49	1271 ± 109
Fe(Wt. %)	7.06 ± 0.3	6.89 ± 0.2	7.28 ± 0.5
Ni(ppm)	93 ± 6	56 ± 3	72 ± 4
Cu(ppm)	78 ± 8	72 ± 3	71 ± 5
Zn(ppm)	187 ± 9	129 ± 9	147 ± 14
Pb(ppm)	66 ± 4	48 ± 2	62 ± 14

Table II.

Summary of the elemental composition of particulate matter samples from Lower Cook Inlet (Cruise RP-4-Di-77A-IV, 4-16 April 1977).

Element	Average of 50 surface samples	Average of 50 samples from 5 m from the bottom
C(Wt. %)	4.01 ± 4.0	2.72 ± 2.5
N(Wt. %)	0.65 ± 0.5	0.41 ± 0.4
Mg(Wt. %)	3.54 ± 0.6	3.47 ± 0.9
Al(Wt. %)	3.64 ± 1.6	8.70 ± 1.6
Si(Wt. %)	31.04 ± 3.4	30.20 ± 4.3
K(Wt. %)	2.15 ± 0.4	2.24 ± 0.4
Ca(Wt. %)	2.20 ± 0.4	2.23 ± 0.3
Ti(Wt. %)	0.55 ± 0.1	0.58 ± 0.07
Cr(ppm)	95 ± 15	99 ± 16
Mn(ppm)	1313 ± 113	1326 ± 159
Fe(Wt. %)	6.22 ± 1.0	6.42 ± 0.8
Ni(ppm)	62 ± 10	63 ± 10
Cu(ppm)	71 ± 15	76 ± 17
Zn(ppm)	165 ± 32	176 ± 34
Pb(ppm)	56 ± 13	56 ± 12

Table III.

Summary of the elemental composition of particulate matter from Lower Cook Inlet and Shelikof Strait (Acona-245, 28 June 3 - 12 July 1977).

Element	Lower Cook Inlet		Shelikof Strait	
	Average of 50 surface samples	Average of 51 samples from 5 m above the bottom	Average of 17 surface samples	Average of 16 samples from 5 m above the bottom
C(Wt. %)	10.77 ± 11.0	6.18 ± 9.0	31.17 ± 11.2	8.40 ± 5.8
N(Wt. %)	1.98 ± 2.0	0.99 ± 1.4	4.89 ± 1.5	1.24 ± 0.8
Mg(Wt. %)	2.86 ± 1.41	3.59 ± 0.82	1.89 ± 0.91	4.01 ± 1.22
Al(Wt. %)	6.98 ± 4.24	8.88 ± 2.34	3.72 ± 2.46	9.49 ± 3.20
Si(Wt. %)	35.75 ± 5.56	38.09 ± 4.92	28.67 ± 10.10	44.71 ± 3.60
K(Wt. %)	1.86 ± 0.86	2.24 ± 0.45	0.89 ± 0.43	2.19 ± 0.63
Ca(Wt. %)	1.84 ± 0.63	2.33 ± 0.32	1.53 ± 0.35	2.08 ± 0.33
Ti(Wt. %)	0.46 ± 0.20	0.58 ± 0.10	0.27 ± 0.09	0.53 ± 0.12
Cr(ppm)	99 ± 30	115 ± 24	75 ± 36	116 ± 29
Mn(ppm)	1138 ± 574	1460 ± 362	981 ± 709	4174 ± 7642
Fe(Wt. %)	5.14 ± 2.11	6.50 ± 0.95	3.15 ± 1.14	6.39 ± 1.71
Ni(ppm)	70 ± 25	81 ± 16	59 ± 19	77 ± 13
Cu(ppm)	99 ± 33	100 ± 31	94 ± 27	112 ± 30
Zn(ppm)	352 ± 158	343 ± 194		
Pb(ppm)	65 ± 19	69 ± 13	60 ± 10	76 ± 22

examples figures 13 and 14 show vertical cross-sections of particulate carbon (expressed as a percentage of the total suspended matter) for the April and July cruises. The July data shows higher particulate carbon concentrations at the surface than at the bottom indicating a vertical stratification of the particulate organic matter. Similar gradients are not observed in the April data, this suggests that the waters are extremely well-mixed with respect to water properties and suspended matter.

Price and Calvert (1973) used the elemental concentrations of major elements in suspended matter to determine the sources and trajectories of terrigeneous components of suspended matter in coastal waters. Specifically the authors used the distributions of particulate aluminum as an indicator of the distribution and trajectories of aluminosilicate minerals. Similarly, other investigators have used particulate carbon as a tracer of particulate organic matter in the oceans (Menzel and Vaccaro, 1964). Riley (1970) suggested that a factor of 2.0 be used to estimate concentrations of particulate organic matter from particulate carbon. Recent investigators have used carbon to nitrogen ratios in particulate matter to distinguish between terrestrial and marine sources of organic matter (Loder and Hood, 1972). The authors found that riverborne organic matter have C:N ratios which range between 15-25. In contrast, ratios for marine organic matter range between 5-15.

The distributions of particulate aluminum and carbon (both expressed as a weight percent at the total particulate matter) and the carbon to nitrogen ratio for the surface samples from the April cruise are presented in figures 15 and 16. The data show that aluminum and carbon are inversely related, indicating that near the mouth of Cook Inlet and to some degree near the mouth Kachemak Bay the percentage of aluminosilicates in the suspended

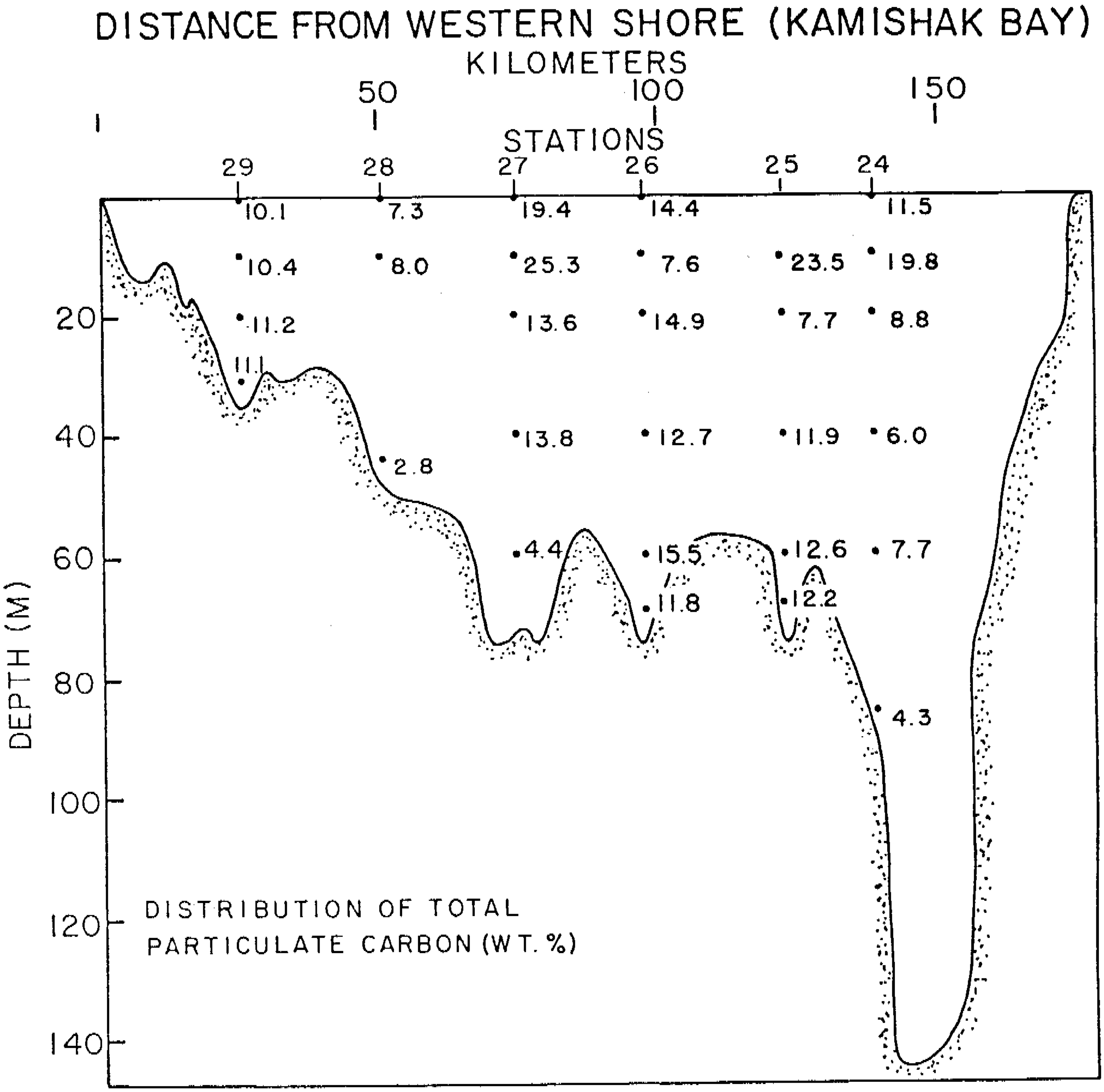

Figure 13. Vertical cross section of the distribution of total particulate carbon for stations 24 thru 29 in Lower Cook Inlet (RP-4-Di-77A-IV, 4-16 April 1977).

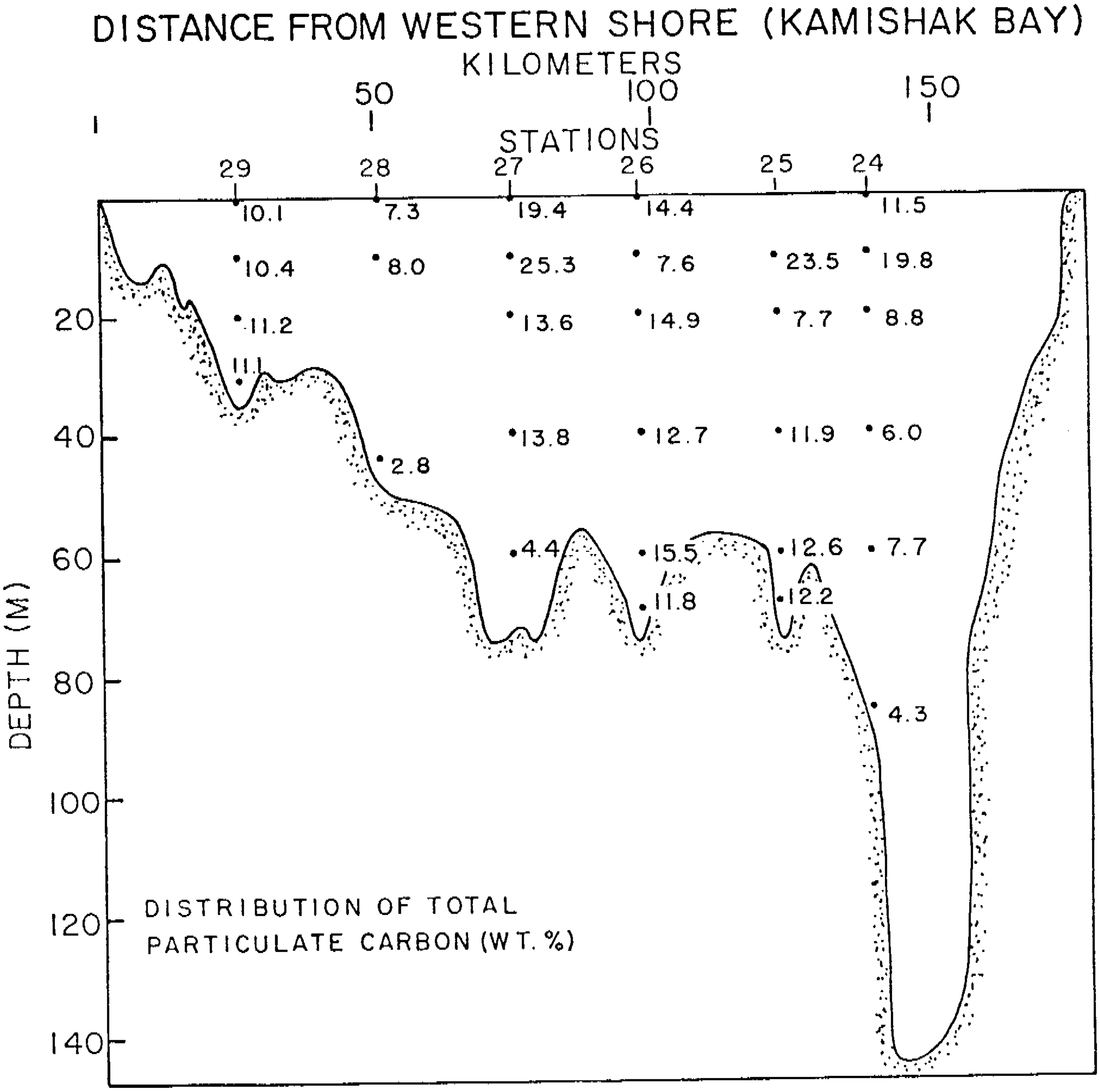

Figure 14. Vertical cross section of the distribution of total particulate carbon for stations 24 thru 29 in Lower Cook Inlet (Cruise Acona-245, 28 June - 12 July 1977).

matter decreases while the percentage of organic matter increases. This is attributed to input of organic-rich particles from the Gulf of Alaska with the inflowing water and to biological production of organic matter on the eastern side of the Inlet. These conclusions are substantiated by the carbon to nitrogen ratios (fig.16) which show values which are indicative of the predominance of marine organic matter (6.5-9.0) at Kennedy and Stevenson Entrances and in the eastern portion of the Inlet. The predominance of the terrestrially derived organic matter is indicated by the high carbon to nitrogen ratios in the western side of the Inlet.

The terrestrially derived aluminosilicates from Lower Cook Inlet, which can be identified by their relatively high aluminum concentrations (>10% aluminum by weight), are traced from Kamishak Bay past Cape Douglas into Shelikof Strait as far south as Cape Nukshak. This suggests that the outflowing brackish water from Lower Cook Inlet carries the terrigenious material around Cap Douglas and into Shelikof Strait where it mixes with the inflowing oceanic water and disperses, eventually losing its identifying characteristics near Katmai Bay.

Similar mixing and dilution patterns are indicated in the trace element data. Figures 17 and 18 show the distributions of particulate Cu and Ni for the surface samples from the April cruise. Highest concentratons of particulate Cu and Ni are located near Kalgin Island at the head of Lower Cook Inlet. These samples are primarily composed of aluminosilicate minerals from the major rivers discharging into Upper Cook Inlet. The trace element concentrations of particles in this region are directly dependent upon the relative abundances of the different aluminosilicate minerals which reach Lower Cook Inlet from these sources. Near the mouth of the Inlet particulate Cu and Ni concentrations decrease by about 40 and 48%,

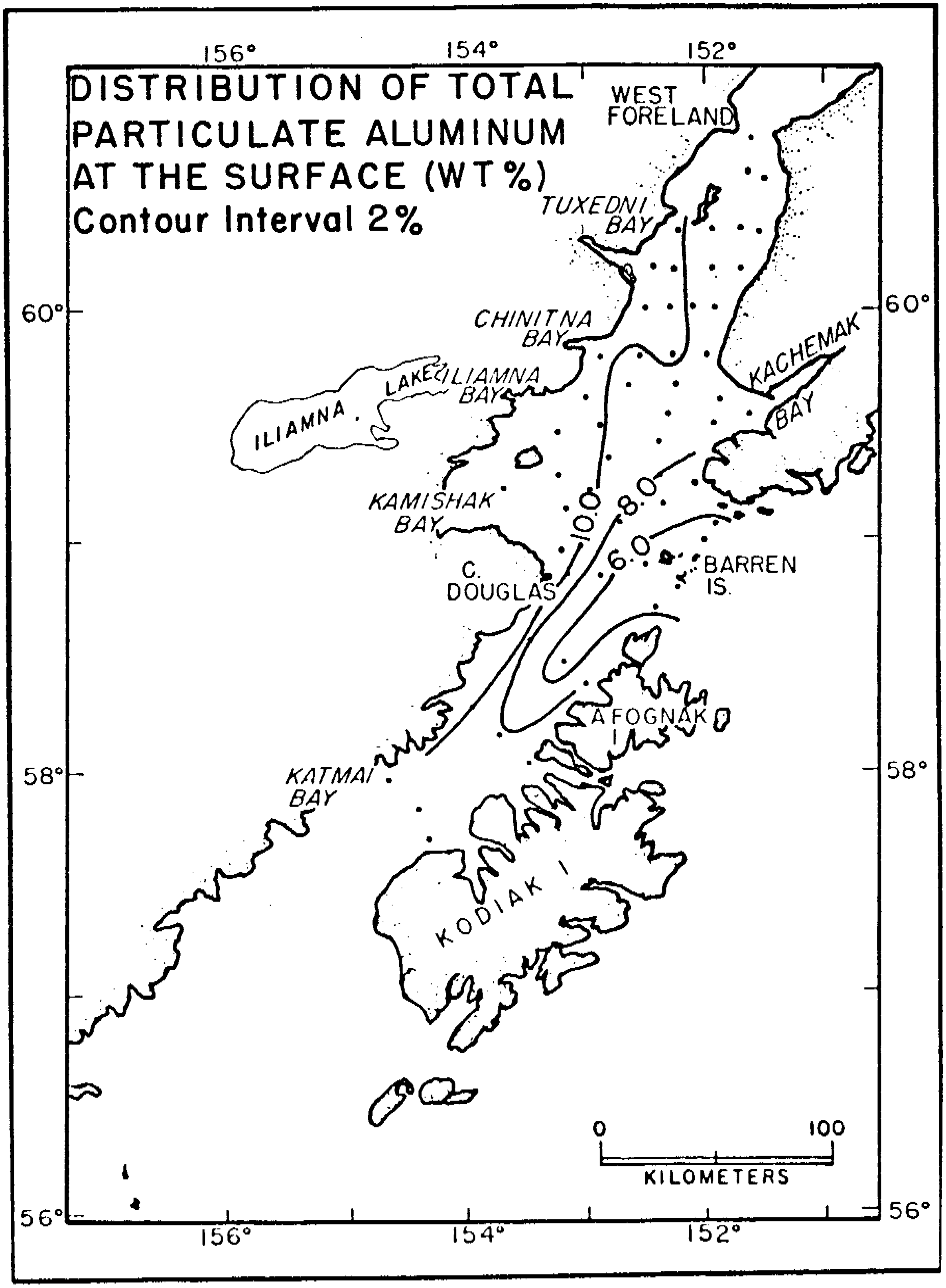

Figure 15. Distribution of particulate aluminum in the suspended matter at the surface in Lower Cook Inlet (Cruise RP-4-Di-77A-IV, 4-16 April 1977).

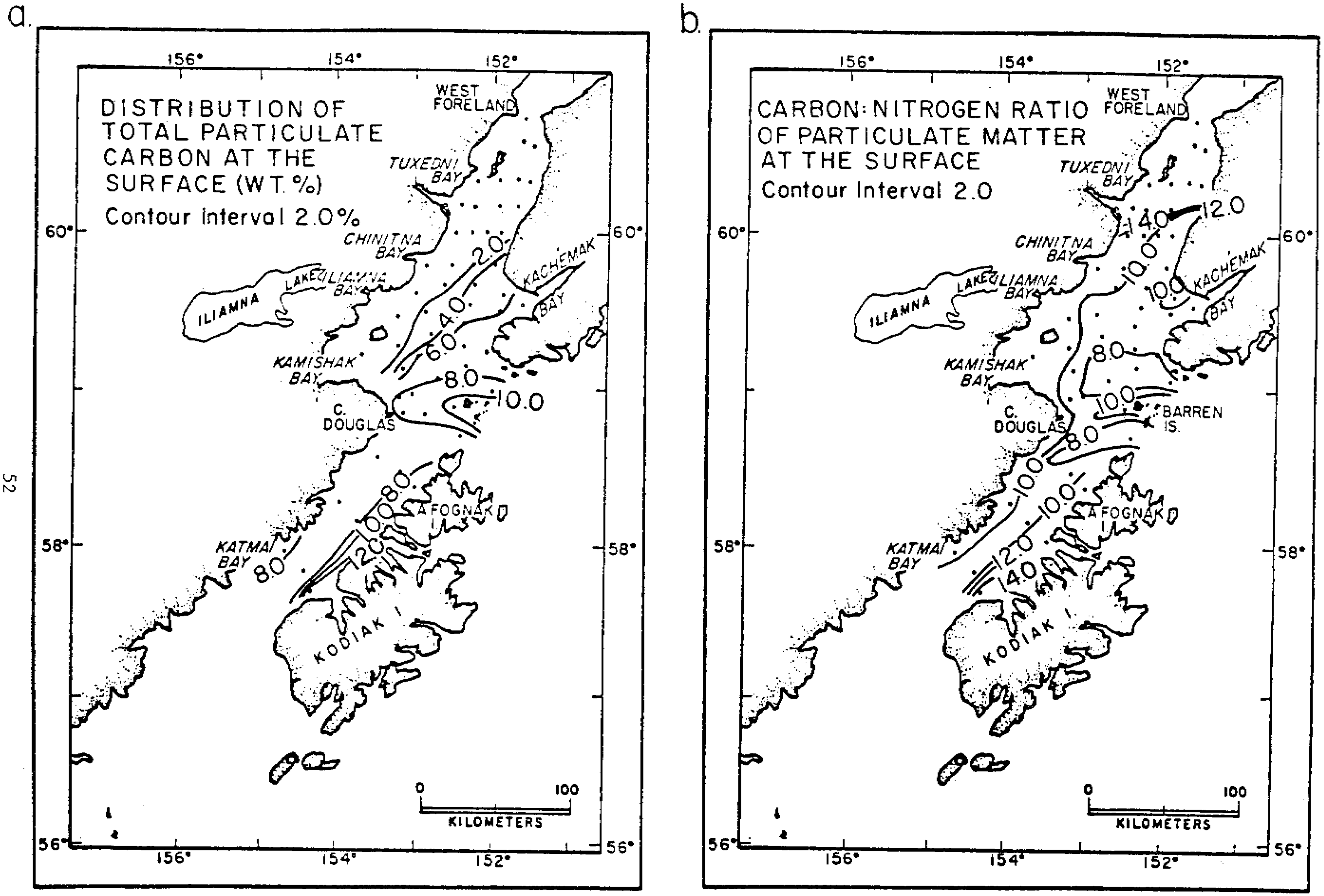

Figure 16. Distribution of: a. total particulate carbon; and b. carbon:nitrogen atom ratios at the surface in Lower Cook Inlet (Cruise RP-4-Di-77A-IV, 4-16 April 1977).

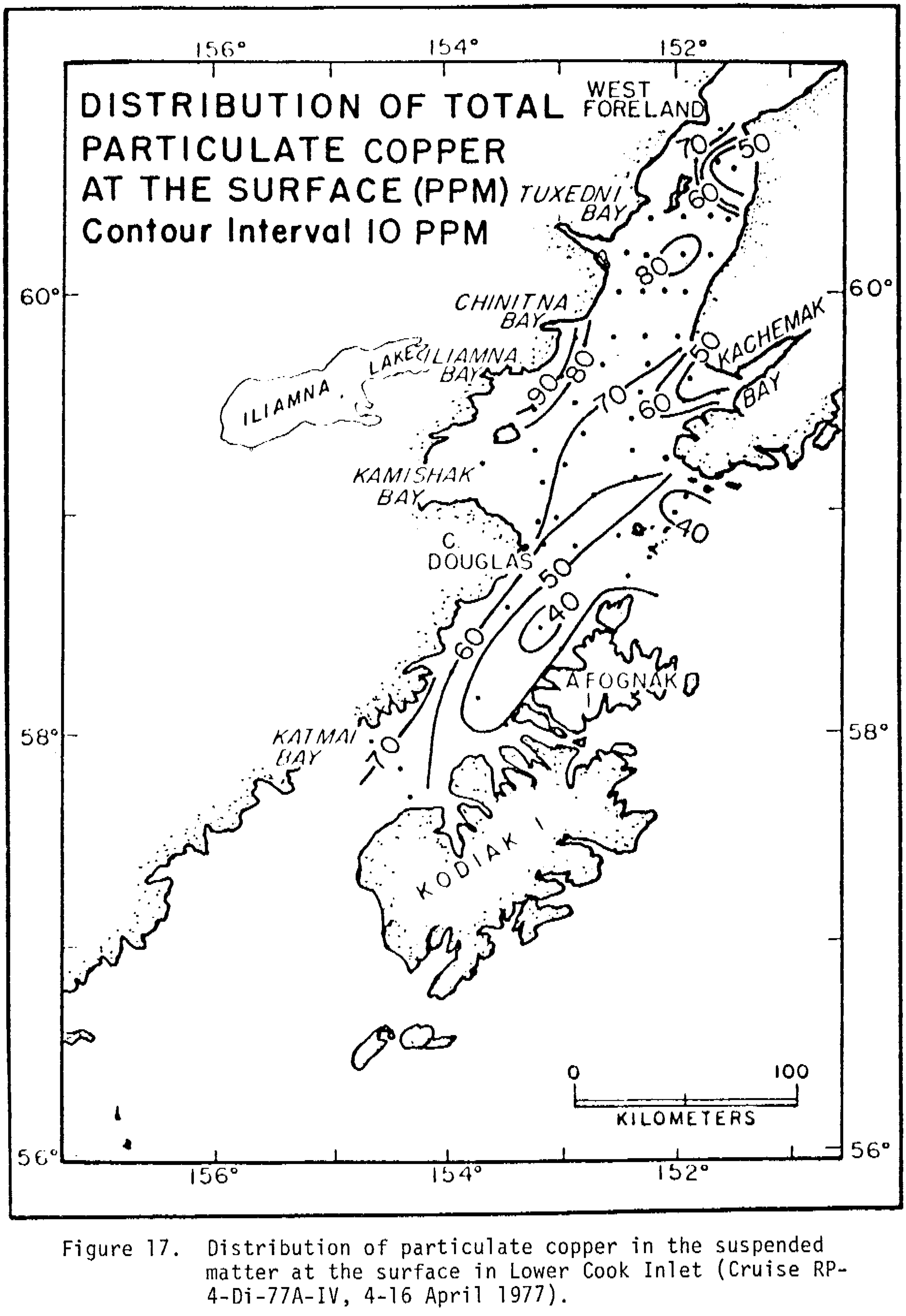

Figure 17. Distribution of particulate copper in the suspended matter at the surface in Lower Cook Inlet (Cruise RP-4-Di-77A-IV, 4-16 April 1977).

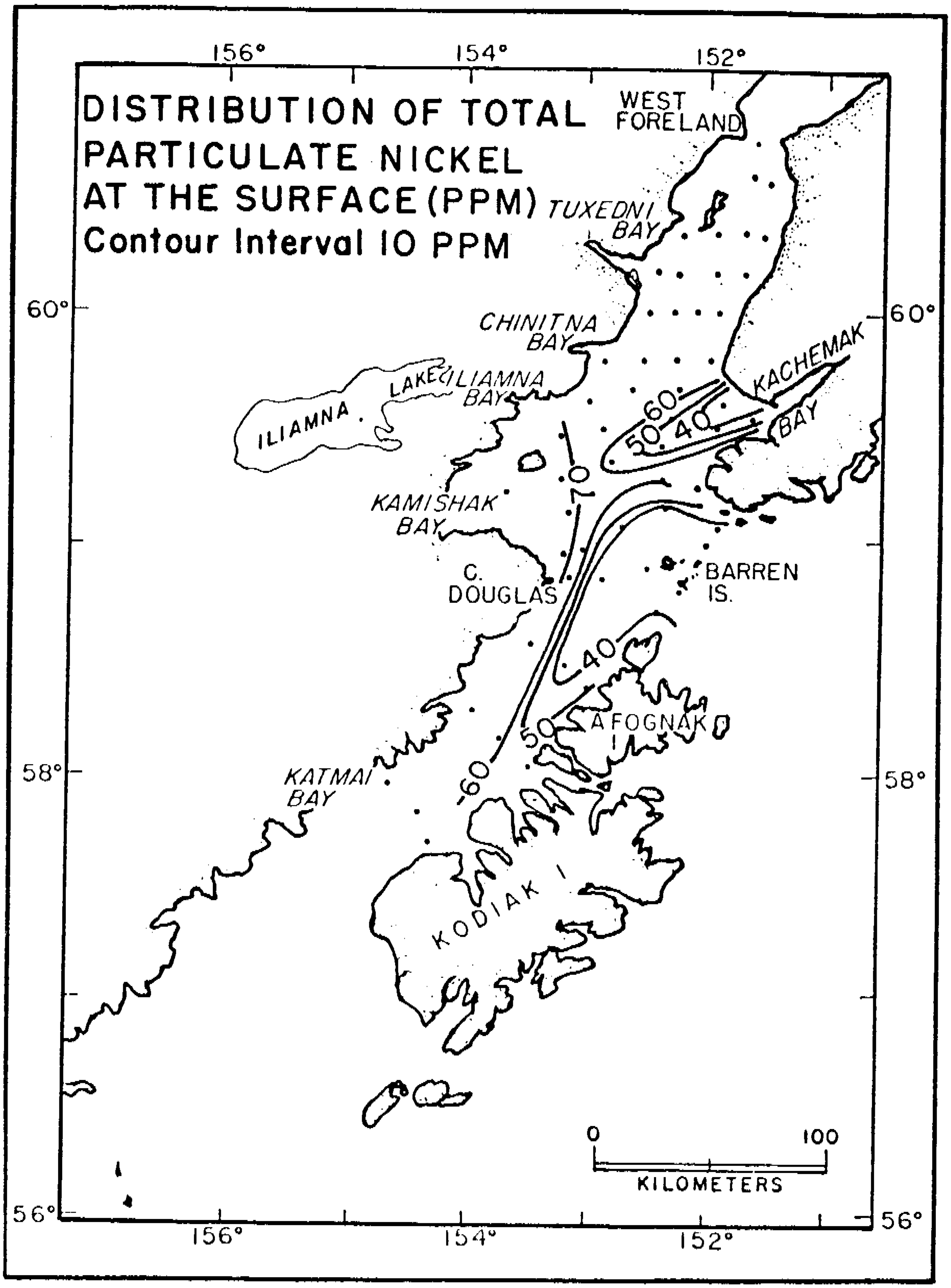

Figure 18. Distribution of particulate nickel in the suspended matter at the surface in Lower Cook Inlet (Cruise RP-4-Di-77A-IV, 4-16 April 1977).

respectively. This decrease may be due to a number of factors including: (1) sedimentation of specific aluminosilicate minerals; (2) dilution by marine organic matter; and (3) release of metals from the particles. At present, dilution by marine organic matter appears to be the dominant factor. However, the other processes may be operative to varying degrees. Studies are presently under way to determine the extent of these processes.

Table III also shows the average elemental composition of 12 surface samples and 16 near bottom samples which were collected from Shelikof Strait during the July cruise. Although the variability is high some trends are evident. The surface samples are depleted in Mg, Al, K, Ti and Fe relative to the samples from Lower Cook Inlet while the bottom samples are enriched in Si and Mn. The depletions of Mg, Al, K, Ti and Fe in surface samples are attributed to dilution by marine biogenic matter which is associated with the inflowing Gulf of Alaska water. The enrichments of Si and Mn in the near bottom samples are anomalies and may indicate a different source for all or part of the near bottom suspended matter.

Table IV is a comparison of the average concentrations of major and trace elements in particulate matter from Lower Cook Inlet with elemental concentrations of particulate matter from the northeast Gulf of Alaska and noutheastern Bering Shelf. The data for the individual lease areas show large variances which are due to local and seasonal variations in the chemical composition of the particulate matter. In spite of these variations some regional differences are observed which can be related to regional differences in the composition of source materials and/or differences in the total amount of terrestrial material that comprise the suspended matter. For example, the data for the northeast Gulf of Alaska and Lower Cook Inlet show differences in the concentrations of C, N, and K which are statistically significant. The enrichments of C and N in the samples from the northeast Gulf of Alaska relative to Lower Cook Inlet are attributed to rapid sedimentation of terrigenous particles in near shore waters (Feely and Cline, 1977) and biological production of organic particles in offshore waters of the Gulf (Larrance, 1977). The enrichment of K in the Lower Cook Inlet samples is attributed to the increased illite/chlorite ratio of the suspended clay minerals which are discharging into Cook Inlet from the Susitna, Matanuska and Knik Rivers (Hein et al., 1978).

The average elemental concentrations of particulate matter from the southwestern Bering Shelf shows significant depletions of Mg, Al, K, Ti, Cr, Mn, Fe, Ni and Cu. These elements are concentrated in terrigenous particles and their depletions in the Bristol Bay samples are attributed to dilution by marine biogenic matter. This conclusion is supported by two independent facts. First, the samples from the southeastern Bering Shelf have a higher particulate carbon content (~19%). Since Feely and Cline (1977) have already shown that the organic matter in the southeastern Bering Shelf has a marine origin and because trace elements are generally thought to be depleted in marine biogenic matter relative to terrigenous matter (Martin and Knauer, 1973), it is reasonable to expect that dilution of the suspended matter with particles of marine origin would have the effect of decreasing the overall concentrations of these elements in the particulate matter. Second, Price and Calvert (1973) state that terrigenous aluminosilicates have Si/Al ratio which range between 2.3 and 3.2. Therefore, an estimate of the biogenous Si content of suspended matter can be obtained by assuming a constant Si/Al ratio to be due to suspended aluminosilicates and any excess to be due to biogenous Si. Using the data

Table IV.

Regional average concentrations of major and trace elements in suspended matter from the Alaskan Outer Continental Shelf lease areas.

Element	Northeast Gulf of Alaska	Lower Cook Inlet	Southeastern Bering Shelf
C(Wt. %)	14.01 ± 8.7	3.36 ± 2.2	17.05 ± 12.4
N(Wt. %)	2.29 ± 1.4	0.53 ± 0.4	2.33 ± 1.9
Mg(Wt. %)	3.78 ± 1.4	3.50 ± 0.7	1.26 ± 0.3
Al(Wt. %)	8.82 ± 3.6	8.67 ± 1.6	3.91 ± 1.6
Si(Wt. %)	31.71 ± 3.7	30.62 ± 3.8	25.97 ± 6.1
K(Wt. %)	1.15 ± 0.4	2.19 ± 0.4	0.48 ± 0.2
Ca(Wt. %)	2.14 ± 0.8	2.22 ± 0.4	1.53 ± 0.6
Ti(Wt. %)	0.61 ± 0.1	0.56 ± 0.1	0.25 ± 0.1
Cr(ppm)	100.7 ± 33	87.1 ± 16	43.2 ± 24
Mn(ppm)	1141 ± 328	1319 ± 136	682 ± 335
Fe(Wt. %)	5.74 ± 2.0	6.32 ± 0.9	2.85 ± 0.6
Ni(ppm)	69.1 ± 23	62.9 ± 10	32.3 ± 18
Cu(ppm)	90.4 ± 26	73.1 ± 16	44.2 ± 29
Zn(ppm)	195.5 ± 38	170.8 ± 33	228 ± 134
Pb(ppm)	52.3 ± 14	56.4 ± 12	53.2 ± 20

from Table I for the rivers discharging into Cook Inlet and the data from Feely and Cline (1977) for the rivers discharging into the northeast Gulf and Bristol Bay an average ratio of 3.2 is assumed to be due to suspended aluminosilicates. Under these conditions >50% of the particulate Si in samples from the southeastern Bering Shelf is estimated to be of biogenous origin as compared to <10% for samples from Lower Cook Inlet and the northeast Gulf of Alaska. While these estimates are subject to large variations and, therefore, are somewhat crude, they do serve to illustrate the importance of knowing the relative contributions of terrestrial and marine sources of suspended matter if trace element variations in particulate matter are to be properly interpreted.

D. Hydrocarbon-Suspended Matter Interaction Studies

The first preliminary results of the oil loading experiment are shown in Table V and Figure 19. The initial oil-sediment loading ratio varies from 0.17 to 1.7 (8.4 mg to 84.5 mg oil added). The salinity of the water was approximately $32^{\circ}/oo$ and the temperature regulated to $10^{\circ}C$. In addition to the amount of sediment accommodated oil, Table V also reflects the quantities of sediment and oil recovered in the two fractions (columns 3-6). One experiment has been performed to date ($N = 3$) at $T = 5^{\circ}C$ ($L_0 = 8.84$) and those results are shown in Figure 19.

In general, the quantity of sediment accommodated oil increases as the concentration of oil added is increased. The curve appears to be reaching a point of saturation, but oil concentrations were not sufficiently high to reach this value. Maximum amount of accommodated oil reached about 5% of the sediment weight under these specific conditions. The single experiment at $5^{\circ}C$ shows significantly higher accommodations (Fig. 19), in

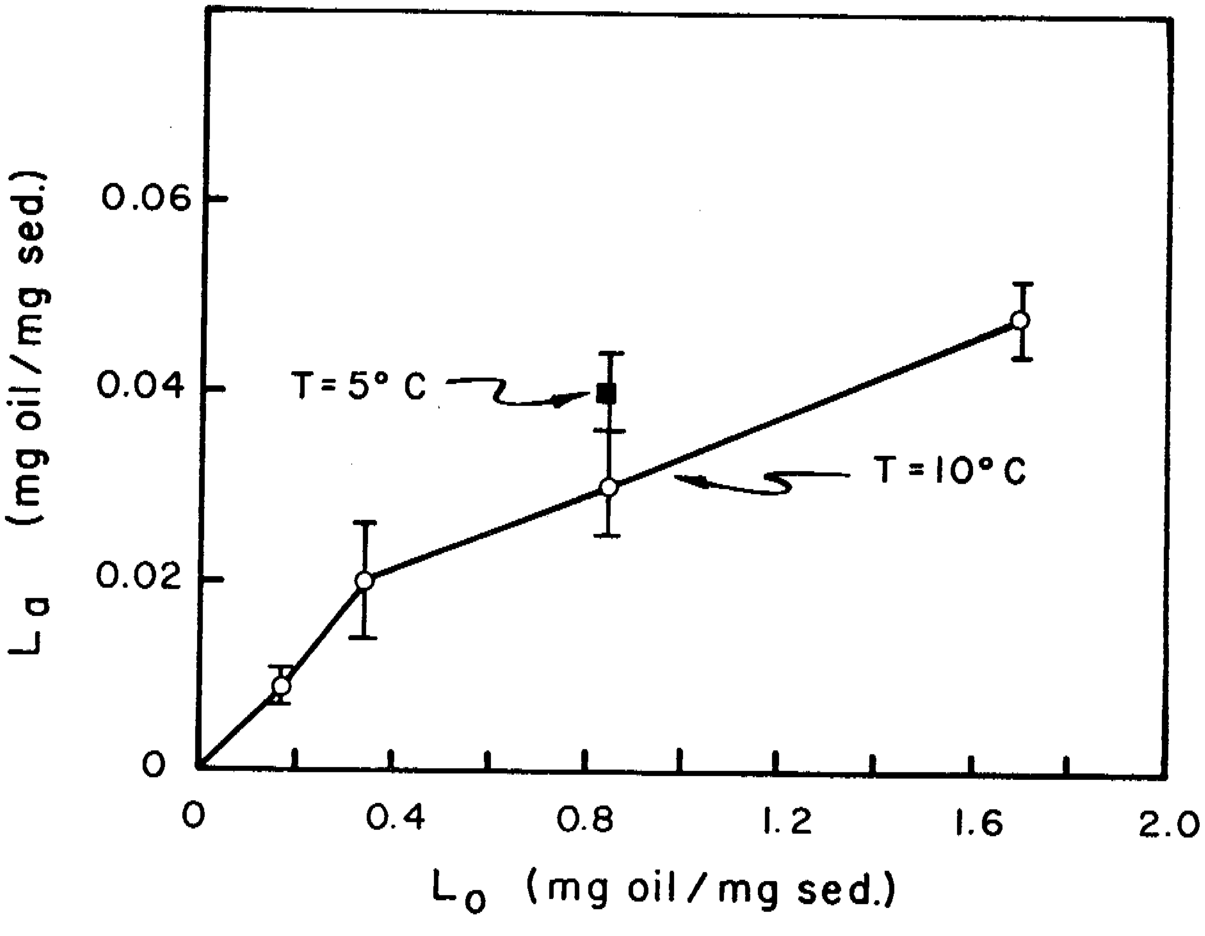

Figure 19. Concentration of accommodated Cook Inlet crude oil (La) on Cook Inlet suspended matter as a function of the initial oil loading (Lo). Experiments were performed at 10°C (o) and 5°C (■) in normal sea water (S = 32°/oo). Concentration of suspended matter was 62 mg/ℓ in each experiment.

agreement with our earlier studies in which the quantity of accommodated oil is inversely proportional to the temperature (Baker et al., 1978).

The amount of total oil recovered from both fractions is reflected in column 5 of Table V. Total oil recoveries varied from 18% to 61%; the latter value approaching the experimental maximum of 80% when uncorrected for evaporative and extractive losses. Low recoveries also were encountered in a similar study using Skagit and Fraser Rivers sediments with Prudhoe Bay crude oil, although the recoveries were not as severe as these (Baker et al., 1978). We have checked for leakage as a possible cause with negative results. The poor extraction efficiency appears to be related to the composition of the oil and of sediment in the mixture. An effort is currently underway to identify the source of the problem.

In order to compare some of the physical properties of the oil-suspended matter aggregates relative to the suspended matter from Lower Cook Inlet, samples of each were subjected to particle size analysis utilizing both a light microscope (AO 3025TU Epi LUME) and a scanning electron microscope (ISI Super Mini SEM II) and the procedures outlined by Feely (1976) as described in Section V of this report. The results of these studies are presented in Figure 20. The size distribution of the ambient suspended matter indicates particles which range between 0.1 and 35.0 μm with a median diameter of 1.9 μm. In contrast the oil-suspended matter aggregates range between 5.0 and 45 μm with a median diameter of 7.5 μm. The oil-suspended matter aggregates were spherical in appearance and contained numerous fine particles. Increased oil loadings in the laboratory experiments did not appear to significantly change the resulting particle size distributions

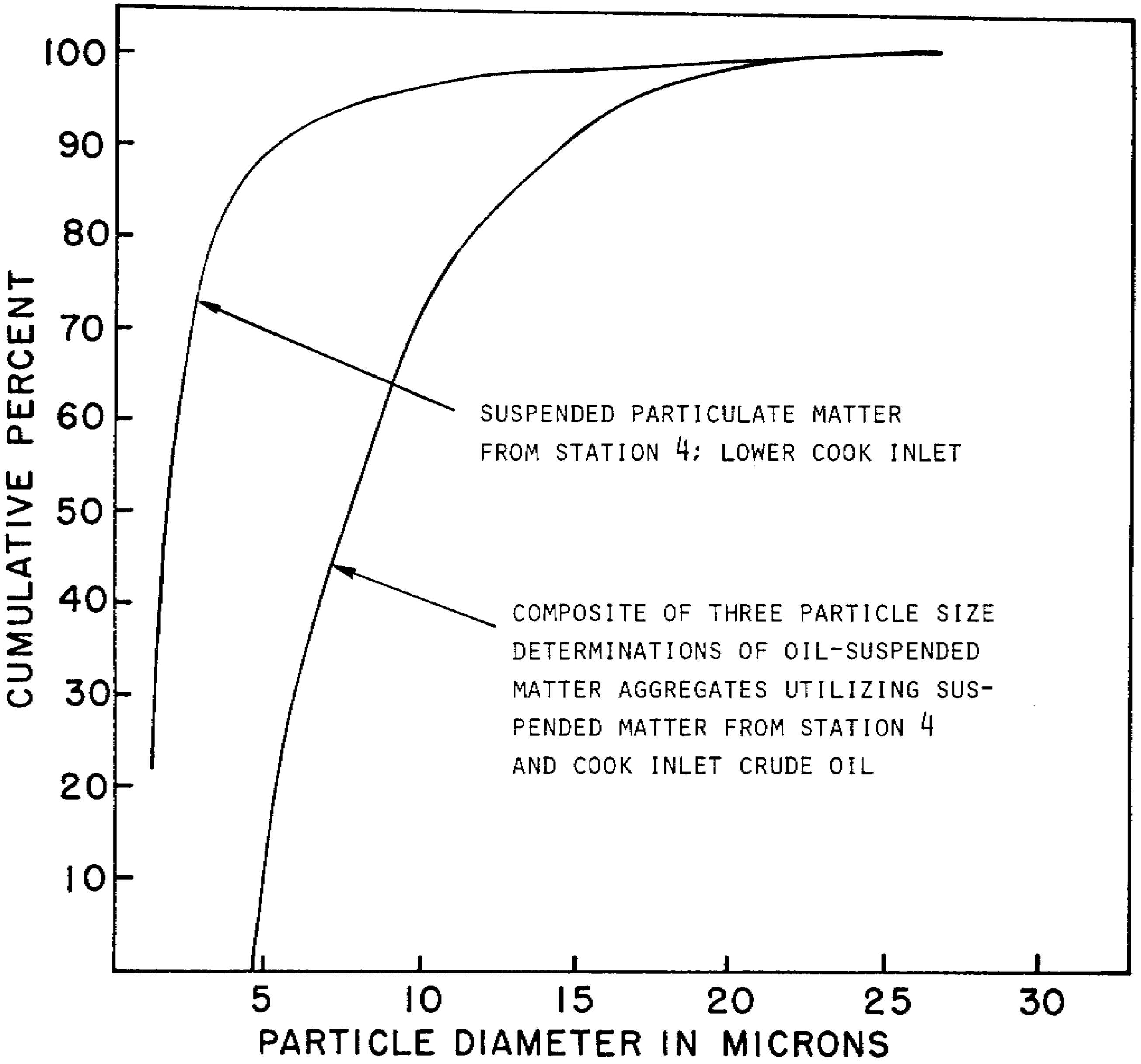

Figure 20. Particle size distributions for surface suspended matter from station 4 in Lower Cook Inlet and oil-suspended matter aggregates resulting from the laboratory interaction studies.

Table V.

The concentration of sediment accommodated Cook Inlet crude oil is shown for various initial oil loadings. All experiments were carried out in 1 liter separatory funnels to which was added 800 mℓ of sea water (S = 32°/oo) and 50 mg of suspended particulate matter obtained from near Kalgin Island. Temperature was held constant at 10°C. Number of replicate experiments is shown in column 2; numerical entries represent the mean and one relative standard deviation.

Amt. Oil Added (mg)	N (No.)	Sed. Recovered Lower Layer (%)	Oil Recovered Lower Layer (%)	Total Oil Recovered (%)	Loading (mg oil/mg sed.)
8.4	5	70 ± 3	3.6 ± 0.5	18 ± 7	0.009 ± 0.002
16.9	7	61 ± 9	3.6 ± 1.3	27 ± 7	0.020 ± 0.006
42.2	3	49 ± 8	2.0 ± 0.0	50 ± 3	0.030 ± 0.006
84.5	3	66 ± 3	3.0 ± 1.7	61 ± 14	0.048 ± 0.004

of the aggregates, although the range of oil loadings was small (20-100 μℓ). These results suggest the oil-suspended matter aggregates maintain an optimal size distribution which is independent of the oil loadings. Therefore unless rapid resolubilization of oil occurs during settling, the aggregates would be expected to settle at rates which are proportional to their size and density. In Cook Inlet this could mean rates which are higher than expected for ambient suspended matter.

Clay minerals and quartz sols (presumably other rock forming minerals as well) usually possess a net electrical charge, brought about by charge dislocation or imperfections within the crystal lattice, or "broken bond" surfaces created by the fracture of mineral grains (Van Olphen, 1963). In the latter case, cations or unions may be adsorbed or chemisorbed to the surface to satisfy the electrical imbalance. The net effect is that the mineral grains repulse each other due to their like charges. Counteracting this force is Van der Waal's force which tends to minimize the surface-free energy of the individual particles through particle agglomeration or growth (Castellan, 1964). In an ionic medium, such as sea water, the electrical double layer is compressed, and the particles are said to flocculate under the effect of Van der Waal's forces.

When oil is added to an ionic clay sol, complex behavior of the system is observed and not readily predictable by theory. How the system behaves depends on the specific interactions between the oil and water, oil and particles, and water and particles. In turn, these relationships depend on the composition of the aqueous medium, size and mineralogy of the particles.

The behavior of a typical Cook Inlet crude oil toward Cook Inlet sediments is analogous to our findings with Prudhoe Bay crude oil and riverine suspended sediments of local origin. For a fixed sediment concentration (i.e., 62.5 mg/ℓ), the quantity of oil harbored by settled solids is proportional to the concentration of oil. In this study, no more than 5% accommodation was observed, whereas in the aforementioned work accommodations up to 100% were observed when Skagit River sediments were used. These sediments were coarser grained (dia $_{med}$ = 2.6 μm) and contained a larger fraction of rock fragments relative to clay minerals. Fraser River sediments were finer grained (dia $_{med}$ = 1.8 μm) and richer in the clay minerals chlorite and illite (Baker et al., 1978). These sediments retained up to 12% of the sediment weight in oil with values of 7% being more typical. Since the sorbed phase was the same for each sediment type, we assume the differences were largely due to mineralogies and particle size. Particle size analysis of suspended matter from station 4 in Cook Inlet shows a median diameter of 1.91 μm (Fig. 20), analagous to that of the Fraser River sediments.

Cook Inlet is a high energy environment, resulting in the selective winnowing and transport of the fine-grained material from the region (Hein, et al., 1978). Areas of notable exception presumably include the protected areas of Kachemak and Kamishak Bays. The dominant locally-derived clay minerals are illite and chlorite, although their percentage of the total suspended load is unknown. The chlorite/illite ratio is approximately 0.9 (Hein et al., 1978), compared to 1.7 for the Fraser River.

The adsorptive characteristics of Cook Inlet sediments appear to be more similar to Frazer River material than to Skagit River sediments. In both cases, oil loadings were generally less than 10%, which appears to be related to differences in mineralogies and particle size. However, we can't rule out differences in oil compositions as a major factor in the agglutinization process. For example, Huang and Elliott (1977) showed that silica particles (eg. Cabosil) stabilized oil-sediment mixtures to different extents, depending on the particular crude oil used. The stabilization was attributed to oil-solid interactions and presumably is the result of oil composition (eg. concentration of surface-active components such as N-O-S compounds or fatty acids).

In this study, as well as in the former example, finer particles tended to agglutinate or attach themselves to the surface slick, rather than flocculate as discrete oiled particles. As a surface oil slick tends to weather, the specific gravity of the oil will tend to increase due to the loss of volatiles, and the incorporation of both water and solid particles into the oil (Gordon, et al., 1976). While these experiments emphasized oil-sediments interactions over short intervals of time (ie., 1 hr), it is likely that sediment retained initially in a surface slick would ultimately form the nucleus of tar balls. There is a need to carry out these experiments over longer periods of time, possibly up to one week, to determine the longer range interactions.

VIII. Conclusions

The most significant conclusions of the suspended matter program in Lower Cook Inlet are listed below.

1. The suspended matter distributions appear to follow the general pattern of circulation in Lower Cook Inlet and Shelikof Strait. The inflowing relatively clear Gulf of Alaska water, which contains significant amounts of biogenic particles, flows northward along the eastern side of Lower Cook Inlet until it reaches Cape Ninilchik, where it mixes with the outflowing

turbid brackish water. The outflowing turbid water moves along the western side of the Inlet past Augustine Island and Cape Douglas into Shelikof Strait where it mixes with the oceanic water and is dispersed. Comparisons of suspended matter and sediment characteristics indicates that net sedimentation of suspended matter in the central basin of Lower Cook Inlet is minimal. However sedimentation may be occurring in the numerous embayments along the coast.

2. Chemical analysis of the suspended material from Lower Cook Inlet reveals that aluminosilicate minerals from the coastal rivers comprise about 80-95% of the suspended matter, with biogenic material making up the rest. Analysis of seasonal variations of C:N ratios of the particulate organic matter indicates that organic matter of marine origin is dominant in the summer where as organic matter of terrestrial origin predominates in winter when primary production is low.
3. Comparisons of regional average concentrations of major and trace elements in the particulate matter indicate regional differences which can be related to differences in the average composition of source material and the relative amounts of biogenic and terrigenous components.
4. Controlled laboratory studies of the interactions between Cook Inlet crude oil and suspended matter from Cook Inlet show that the accommodation capacity of suspended matter for crude oil increases with the concentration of added oil. Important

parameters in the accommodation process include: The chemical nature and viscosity of the oil; the mineralogical composition and size distribution of the suspended matter; temperature; and degree of mixing.

IX. Needs for Further Study

The recommendations for future studies with respect to the suspended matter program are presented below.

1. The results of the suspended matter distribution studies show that while concentration gradients for suspended matter in Lower Cook Inlet are extremely high, little net sedimentation occurs in the central basin of Lower Cook Inlet. Therefore, the embayments along the coasts of Lower Cook Inlet and Shelikof Strait may be receiving most of the fine grained particulate materials which are discharged from the coastal river. Since suspended particles have been shown to efficient scavengers of pollutants and because many of the living resources indigenous to Lower Cook Inlet are suspension and detrital feeders, future studies should be devoted to determining where the suspended material ultimately resides.
2. At present the oil-suspended matter interaction studies have demonstrated that increased oil loadings have resulted in increased accommodation of the oil by suspended matter. The upper limit, if there is one, of the accommodation capacity should be determined. Also, in the future, studies should be initiated to evaluate the nature and extent of resolubilization of oil from particles. Experiments of this nature will allow for accurate evaluation of the subsursurface oil transport in association with particulate matter.

X. Summary of Second Quarter Operations

A. Task Objectives

The primary objectives of the particulate matter program during the second quarter have been to complete the chemical analysis of the samples collected during the spring, summer and fall cruises and to recover the sediment traps that were deployed in October.

B. Field Activities from 1 January - 1 April 1978

1. Ship Schedule
    a. DISCOVERER Cruise (RP-4-Di-78A-I, 5-24 March 1978)
2. Participants from PMEL
    b. Ms. Jane Hannuksela, Oceanographer

C. Laboratory Activities from 1 January - 1 April 1978

During the second quarter most of our laboratory work has been concerned with the analysis of the samples from the summer and fall cruises and with the oil-suspended matter interaction studies. We have completed all of the analyses and the completed data is presently being compiled according to the format designed by EDS and will be submitted to the project office by the end of the next quarter.

D. Laboratory Procedures

The laboratory methods are described in Section V of this report.

E. Sampling Protocol

The sampling methods are described in Section V of this report.

F. Data Analysis

The data from the summer cruises are being reduced and compiled according to the formats designed by EDS. These data will be submitted to the project office by the end of the next quarter.

G. Results

The results of our field activities during the second quarter will be described in a future report.

XI. Publications and Presentations

The following are a list of publications and presentations that have resulted from this project.

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ANNUAL REPORT

Identification of Natural and Anthropogenic Petroleum Sources in the Alaskan Shelf Areas Utilizing Low Molecular Weight Hydrocarbons

Research Unit #153

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April 1978

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1. GENERAL SUMMARY

1.1 Objectives

The low molecular weight hydrocarbon program was initiated on the OCS of Alaska in response to the environmental guidelines set forth in the Environmental Study Plan for the Gulf of Alaska, Southeastern Bering Sea and the Beaufort Seas (January 1975). Briefly, the purpose was to establish the spatial and temporal variations (seasonal and diurnal) in the dissolved hydrocarbon fraction composed of methane, ethane, ethene, propane, propene, isobutane, and n-butane. These data are being collected in order to establish baseline levels of naturally occurring hydrocarbons in the lease areas prior to exploration, development, and production of fossil fuel reserves as these components have proven to be valuable indicators of petroleum input arising from drilling, production, and transportation of crude oil and refined products. In addition to the ease with which these components may be analyzed, they also provide a practical procedure by which the accumulation of petroleum hydrocarbons may be documented.

In support of baseline program, attention is now being focused on the natural sources of hydrocarbons and their fate. These specialized studies focus on the air-sea exchange of the LMWH, in situ production of gases in the water column and from the underlying sediments, and the unique identification of petroleum tracer compounds within this suite of hydrocarbons, including the low molecular weight aromatics (e.g. benzene, methylethyl substituted benzenes, etc.). These data are required as necessary information relative to the compositional and residence time characteristics of these components.

1.2 Implications to Oil and Gas Development

These studies were enacted as a part of the baseline characterization of dissolved natural hydrocarbons on the OCS of Alaska. The hope was to establish establish concentration levels, temporal and spatial variability of hydrocarbon components common to petroleum or natural gas resources prior to actual production. These measurements were felt to be an invaluable precursor to future monitoring efforts.

A cursory examination of our data to date indicates that the LMWH will be excellent tracers of petroleum input in most of the OCS areas investigated. Although methane occurs ubiquitously over the shelf regions of Alaska in moderate concentrations, the concentrations of the C_2-C_4 hydrocarbons are everywhere low (except localized areas of Cook Inlet and Norton Sound), thereby increasing their effectiveness as tracers of petroleum input. Of course, the value of these components as tracers will depend critically on the magnitude of the input, whether it is at depth or at the surface, and the prevailing hydrographic and meteorological conditions at the point of input. The extent to which microbial metabolism of the volatile hydrocarbon fractions is important is not clear at this time.

Studies to date also have revealed useful compositional parameters for distinguishing hydrocarbon sources. The most valuable of these is the ethane: ethene and propane:propene ratio. The low abundance of the unsaturates in crude oil coupled with low abundance of alkane associated with biological system gives a clear unequivocal indicator of petrogenic input. These ratios have been effectively tested in both Cook Inlet and Norton Sound.

Ancillary to the objectives of this program, methane has been shown to be quasi-conservative tracer of meso-scale circulation. The near-bottom distribution of methane in Norton Sound clearly supports the general cyclonic circulation prevelent on the outer sound. Also, the clockwise gyre located south and west of Kayak Island in the Gulf of Alaska is graphically evident in the surface distribution of methane.

2. INTRODUCTION

2.1 General Nature of Study

The development of petroleum resources in the Alaskan OCS may result in the release of toxic hydrocarbons to the marine environment with possible deleterious effects on the pelagic, benthic, and intertidal biota. Increases in the natural levels of petroleum-derived hydrocarbons are likely to occur from the normal activities associated with exploration, production and transportation of crude and refined products within the region. Thus, it is of environmental significance that baseline levels of both naturally occurring and petroleum-derived hydrocarbons be established prior to the development of fossil fuel resources in the area, and that attention be focused in the sources and residence times of these components.

Petroleum contains three broad classes of hydrocarbons: paraffins, naphthenes, and aromatics, but few olefinic hydrocarbons. The proportions of each varies in petroleum, depending on the geologic and geographic sources, but on the average paraffins represent about 30 percent of the total (NAS, 1975). In contrast, many of the gas wells in Upper Cook Inlet are producing methane in excess of 98 mole percent (Kelly, 1968), the remainder being small quantities of ethane and propane.

It is presently believed that the most toxic fractions of crude oil are the low boiling point aliphatics and aromatics as well as the polynuclear aromatics (Blumer, 1971). Also associated with these complex fractions are the LMWH, in varying amounts. While these compounds are of lower toxicity than the aforementioned fractions (Sackett and Brooks, 1974), they are more soluble and, hence, are likely to be dispersed by normal mixing processes. Although the evaporation rates of the low molecular weight hydrocarbons appear to be quite rapid from a surface oil slick (McAuliffe, 1966), this does not preclude their incorporation in the water column from subsurface injection (e.g., ruptured pipeline) or from severe wave-induced turbulence.

The occurrence of light hydrocarbons in the water column may arise from both petroleum production activities and natural marine sources. Gaseous hydrocarbons may exchange across the sea surface in response to a concentration gradient (Broecker and Peng, 1974), diffuse from underlying sediments (Frank et al., 1970), escape in the form of bubbles from natural occurring gas and oil seeps (Link, 1952; Geyer and Sweet, 1973), or be produced by in situ biological processes (Lamontagne et al., 1973).

Methane (CH_4) is a significant component of natural gas and is also produced in anoxic sediments by bacterial CO_2 reduction and fermentation reactions (Claypool, 1974). Thus, the presence of excess methane in the water column overlying organic-rich sediments is not an unequivocal indicator of a petroleum source, unless viewed jointly with the distribution of the heavier fractions, C_2-C_4 (Brooks and Sackett, 1973).

Above saturation values of methane, ethylene, and propylene also have been observed in the surface layers of open ocean and are believed to be related to biological activity or photochemical reactions involving organic matter (Swinnerton and Lamontagne, 1974; Lamontagne et al., 1973).

2.2 Objectives

In conjunction with and in support of the OCSEAP program, the LMWH studies were carried out in the northeast Gulf of Alaska, southeastern Bering Sea, Norton Sound, southeastern Chukchi Sea, and Lower Cook Inlet. The objectives of the program are to determine the distributions and natural sources of methane, ethane, ethene, propane, propene, isobutane, and n-butane prior to drilling activity. Observational activities include areal and seasonal coverage to denote biological processes, benthic sources, as well as short-term time series to elucidate diurnal changes.

As a secondary objective, known offshore seeps are being investigated to ascertain the composition of natural gas seeps and to evaluate the merits of naturally injected LMWH as tracers of petroleum input. The success of this program depends critically on seep composition and activity, depth of water and unconsolidated sediment cover, mean current fields, and topographic structures (Fischer and Stevenson, 1973).

2.3 Relevance to OCSEAP

The principal concern surrounding the distributions, sources, and sinks of LMWH is not their direct impact on biota, but rather their role as tracers of more toxic hydrocarbon fractions commonly found in crude oils. Of particular value is the use of LMWH to identify probable trajectories of the toxic dissolved fractions (e.g., PAH) during a spill, well blowout, or pipeline rupture. Because some of the hydrocarbons common to petroleum are also manufactured by marine organisms, it becomes necessary to evaluate the normal background levels of hydrocarbons before an accurate assessment of anthropogenic input can be made.

Accidental introduction of crude oil onto the surface of the ocean can be readily traced by a variety of visual techniques (e.g., remote sensing). However, the dispersion of soluble hydrocarbon fractions cannot be so easily traced, except with the expenditure of considerable time in sampling and laboratory analysis. In all likelihood, the results would not be available for days, or possibly weeks. The LMWH becomes valuable short-term tracers of the dissolved hydrocarbon fraction because of their relatively high concentration in crude oils, and the ease of analysis.

The success of the method depends on the nature of the accident, hydrographic and meteorological conditions, input concentration of hydrocarbons, and the natural ambient levels against which increases can be measured. For example, observations conducted in the Gulf of Mexico show that propane and butane are enriched by factors of 10^3 to 10^4 over ambient background levels in areas of known petroleum input (Brooks and Sackett, 1973).

The overall objective is to provide the criteria for an early warning detection of petroleum-derived hydrocarbons and to establish the feasibility of using light hydrocarbons as dispersion tracers, particularly in reference to near-bottom mixing and resuspension processes. In the event of a spill, it is likely that the C_1-C_4 fraction may be useful in guiding a sampling protocol for the relatively soluble toxic fractions of crude oil (e.g., Norton Sound gas seep).

3. METHODOLOGY

3.1 Sample Concentration

LMWH are stripped from 1 ℓ volume of seawater using the procedure recommended by Swinnerton and Linnenbom (1967). A diagram of the gas phase equilibrator is shown in Figure 3-1. Although the system actually used in these studies is somewhat simpler in detail than that shown in Figure 3-1, the principle remains the same.

Hydrocarbons are removed in a stream of ultra-pure He (120-140 mℓ/min) and concensed on a single activated alumina trap maintained at -196°C. Approximately 10 minutes of stripping are required to quantitatively remove the hydrocarbons (> 98%) from solution, after which time the trap is warmed to 90-100°C and the absorbed gases are swept into the gas chromatograph (GC).

3.2 Gas Chromatography

The alkanes are chromatographed on a 60/80 mesh Poropak Q® column (3/16" x 4', stainless steel) at a flow rate of 50 mℓ/min and detected sequentially as they emerge from the columns. In order to obtain optimum peak resolution between the alkanes, the Poropak Q® column was connected in series with a short column (3/16" x 2", stainless steel) of activated alumina impregnated with 1 percent silver nitrate by weight. This modification, coupled with temperature programming from 110-140°C, has resulted in sharper peaks, better separation and reduced retention times for all components (Figure 3-2). The GC utilized was a Hewlett Packard® model 5711, equipped with dual FID's.

3.3 Data Quality Control

3.31 Accuracy

The LMWH analysis was referenced to specially prepared hydrocarbon mixtures supplied and certified by Matheson Gas Products. The concentrations of the

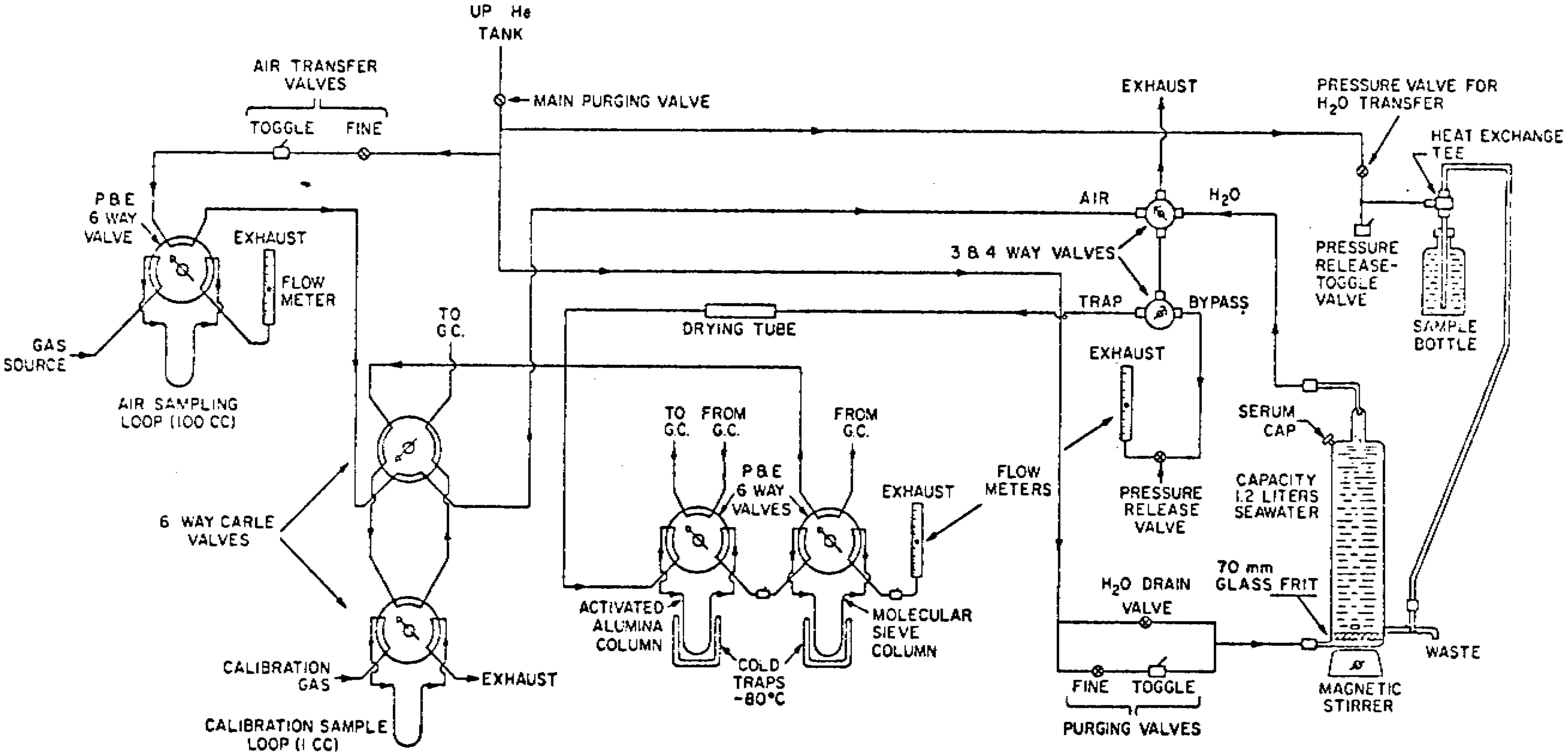
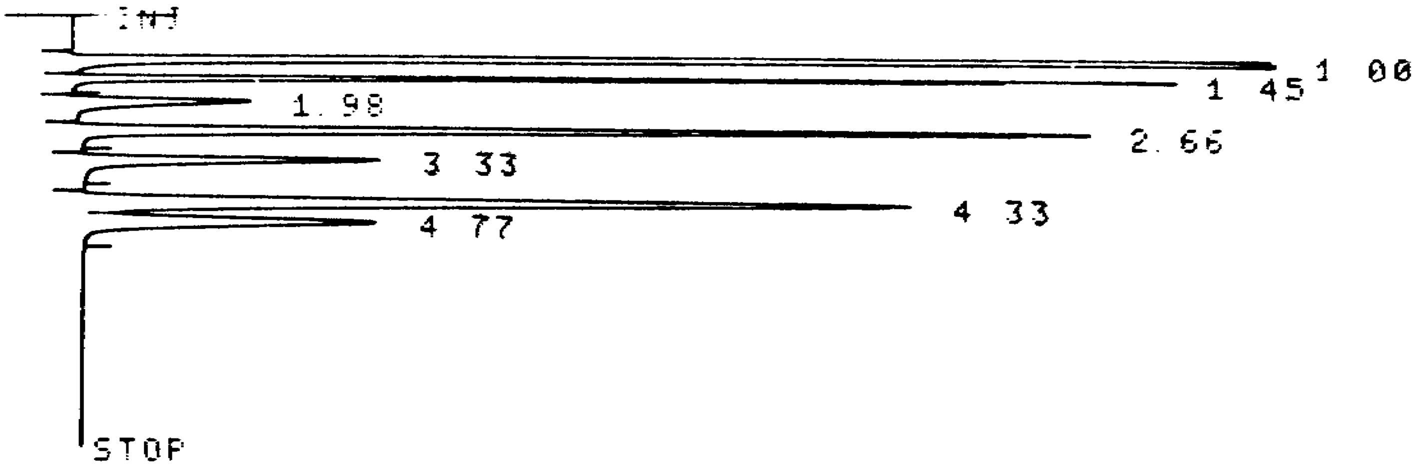


Figure 3-1. Low molecular weight hydrocarbon extraction system (Swinnerton and Linnenbom, 1967; Swinnerton et al., 1968). The extraction system shown is a recent modification given to us by Mr. R. Lamontagne of the Naval Research Laboratories, Washington, D. C.



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   RT    TYPE       AREA
 1 00              173637
 1 45     M         15983
 1 98                5919
 2 66     M         23254
 3 33                9096
 4 33               29686
 4 77     M         12696


HP 3380A
DLY OFF          STOP 10          REJECT   100
MV/M    10       ATTN      4
```

Figure 3-2. Chromatogram of the low molecular weight hydrocarbons methane (102.7 ppmv), ethane (5.0 ppmv), ethene (1.9 ppmv), propane (5.0 ppmv), propene (2.0 ppmv), iso-butane (2.0 ppmv), and n-butane (5.1 ppmv) in order of elution. Values above the peak apexes are the retention times in minutes.

Table 3-2 Precision error associated with standard replicate injections. Two cases are shown with 4 replicates in each set. The relative error is the quotient of the standard deviation and the mean $(\overline{X})$. Concentration of each component is given in column 2 as ppmv. Sample loop volume was nominally 1 cm^3 at 0°C and 1 atm. total pressure.

Component	Concentration ppmv	1	2	3	4	$\overline{X}$	RE	1	2	3	4	$\overline{X}$	RE
Methane	102.7	159,913	161,696	159,559	159,348	160,129	0.007	173,043	175,398	172,700	173,414	173,639	0.007
Ethane	5.0	13,688	13,842	13,718	13,688	13,734	0.005	15,893	16,097	15,912	15,831	15,933	0.007
Ethene	1.9	4,937	4,978	4,984	5,008	4,977	0.006	5,976	6,061	6,219	6,029	6,071	0.017
Propane	5.0	20,379	20,401	20,363	20,321	20,366	0.002	23,371	23,986	24,081	23,472	23,728	0.015
Propene	2.0	7,645	7,747	7,688	7,664	7,686	0.006	9,365	9,417	9,351	9,120	9,313	0.014
n-Butane	2.0	11,403	11,307	11,185	11,478	11,343	0.010	30,853	31,493	31,587	31,264	31,299	0.010
iso-Butane	5.1	27,097	27,076	26,945	27,086	27,051	0.003	12,868	12,977	13,054	12,844	12,936	0.008

Table 3-3 Total sampling and analysis error. Three cases were selected in which either 3 or 4 replicates were analyzed. The relative error (R.E.) is the quotient of the standard deviation and the mean ($\overline{X}$). The designation "T" represents a trace amount of the component (i.e., concentration $\leq$ 0.03 nℓ/ℓ).

	Southeastern Bering Sea Station PM022 Depth 22 m						Northeast Gulf of Alaska Station PM027 Depth 67 m					Norton Sound, Alaska Station N20 Depth 0 m				
Component	1	2	3	4	$\overline{X}$	R.E.	1	2	3	$\overline{X}$	R.E.	1	2	3	$\overline{X}$	R.E.
Methane	83.5	88.8	87.2	82.9	85.6	0.03	719.3	716.1	723.4	719.6	0.01	111.0	111.7	111.5	111.4	0.00
Ethane	0.60	0.57	0.61	0.60	0.60	0.03	0.34	0.33	0.34	0.34	0.02	0.18	0.25	0.25	0.23	0.19
Ethene	2.81	3.03	2.77	2.82	2.86	0.04	1.10	1.12	1.12	1.11	0.01	0.78	0.76	0.76	0.77	0.02
Propane	0.31	0.30	0.30	0.30	0.30	0.02	0.22	0.22	0.23	0.22	0.02	0.08	0.09	0.10	0.09	0.11
Propene	0.88	0.86	0.86	0.91	0.88	0.03	0.34	0.31	0.35	0.33	0.06	0.33	T	0.36	0.34	0.06
n-Butane	0.11	0.06	0.06	0.12	0.09	0.36	T	T	T	-	-	0.00	0.00	0.00	-	-
iso-Butane	0.00	T	T	T	-	-	T	T	T	-	-	T	T	T	-	-

individual components were adjusted to meet the naturally occurring hydrocarbon levels expected in the OCS study areas, although concentrations less than 1 ppmv could not be reliably prepared. To confirm the analysis, one of the tank standards was sent to NBS for LMWH analysis, the results of which are given in Table 3-1. The NBS analyzed standard was then used to calibrate the remaining hydrocarbon standards. With the possible exception of ethane and propane, hydrocarbon components were within the stated accuracy of ± 5 percent quoted by Matheson. Thus, the uncertainty given by NBS in their analyses represents a measure of the accuracy.

Table 3-1 Analysis of Matheson certified hydrocarbon standard by National Bureau of Standards

	Matheson	NBS
Component	Nominal Concentration ppmv	
Methane	23 ± 1	21.8 ± 0.8
Ethane	1 ± 0.1	1.3 ± 0.1
Propane	2 ± 0.2	1.25 ± 0.02
n-Butane	1 ± 0.1	1.1 ± 0.02

3.32 Precision

Precision of analysis was accomplished in two ways. First, precision errors associated with standard injection and GC response were determined by replicate injection of the standard gases. Injection of gas standard was accomplished with the aid of a Carle® sampling valve fitted with a calibrated 1 cm sample loop. The results of this experiment are depicted in Table 3-2, together with estimates of the relative error. It is readily seen that individual component precisions (1 σ) are better than 1 percent in most cases.

The overall error in precision, which includes water sampling, sample stripping, and GC response characteristics, was estimated from replicate analysis of seawater from various depths. Water samples were taken in a 10 ℓ Niskin® sampler and subdivided for replicate analyses. The replicate study was repeated several times in each survey region in order that precision errors could be established at various concentration levels. Representative examples of this study are shown in Table 3-3 in terms of the mean concentration ($\overline{X}$) and the relative error (RE). Ignoring the results obtained for the butanes, since their concentration was everywhere at or below the detection limit ($\leq$ 0.03 nℓ/ℓ), the relative precision error was generally less than 5 percent. In the case of the replicate study from the surface waters of Norton Sound, the relatively poor precision observed in ethane and propane is due to the low concentrations.

The detection limit for each component was estimated from the nominal background noise. Interpreted peak areas less than 200 counts were considered insignificant, placing a defined lower limit on the detectability. The values are, based on the data shown in Table 3-4, methane - 0.12 nℓ/ℓ, ethane - 0.06 nℓ/ℓ, ethene - 0.07 nℓ/ℓ, propane - 0.04 nℓ/ℓ, propene - 0.04 nℓ/ℓ, isobutane - 0.03 nℓ/ℓ, and n-butane - 0.03 nℓ/ℓ.

Table 3-4 Analytical precision of the LMWH analysis determined from replicate injection of standards

Component	Concentration ppmv	A Unit	σ A Areas	% Error	N No. Samples
Methane	102.7	173793	1160	0.7	8
Ethane	5.0	15804	102	0.6	8
Ethylene	1.9	5254	77	1.5	8
Propane	5.0	25085	229	0.9	8
Propylene	2.0	9980	186	1.8	8
Isobutane	5.1	30584	454	1.5	8
n-Butane	2.0	11970	270	2.2	8

4. REVIEW OF RESULTS

4.1 General Statement

Field observations during FY77 were limited to two cruises to Lower Cook Inlet. The preliminary results from these field activities were reported in the previous quarterly report (Cline, 1977a). In this report, a brief review of the hydrocarbon data from Cook Inlet will be presented, together with a discussion of these observations in the broader context of the Alaskan Shelf hydrocarbon distributions. Discussion will also compare the findings of principal investigators in other OCS areas (e.g., MAFLA).

A summary of past cruise activities are shown in Table 4.1, including number of stations occupied and samples analyzed. All samples were analyzed within 2 hours of collection and none have been archived. All results to date have been submitted to NODS/EDS for archiving.

In the following discussion, each lease area will be treated individually.

Table 4.1 Summary of cruise activities to the present. A more detailed summary is available in the appropriate quarterly reports.

Lease Area	Cruise Date	No. Stations	Samples Analyzed
S. E. Bering Sea	9/14/75 - 10/1/75	72	316
S. E. Bering Sea	6/25/76 - 7/8/76	55	319
N. E. Gulf Alaska	10/21/75 - 11/9/75	51	274
N. E. Gulf Alaska	4/13/76 - 4/30/76	47	355
N. E. Gulf Alaska	7/19/76 - 7/31/76	47	276
Norton Sound/ Chukchi Sea	9/8/76 - 9/24/76	79	339
L. Cook Inlet/ Tarr Bank	4/4/77 - 4/22/77	44	141
L. Cook Inlet/ Kodiak Shelf	7/28/77 - 7/16/77	102	500

4.2 Lower Cook Inlet

During 1977, two cruises to Lower Cook Inlet were planned and executed as shown in Table 4.1. The first of these was conducted during April, prior to the spring bloom, the second in early July. The results obtained from the first cruise were subject to numerous analytical difficulties, which were later resolved. In this report only the salient features of these two cruises will be discussed.

The sampling grid employed during both cruises is illustrated in Figure 4.1, including the stations in Shelikof Strait. This is the same grid used to assess suspended matter distributions (see Feely and Cline, 1977). During the July cruise, transit above the Forelands aboard the R/V ACONA was possible although these stations are not shown on Figure 4.1, but are shown in the subsequent areal distribution maps.

4.21 Methane

The seasonal distribution of methane at the surface is variable and reflects the relative activity of the various sources. During early spring (Figure 4-2), the concentration of methane in the lower inlet is between 100-200 nℓ/ℓ (STP) with higher concentrations found to the north. The tongue of methane-deficient water entering the lower inlet is the relatively high salinity gulf water that has entered the lower inlet via Kennedy Entrance (SAI, 1977). At the time of these measurements, the surface temperature and salinity was 5°C and $32^{\circ}/oo$ in the lower inlet. Using the Bunsen solubility coefficients of Yamamoto et al. (1976), and assuming a CH_4 mixing ratio in the atmosphere of 1.4 ppmv (Lamontagne et al., 1974), the equilibrium concentration of methane would be about 56 nℓ/ℓ (STP). Surface concentrations in the lower

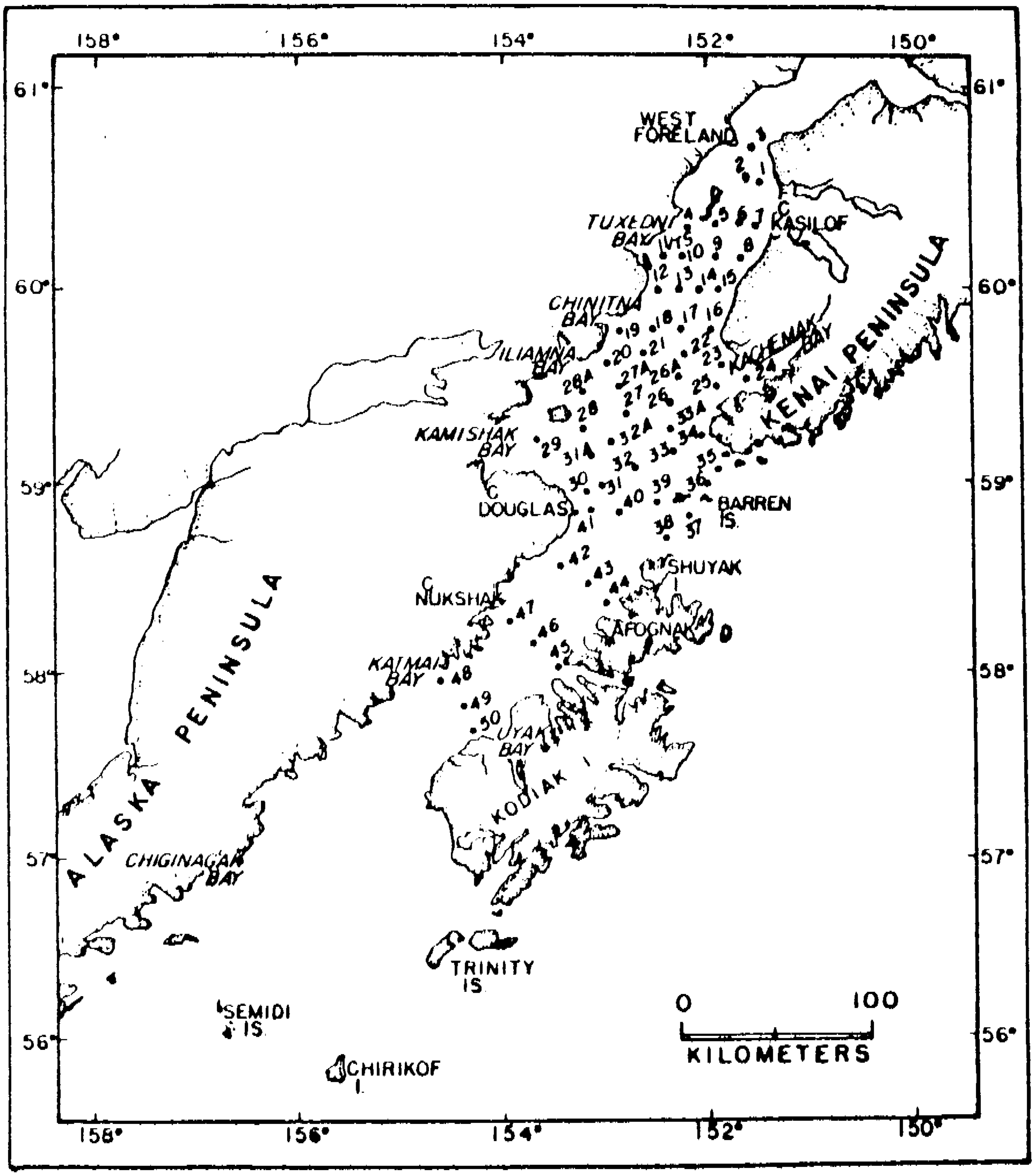

Figure 4-1. Station locations occupied in April and July 1977 in Cook Inlet and Shelikof Strait. Stations occupied in July above the Forelands are not shown.

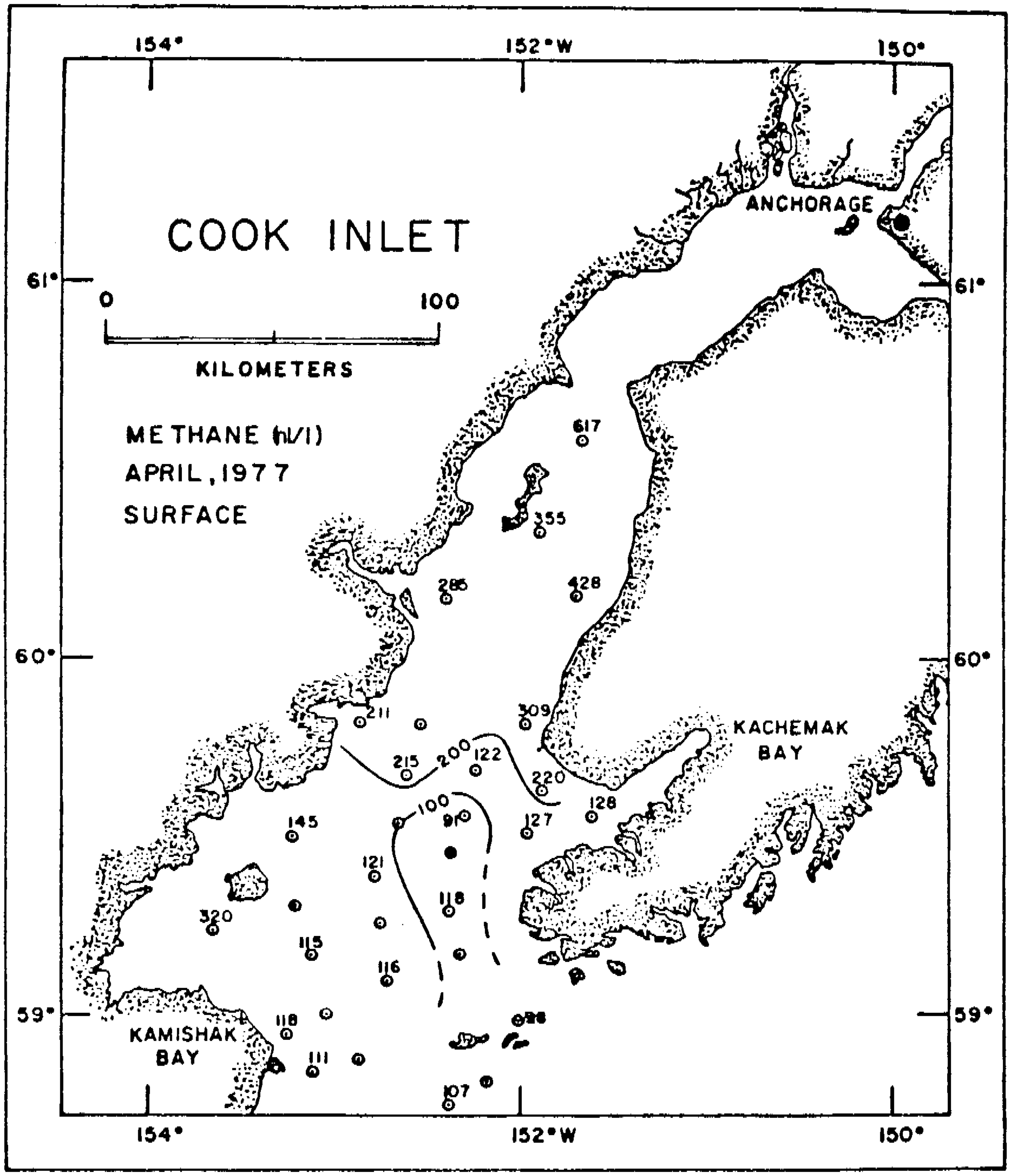

Figure 4-2. Distribution of methane (nℓ/ℓ, STP) in the surface layers during April 1977. Concentrations are not shown at all stations for the purpose of clarity.

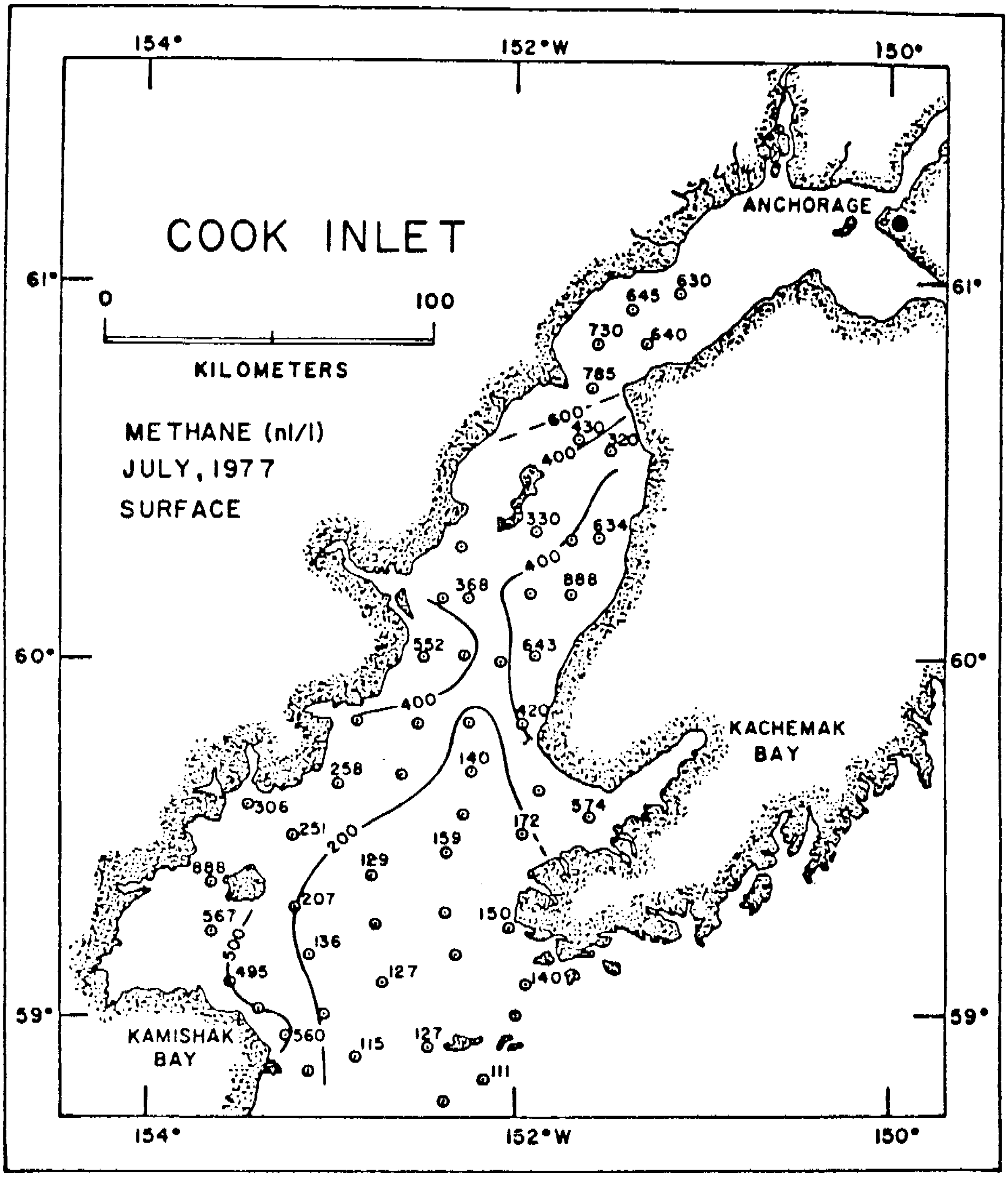

Figure 4-3. Distribution of methane (nℓ/ℓ, STP) in the surface waters during July 1977. Concentrations are not shown at all stations for the purpose of clarity.

inlet are at least a factor of two above saturation, increasing to factor of 11 near the Forelands. Because of large tidal excursions in the inlet (SAI, 1977), vertical turbulence is great and little or no vertical structure was observed in the distribution of methane (Cline, 1977a).

A similar surface distribution was observed in July, but the concentrations were higher than observed in April (Figure 4-3). The intrusion of methane - deficient waters in the lower inlet is again evident, penetrating to a point just north of Anchor Point. Concentrations of methane in the near-shore areas approach 900 nℓ/ℓ (Kamishak Bay) and presumably reflect the influence of methane production from the bottom sediments. The supersaturation ratio varies between approximately 2 near the Barren Islands and 16 in Kamishak Bay and near Ninilchik. High concentrations observed north of the Forelands may be, at least in part, petrogenic in origin. More of this discussion will follow below.

Similar to the situation observed in spring, the near-bottom concentrations of methane were similar to the surface distributions (Cline, 1977a). Near-bottom concentrations were locally higher, reaching a maximum value of 1320 nℓ/ℓ in Kachemak Bay. Values in excess of 800 nℓ/ℓ were common in Kamishak Bay and near Ninilchik. Microbial production of methane from bottom sediments appears to be important in these areas.

4.22 Ethane and Ethene

The concentration of ethane in the surface layers is depicted in Figure 4-4 for the month of July 1977. The highest concentrations of C_2H_6 were observed north of the Forelands in Trading Bay, which is the location of the McArthur oil field. Ethane-rich waters move south through the Forelands and pass to the east of Kalgin Island in response to the general estuarine circulation of the inlet. Salinity for the same period of time reflects a similar distribution (Figure 4-5).

On the west side of the lower inlet, the average concentration of ethane is 0.4 nℓ/ℓ, increasing to values greater than 0.5 nℓ/ℓ toward the east. The distribution of ethane is analagous to that of salinity and represents zonal differentiation due to estuarine flow and Coriolas force. Higher concentrations of ethane observed near Anchor Point appear to be related to the occurrence of ethene (see Figure 4-6).

Near-bottom distribution of ethane is analagous to that observed in the surface layers. This is not surprising given the poor vertical stratification that existed at the time of the measurements.

For the month of July 1977, the surface distribution of ethene is depicted in Figure 4-6. Concentration north of the Forelands was uniformly 0.5 nℓ/ℓ and reflects little biological activity. To the south, higher concentrations were observed in Kachemak Bay (6.9 nℓ/ℓ) and north of Anchor Point (> 4 nℓ/ℓ). In the former case, the high surface value was not supported by higher concentrations at depth indicating a surface production (Cline, 1977a). In view of the high biological productivity of this area, the occurrence of ethene is probably related to elevated levels of biological productivity (Larrance et al., 1977). During early July 1976, primary productivity ranged from 1-5 gC/m^2-day in the lower inlet; we assume conditions were similar in 1977. Because of little vertical stratification, the near-bottom distribution of ethene was similar to that observed in the surface layers (Cline, 1977a).

In April, the concentration of ethene varied from 0.2 nℓ/ℓ near Kalgin Island to a high value of 2.1 nℓ/ℓ in Kachemak Bay (Cline, 1977a). The average value for the entire inlet was 0.5 ± 0.4 nℓ/ℓ, substantially lower than average conditions observed in July (Figure 4-6). In early April of 1976, primary

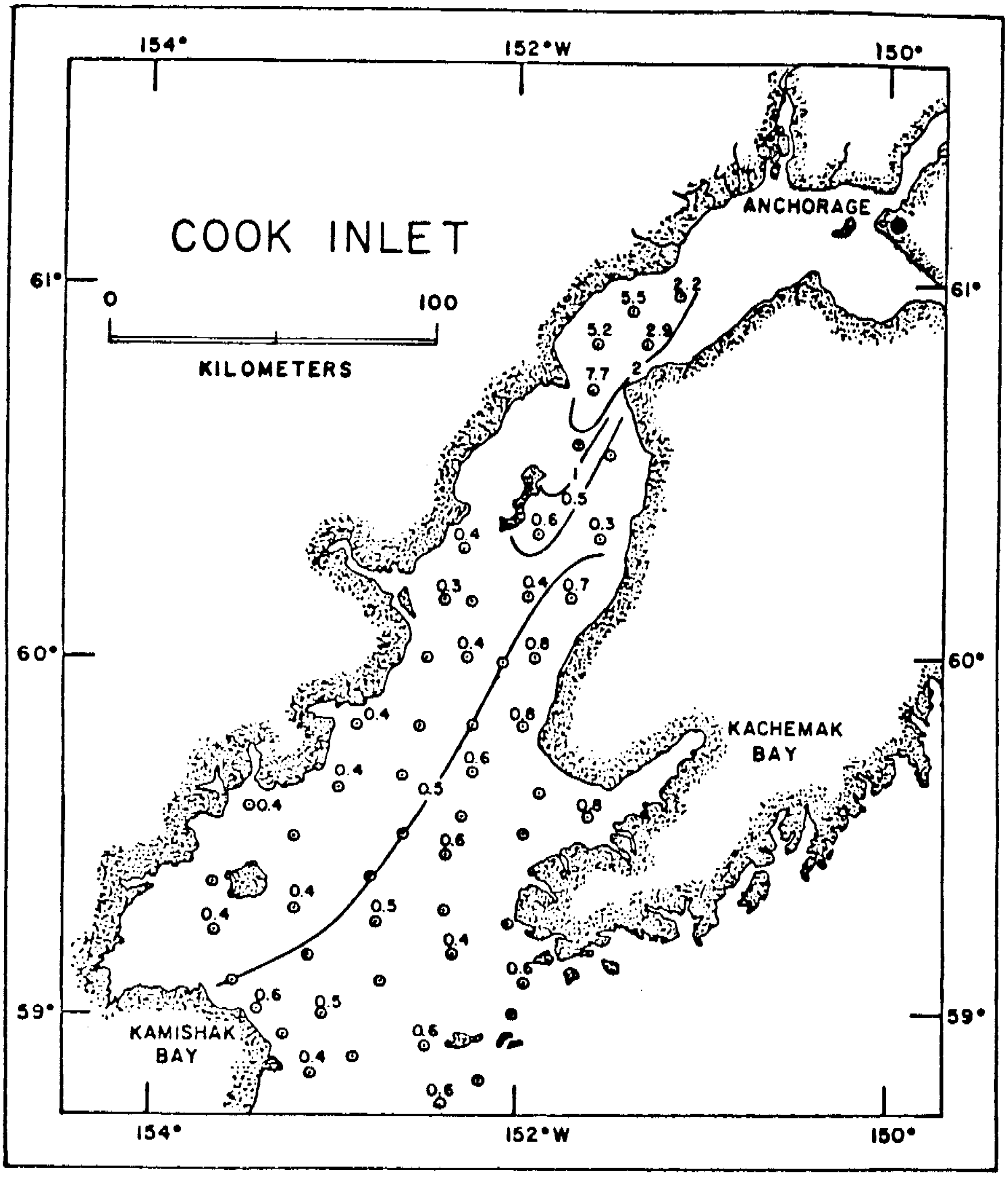

Figure 4-4. Distribution of ethane (nℓ/ℓ, STP) in the surface layers during July 1977. Concentrations are not shown at all stations for the purpose of clarity.

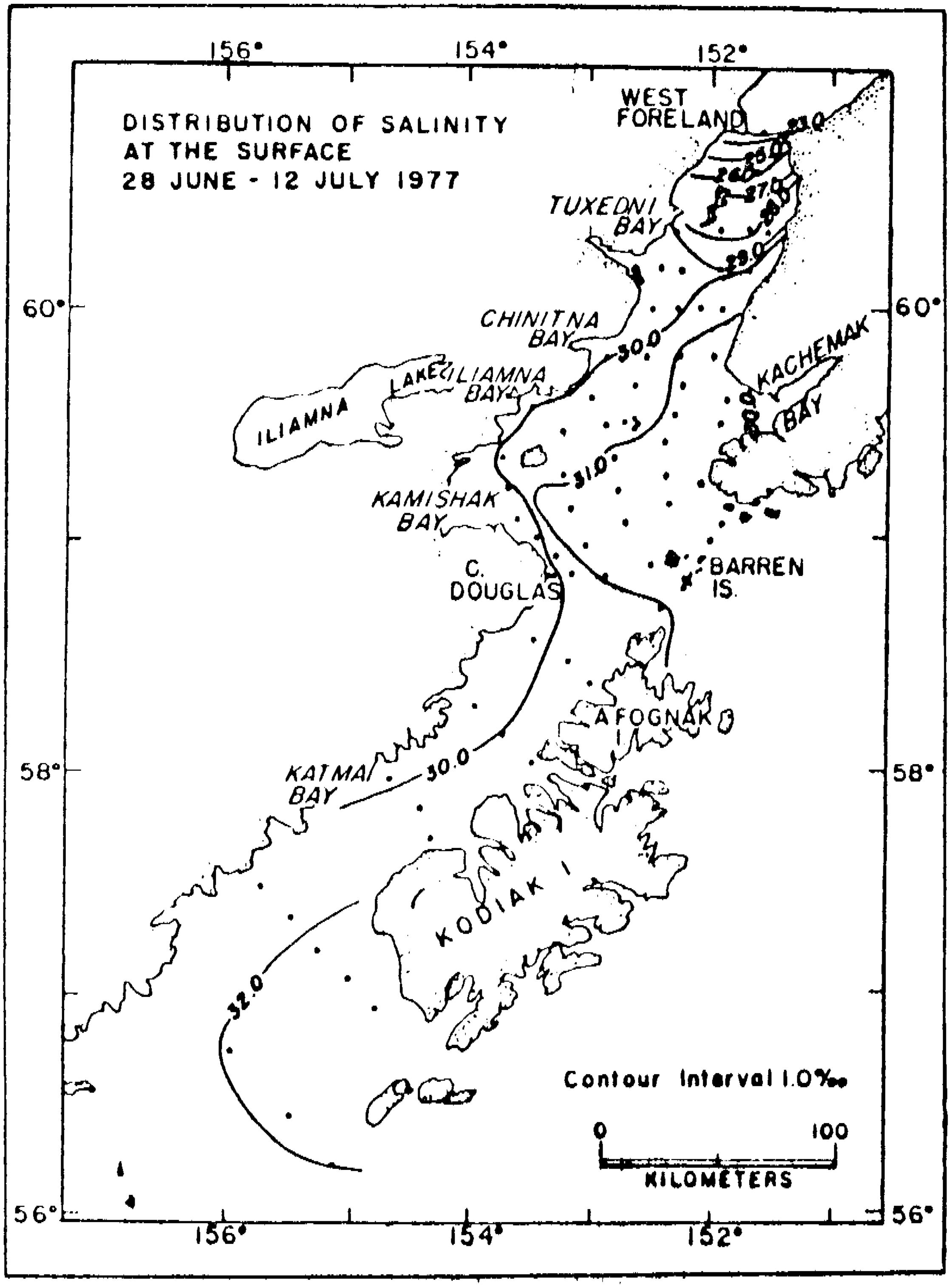

Figure 4-5. Distribution of salinity (°/oo) at the surface during July 1977.

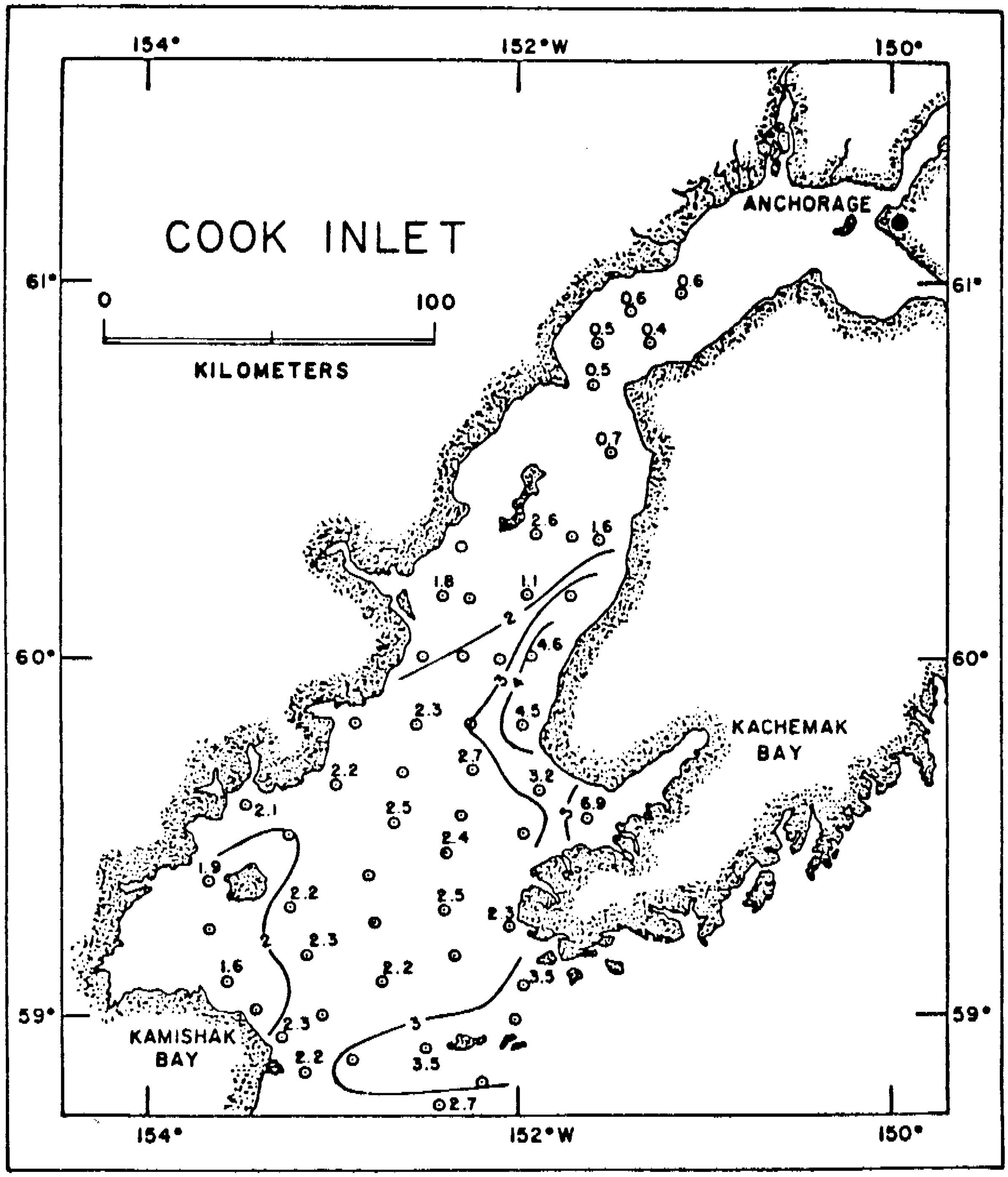

Figure 4-6. Distribution of ethene (nℓ/ℓ, STP) in the surface layers during July 1977. Concentrations are not shown at all stations for the purpose of clarity.

productivity in Kachemak Bay was generally less then 1 mgC/m^2-day (Larrance et al., 1977).

4.23 Propane and Propene

The distribution of propane in surface layers during July 1977 is reflected in Figure 4-7. Concentration of C_3H_8 was high north of the Forelands (> 1 nℓ/ℓ), decreasing to values less than 1 nℓ/ℓ toward the south. Zonal variation was again apparent as the concentrations on the west side averaged 0.2 nℓ/ℓ compared to 0.4-0.5 nℓ/ℓ in the east. In April, the average concentration in the surface layers was 0.2 ± 0.1 nℓ/ℓ, reflecting the low biological or photochemical imput.

The distribution of propene in the surface layers during July 1977 was similar to that of ethene. A high concentration of 2.5 nℓ/ℓ was observed in Kachemak Bay in contrast to more typical values of 0.5-0.7 nℓ/ℓ observed in the central area of Lower Cook Inlet. Above the Forelands, the concentrations rarely exceeded 0.1 nℓ/ℓ, again reflecting the low biological input in this area due to high suspended loads.

4.24 Butanes

In all OCS areas sampled to date, both n- and i- butanes are generally at or below the detection level of 0.05 nℓ/ℓ. However, north of the Forelands during July 1977, concentrations of the C_4 isomers approached 1 nℓ/ℓ and represents a level significantly above background. Analagous to the high concentrations of ethane and propane, the origin is probably thermogenic in nature.

4.3 NEGOA

Between October 1975 and July 1976, three cruises were conducted in the NEGOA region, covering the major seasons (see Table 4.1). The results of these

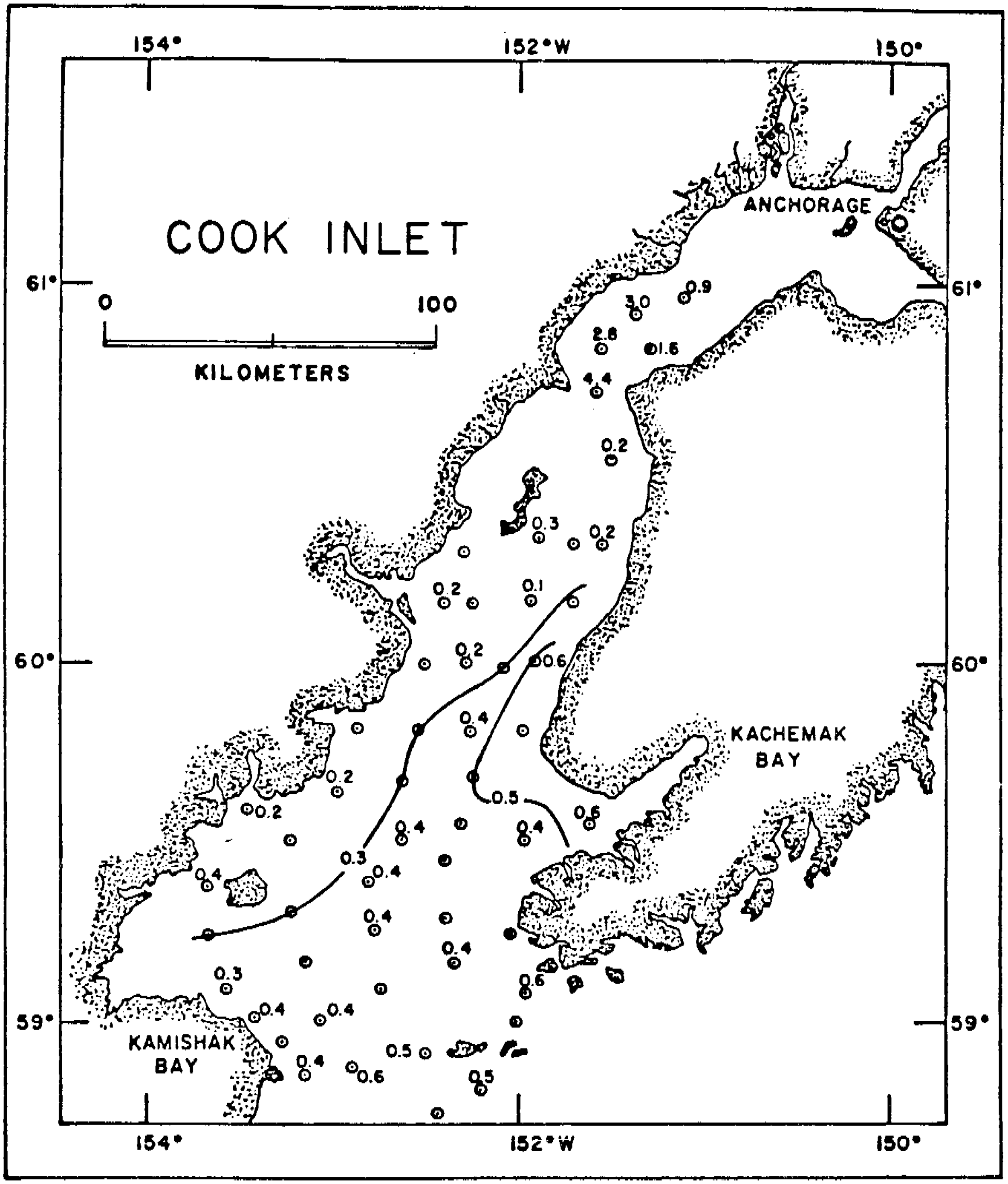

Figure 4-7. Distribution of propane (nℓ/ℓ, STP) in the surface layers during July 1977. Concentrations are not shown at all stations for the purpose of clarity.

cruises have been reported elsewhere (Cline and Feely, 1976; Cline, 1977b), the salient features will be discussed here.

The sampling grid employed during all three cruises is shown in Figure 4.8.

4.31 Methane

The surface distribution of methane is shown for the three seasons in Figures 4-9 thru 4-11. The surface shelf waters uniformly contain more than 100 mℓ/ℓ of methane during all seasons, representing a minimum supersaturation level of approximately 200 percent. Locally, surface concentrations may exceed 300 nℓ/ℓ, typically southwest of Kayak Island, and may be related to the anticyclonic gyre (Galt and Royer, 1975) observed in that region (Figures 4-9, 4-10, and 4-11). In July of 1976, high concentrations of methane (600 nℓ/ℓ) were observed in the vicinity of Icy Bay and may have related to sustained high productivity levels that were observed at the same time. In this instance, the surface concentrations of methane exceeded the concentrations near the bottom, implying that high levels of productivity had resulted in in situ methane production in the water column (Cline, 1977b). The highest concentration of methane was 1680 nℓ/ℓ observed at the entrance to Yakutat. This value represents a supersaturation concentration with respect to the overlying atmosphere of approximately 30. As we shall see later, the high concentrations of methane were supported by unusually high concentrations of ethane and propane. Whether these elevated concentrations are related to primary productivity or represent the surface entrainment of petrogenic hydrocarbons from the interior Yakutat Bay, it cannot be ascertained at this time.

With the exception of localized accumulations of methane in the surface layers, the concentraion of methane over the shelf varies from 100-300 nℓ/ℓ,

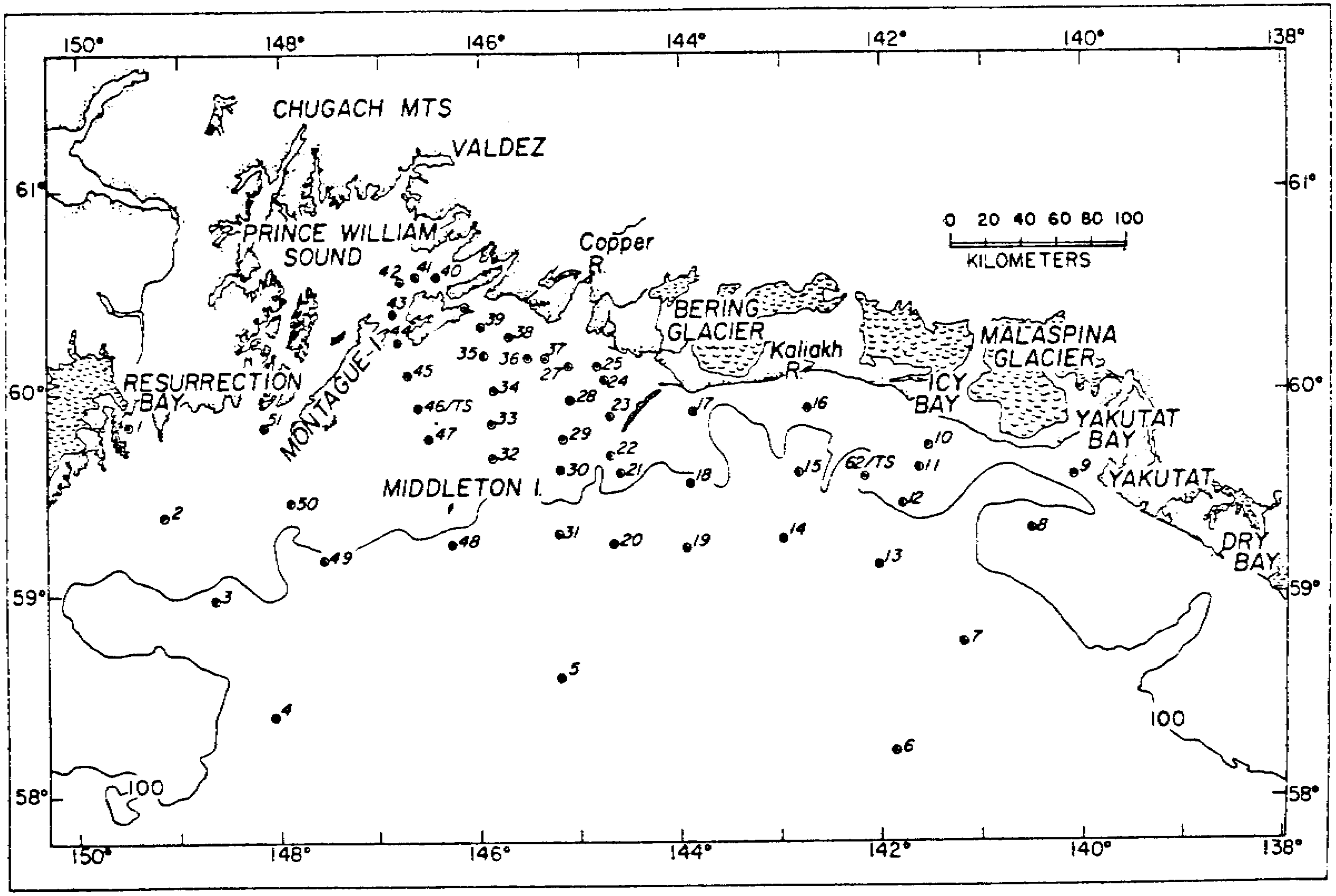

Figure 4-8. Station locations in the northeast Gulf of Alaska.

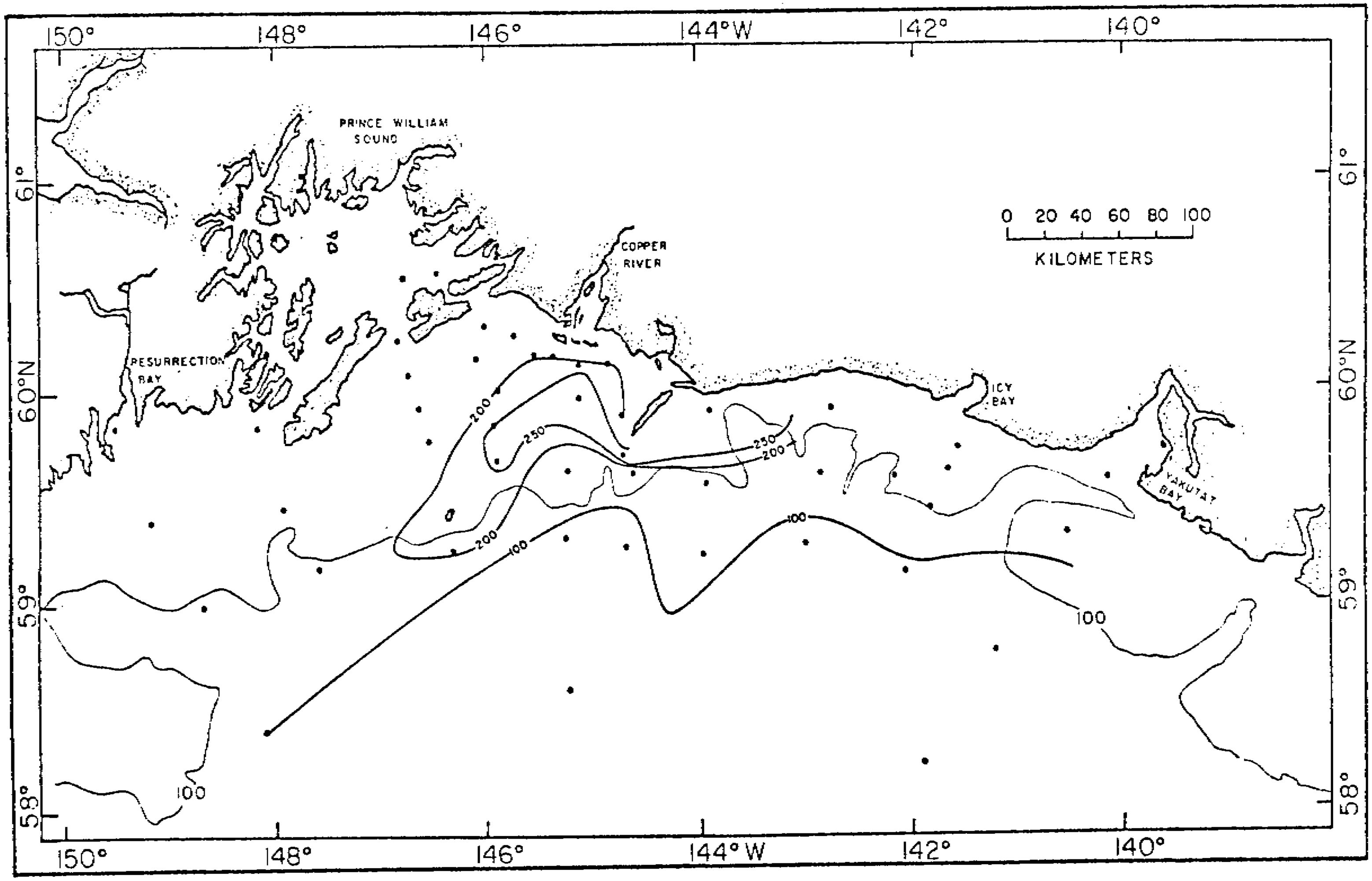

Figure 4-9. Areal distribution of methane in the surface waters during Oct.-Nov. 1975. Concentrations are expressed in nℓ/ℓ (STP).

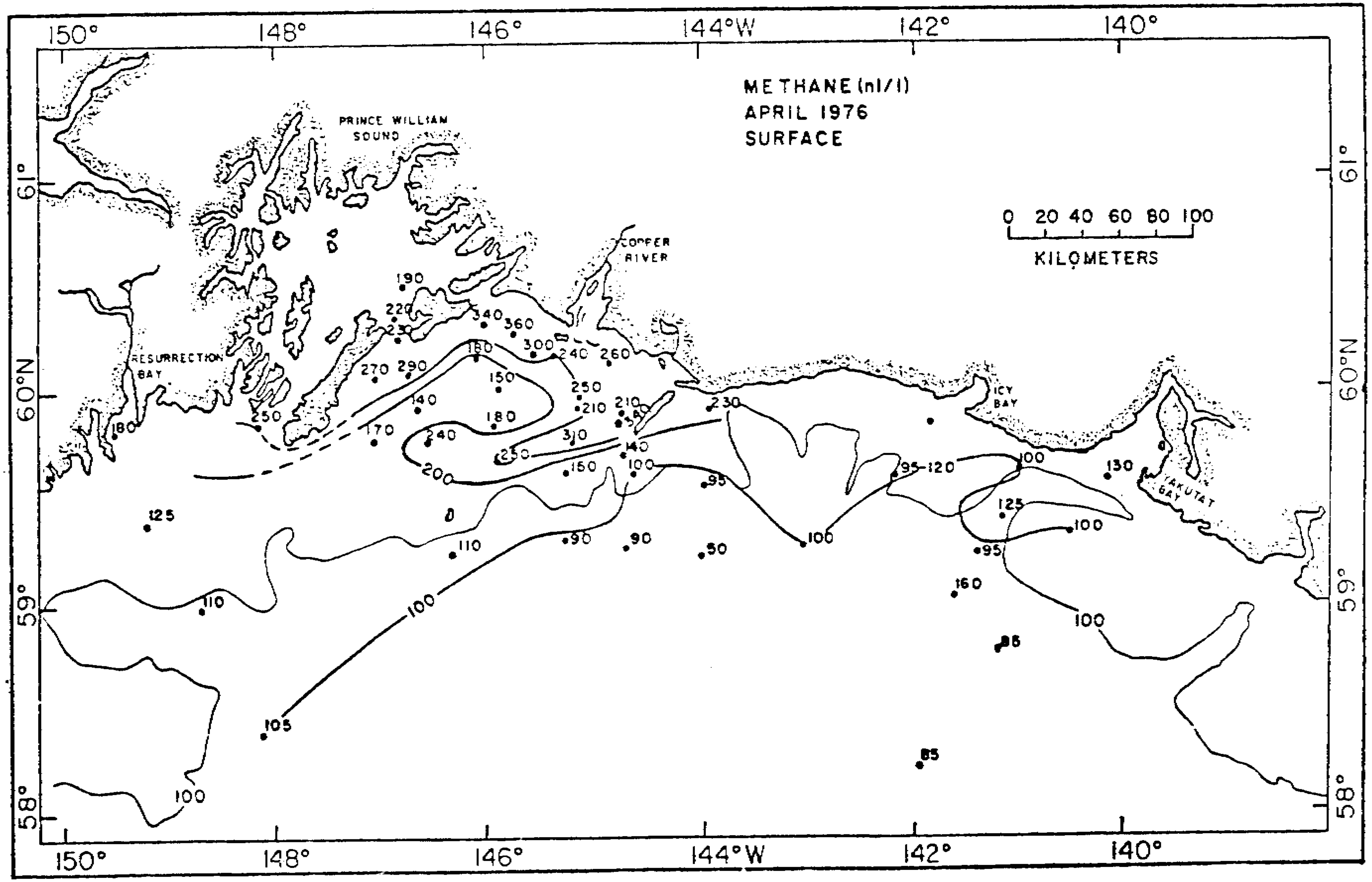

Figure 4-10. Areal distribution of methane in the surface waters during April 1976. Concentrations are expressed in nℓ/ℓ (STP).

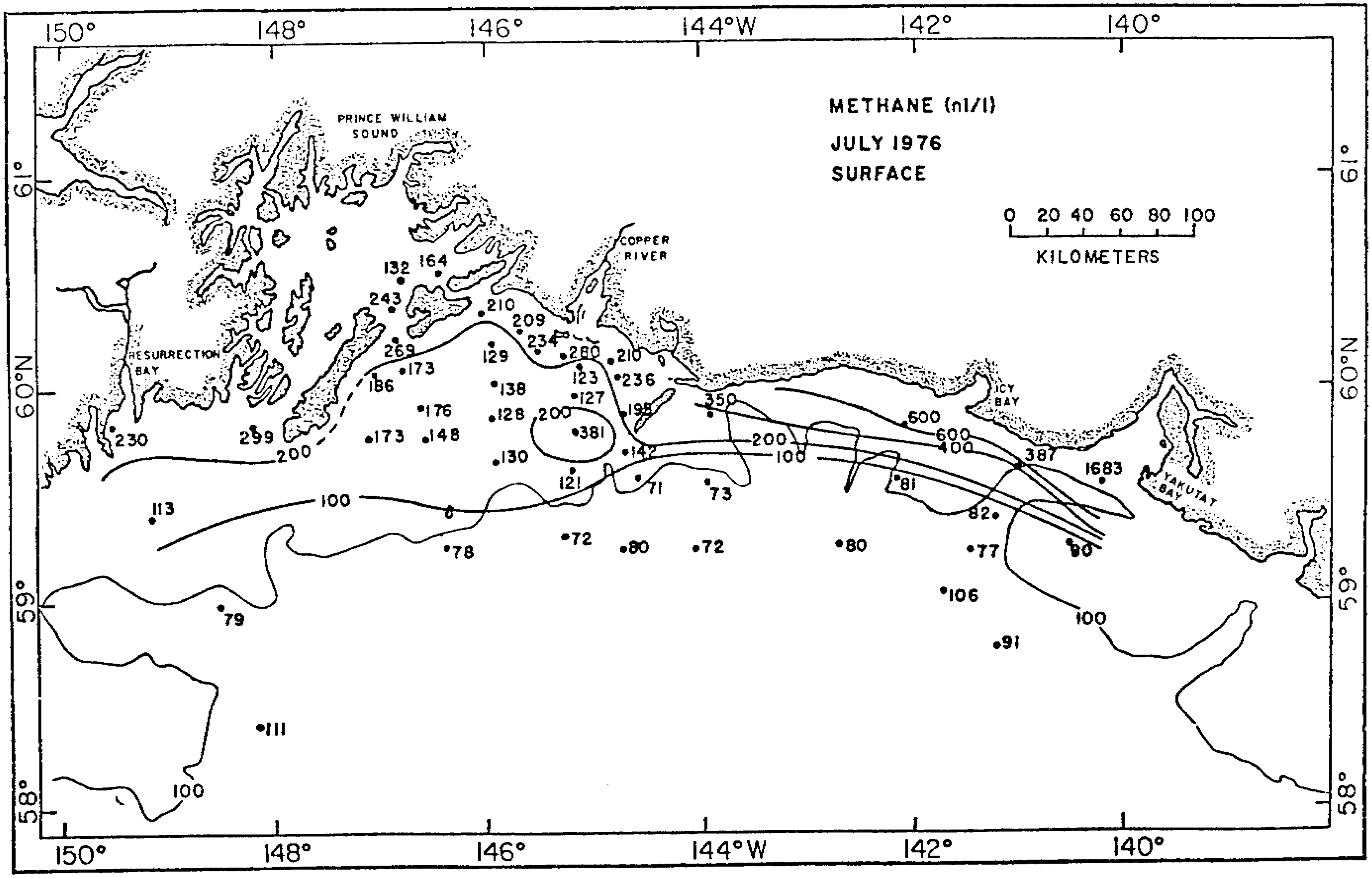

Figure 4-11. Areal distribution of methane in surface waters during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

with offshore values less than 100 nℓ/ℓ. Offshore concentrations are presumably approaching saturation with the overlying atmosphere.

In general, the concentrations of methane are much higher near the bottom than in the surface layers, reflecting the proximity of these waters to the bottom source. Unusually high levels are observed in the region surrounding Tarr Bank where fine-grained organic-rich sediments are prevalent. In October-November 1975 the major source of methane was the Hinchinbrook Sea Valley near Montague Island with a characteristic near-bottom drift of the waters toward the east (Cline, 1977b). In July 1976, the major source appeared to be north of Tarr Bank with little indication of advective drift. Concentrations of methane in April 1976 were substantially lower than those observed in October-November 1975 and July 1976. Again there appeared to be little preferred advection as was noted in October-November 1975 with the concentration of methane largely reflecting the distribution of fine-grained sediments.

In general, the concentration of dissolved methane near the bottom is highly variable, suggesting temporal sources and/or highly variable circulation patterns. Our observations would suggest that seasonally methane concentrations range from a low of 100 nℓ/ℓ to approximately 1500 nℓ/ℓ. More typically, the region south of Prince William Sound between Montague Island and Kayak Island is distinguished by variable concentrations of methane, usually above 400 nℓ/ℓ. At the present time there is no reason to believe that these concentrations are not the result of biogenic methane production. Later in the discussion, it will become apparent that methane accumulation is largely unsupported by similar advances in the concentrations of ethane and propane, suggesting a microbial origin.

4.32 Ethane and Ethene

The concentration of ethane in the surface layers was rather uniform throughout the seasonal studies just concluded. From observations conducted in

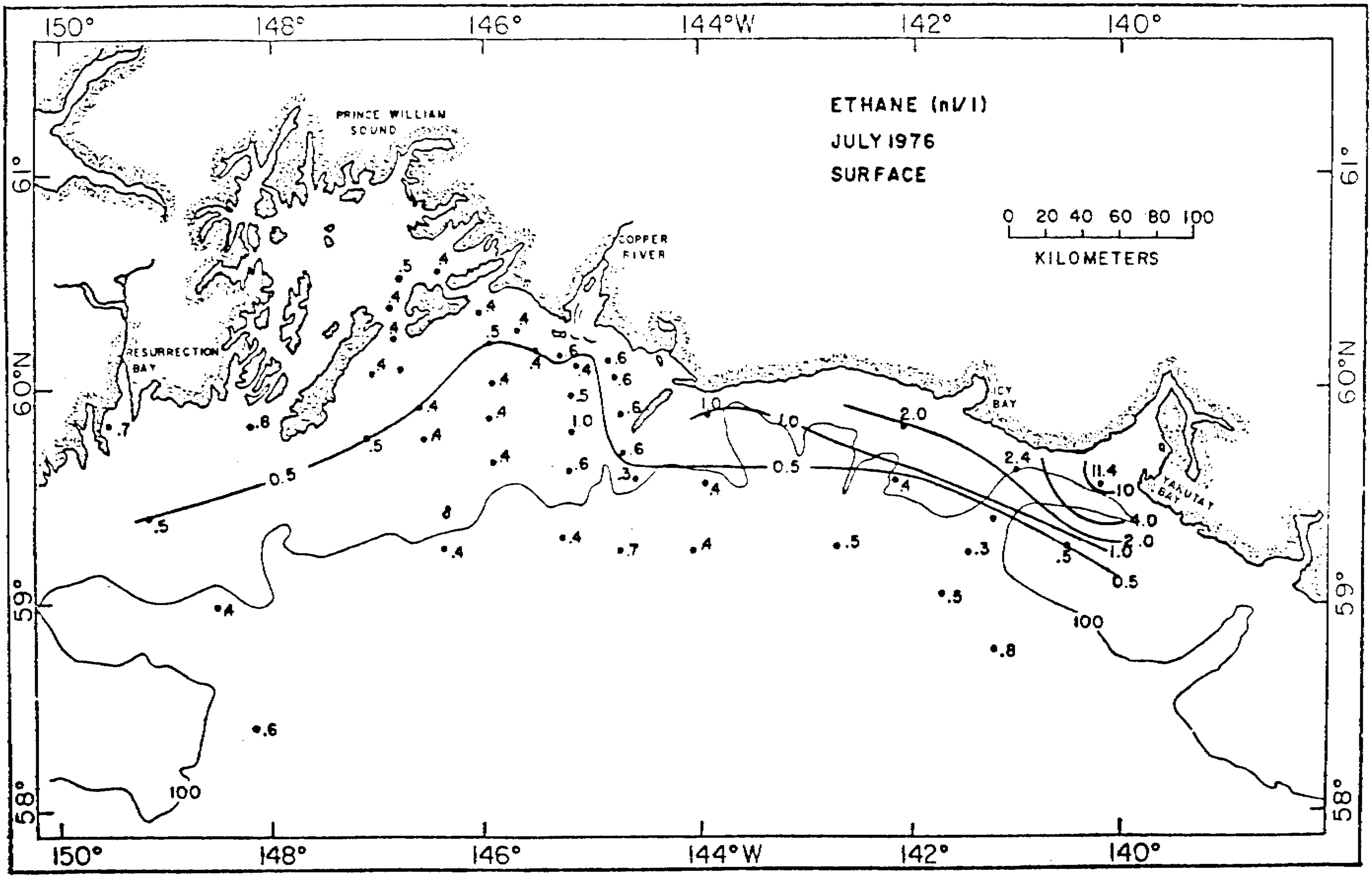

Figure 4-12. Areal distribution of ethane in the surface waters during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

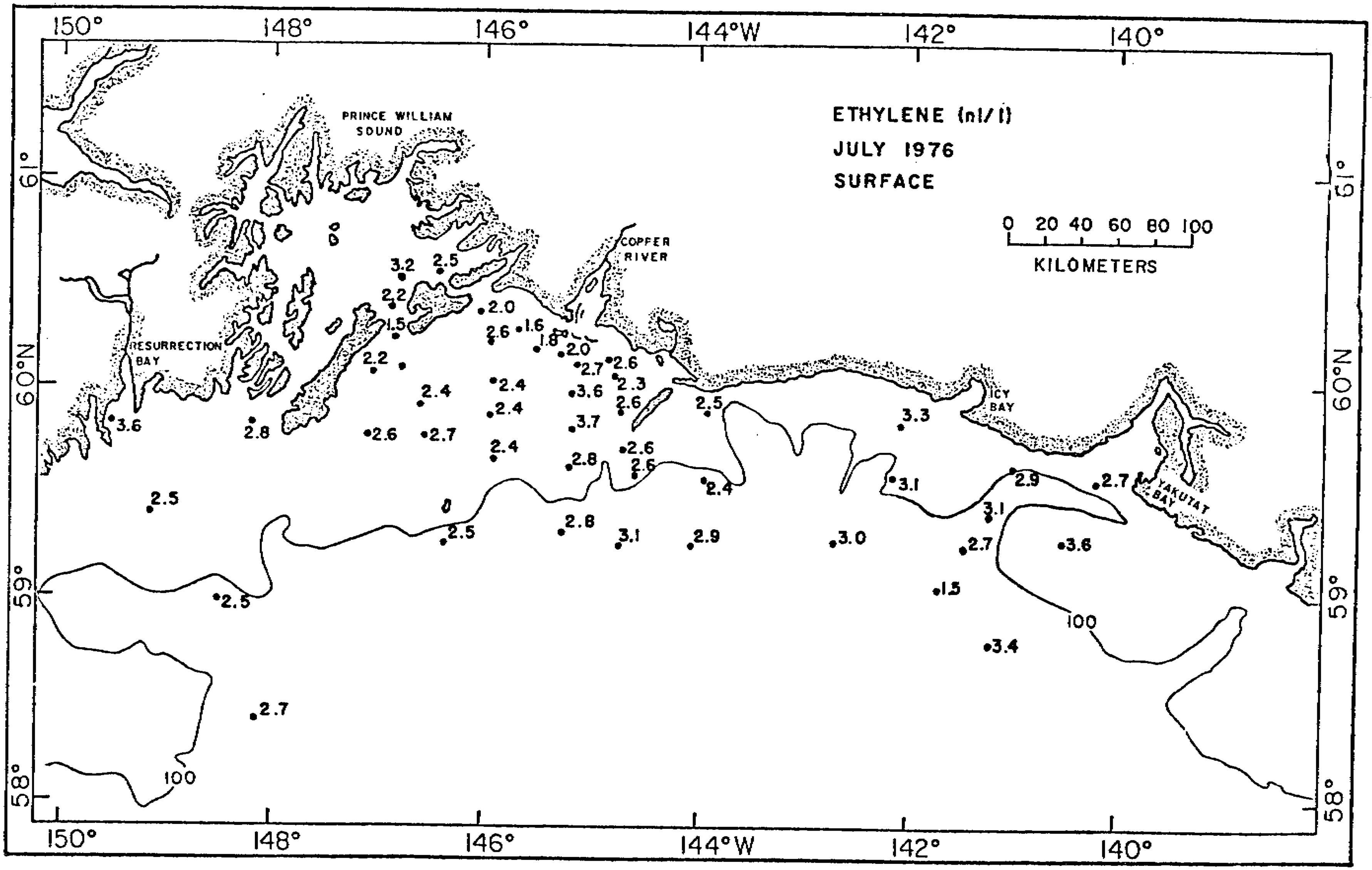

Figure 4-13. Areal distribution of ethene in the surface waters during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

October-November 1975 and again in April 1976, the concentration of ethane varied little, averaging 0.2 to 0.5 nℓ/ℓ (Cline and Feely, 1976; Cline, 1977b). There were no apparent localized sources for ethane and we conclude that these minimal concentrations probably reflect near equilibrium conditions with respect to the atmosphere. In July 1976, however, the average concentration in the Tarr Bank area rose to approximately 0.5 nℓ/ℓ with a strong source evident near Yakutat Bay (Figure 4-12). The highest concentration of ethane observed was 11.4 nℓ/ℓ and was associated with similarly high concentrations of methane and propane. The local region near Yakutat Bay appeared to be undergoing a strong plankton blume at the time of the measurements (Jerry Larrance, personal communication) and these elevated LMWH levels may have been associated with that phenomenon. However, ethene concentrations in the same region were not unusually high for this season (Figure 4-13), suggesting that the source may have been a gas and/or oil seep. All measurements conducted to date in the shelf areas of Alaska, as well as in Puget Sound (Baker et al., 1978), show that the concentration of ethene exceed that of ethane by a factor of 2 or more during periods of high productivity or light incidence. To find the highest concentrations of ethane and propane at the surface rather than the bottom suggests that the source was within Yakutat Bay and was advected seaward in accord with normal estuarine circulation.

Seasonal variations of ethane concentrations within 5 m of the bottom were uniform, ranging from 0.2 to 1.3 nℓ/ℓ (Cline, 1977b). The average, however, is near 0.4 nℓ/ℓ; the high value noted above was observed at a single station over Tarr Bank, and may have been spurious.

4.33 Propane and Propene

Surface concentrations of propane, not unlike ethane, showed little areal or seasonal variations (Cline, 1977b). In the region south of Prince William

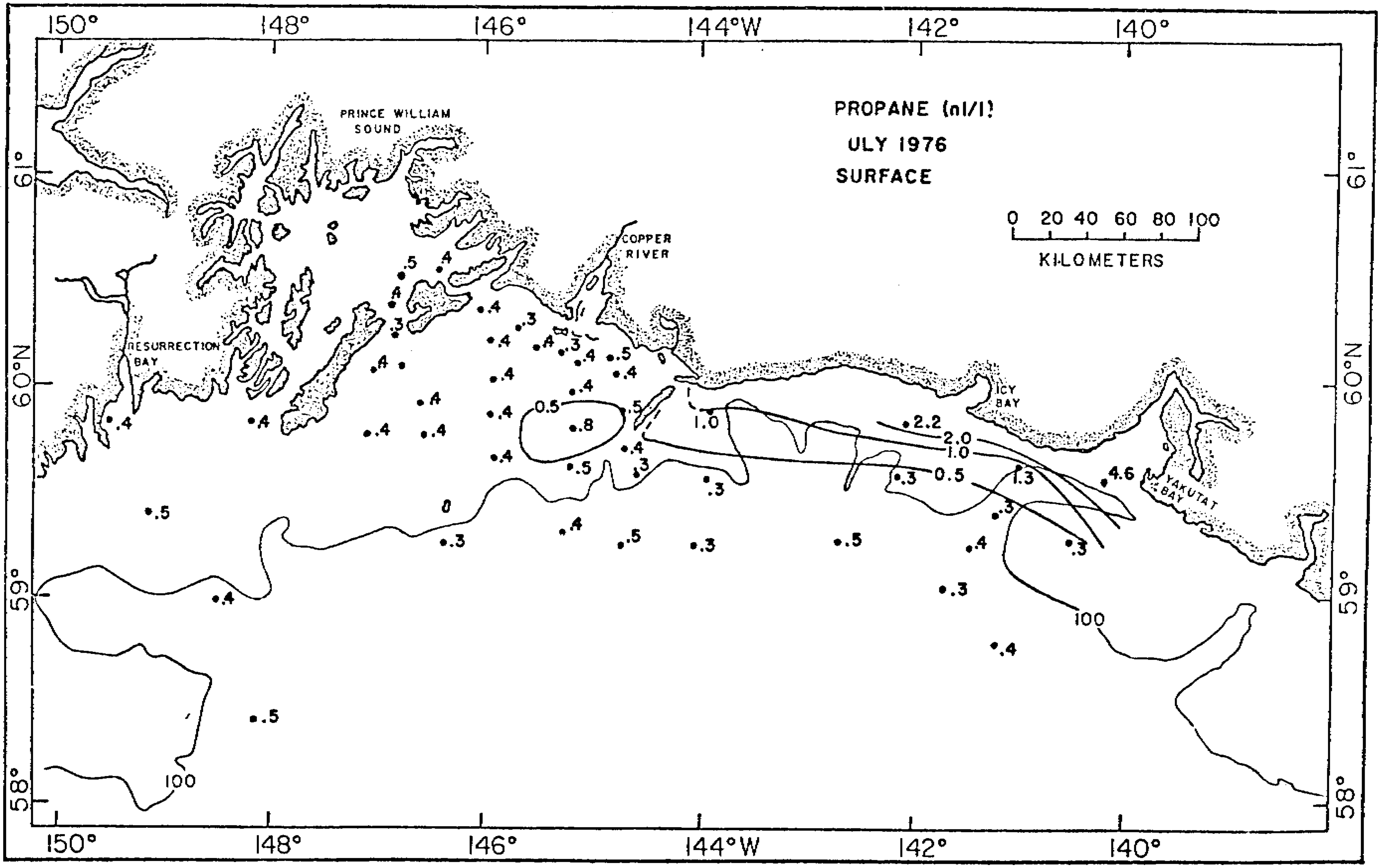

Figure 4-14. Areal distribution of propane in the surface waters during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

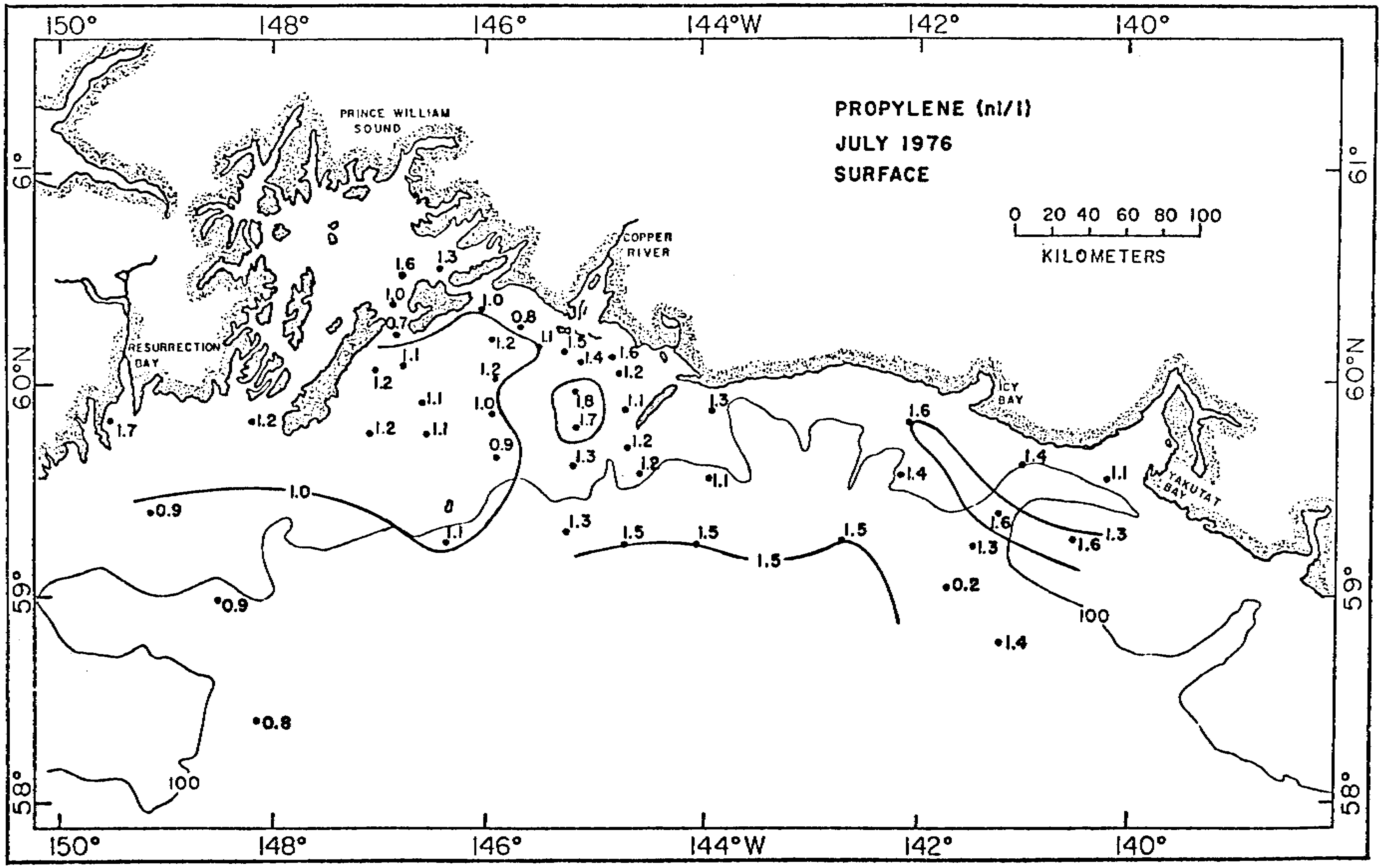

Figure 4-15. Areal distribution of propene in the surface waters during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

Sound, the concentration of ethane was approximately 0.4 nℓ/ℓ, decreasing 0.2 nℓ/ℓ toward the east. As noted earlier, a relatively high concentration of propane was observed at the entrance to Yakutat Bay during the July 1976 cruise (Figure 4-14), but was not accompanied by similar increases in propene (Figure 4-15).

Near-bottom concentrations of propane are spatially and temporally invariant (Cline and Feely, 1976; Cline, 1977b). Concentrations were near 0.2 nℓ/ℓ, except in July near Hinchinbrook Island and Tarr Bank, where concentrations approached 0.6 nℓ/ℓ. These values are within the normal variability observed over the slope and do not suggest the presence of either gas or oil seeps.

4.34 Butanes

Iso- and n-butanes were everywhere present at or below the detection limit of 0.05 nℓ/ℓ. This was true in both the surface waters as well as at depth.

4.4 Southeastern Bering Sea (Bristol Bay)

Observations for low molecular weight hydrocarbons were conducted in September-October 1975 and again in June-July 1976. These measurements represent conditions as they existed during the fall and summer seasons. The results of these cruises have been reported elsewhere (Cline and Feely, 1976; Cline, 1977b), but the salient features will be discussed here.

The sampling grid employed during both cruises is shown in Figure 4.16.

4.41 Methane

Surface concentrations of methane were generally low in the fall of 1975, ranging from values in excess of 150 nℓ/ℓ near Herendeen Bay on the Alaskan Pennisula to values less than 60 nℓ/ℓ near the Kvichak and Kushkokwim Rivers. Surface waters in equilibrium with the atmosphere should contain approximately 50 nℓ/ℓ of methane, assuming a partial pressure of methane of 1.4 ppmv

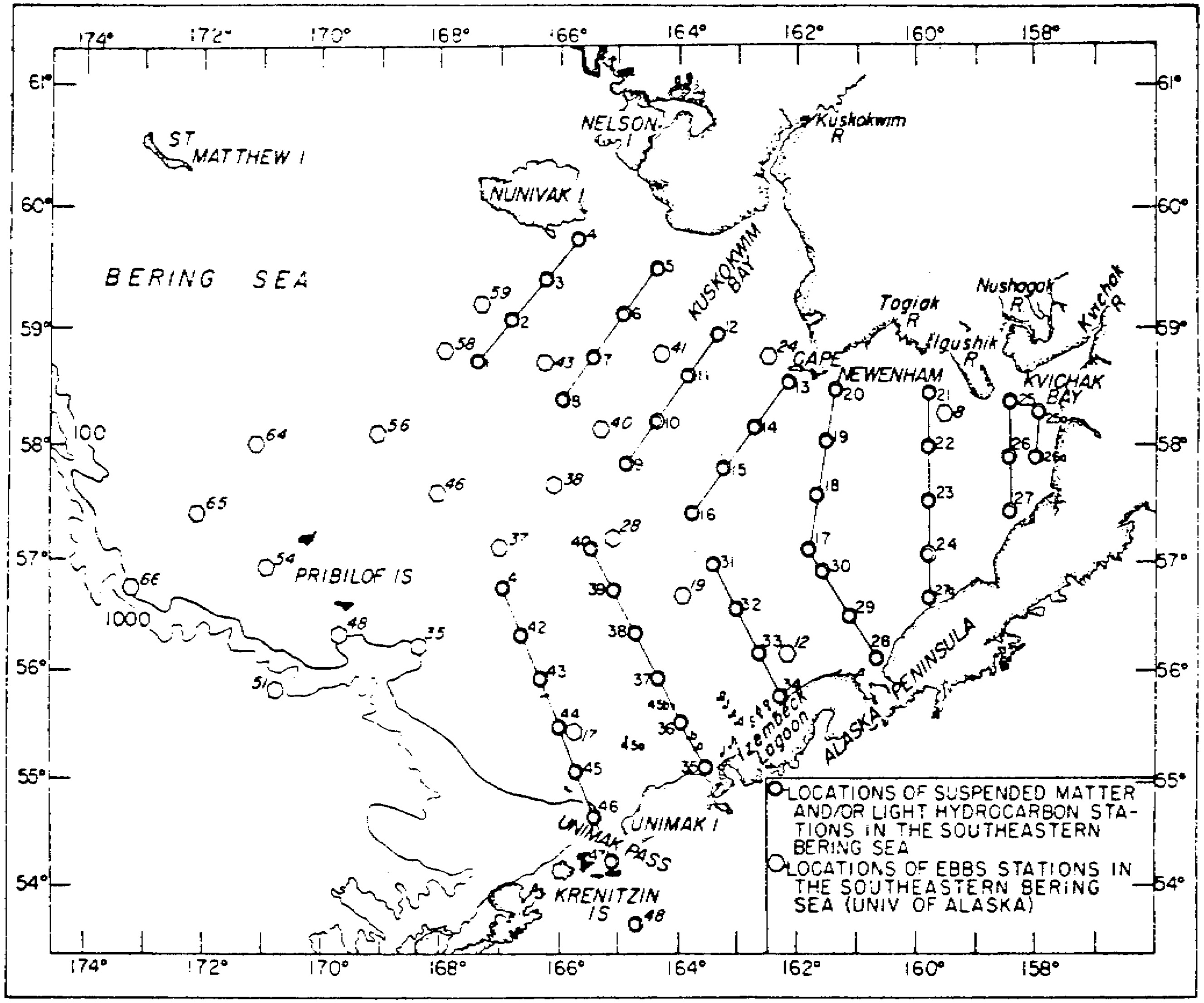

Figure 4-16. Station locations in the southeastern Bering Sea. PMEL stations are indicated by open circles, IMS stations are indicated with open hexagonal symbols. Both series of stations were sampled for low molecular weight hydrocarbons.

(Lamontagne, et al., 1974). Thus, the near equilibrium state reflected the quiescent biological condition that existed at that time (Cline and Feely, 1976).

In contrast, methane concentrations in the surface layers during the following summer were considerably above saturation, particularly near Herendeen Bay (Figure 4-17). With the exception of outer central Bristol Bay, concentrations of methane were consistently above 100 nℓ/ℓ, the highest value being nearly 1600 nℓ/ℓ near Herendeen Bay. The distribution of methane during July 1976 is similar to the temperature distribution suggesting that the local production of methane is modified by the intrusion of methane-depleted waters from the west (Cline and Feely, 1976). The high concentrations in the surface waters observed near the Alaskan Penninsula is presumably due to the influence of the lagoons. Organic-rich muds in these shallow embayments are apparently a large source of biogenic methane.

The near-bottom distribution of methane for the two seasons is shown in Figures 4-18 and 4-19. The high concentrations of methane observed in the fall of 1975 in the region of the Golden Triangle (see Figure 4-18) was not observed in the summer of 1976. This would suggest that methane present in the near-bottom waters was the result of intrusion or was locally produced from surficial sediments. With the aforementioned exception, the concentrations of methane near the bottom were systematically higher than those observed in the fall of 1975 (Figure 4-18), in concert with conditions prevailing in the surface layers. In all likelihood, a portion of the surface increase is due to vertical flux from below although we cannot rule out the possibility of significant production of methane in the surface layers during periods of high primary productivity.

In the most general sense, both temporally and spatially, methane in the near-bottom waters varied between 100-400 nℓ/ℓ, excluding the prominent

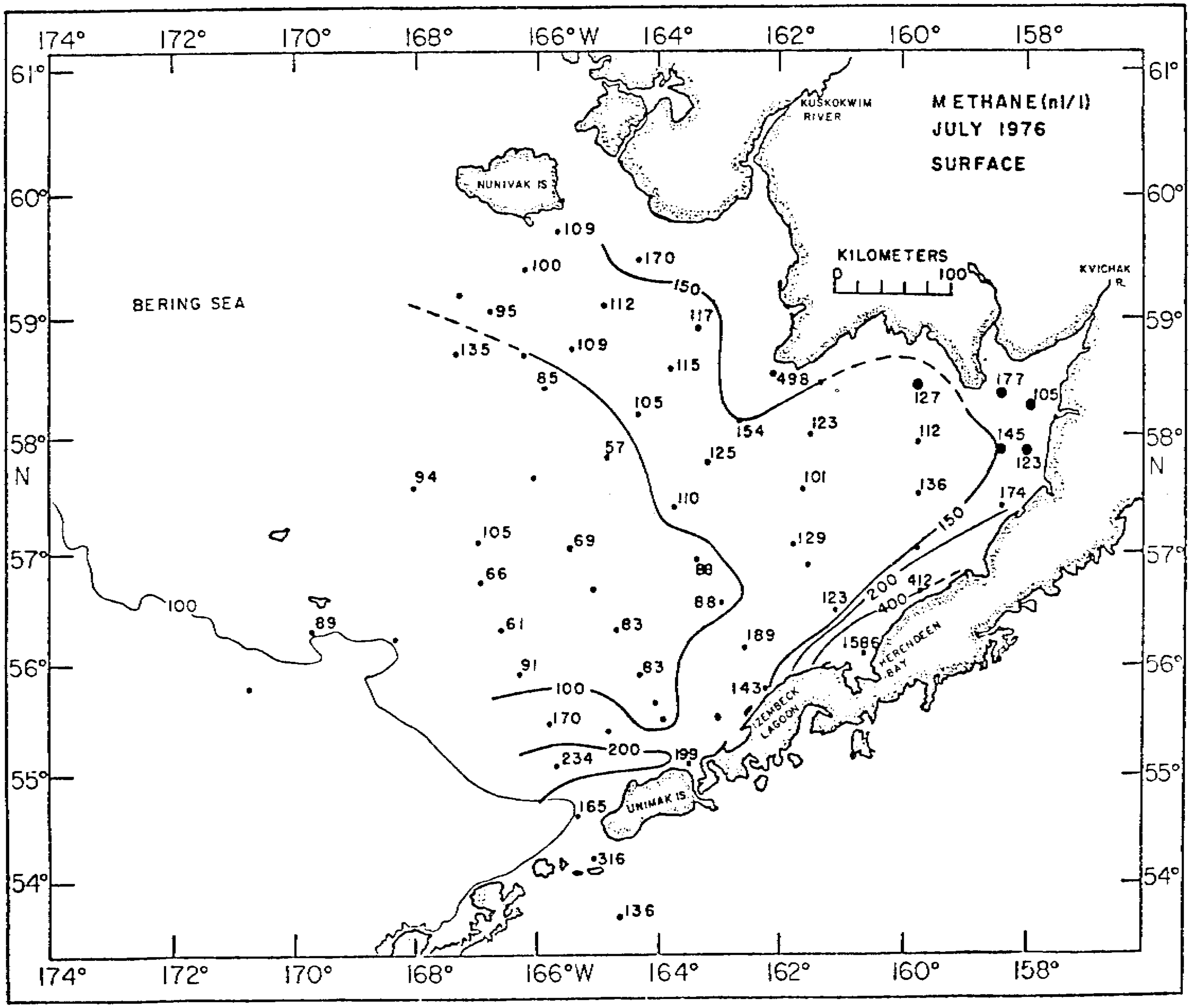

Figure 4-17. Areal distribution of methane in the surface waters during June-July 1976. Concentrations are expressed in nℓ/ℓ (STP).

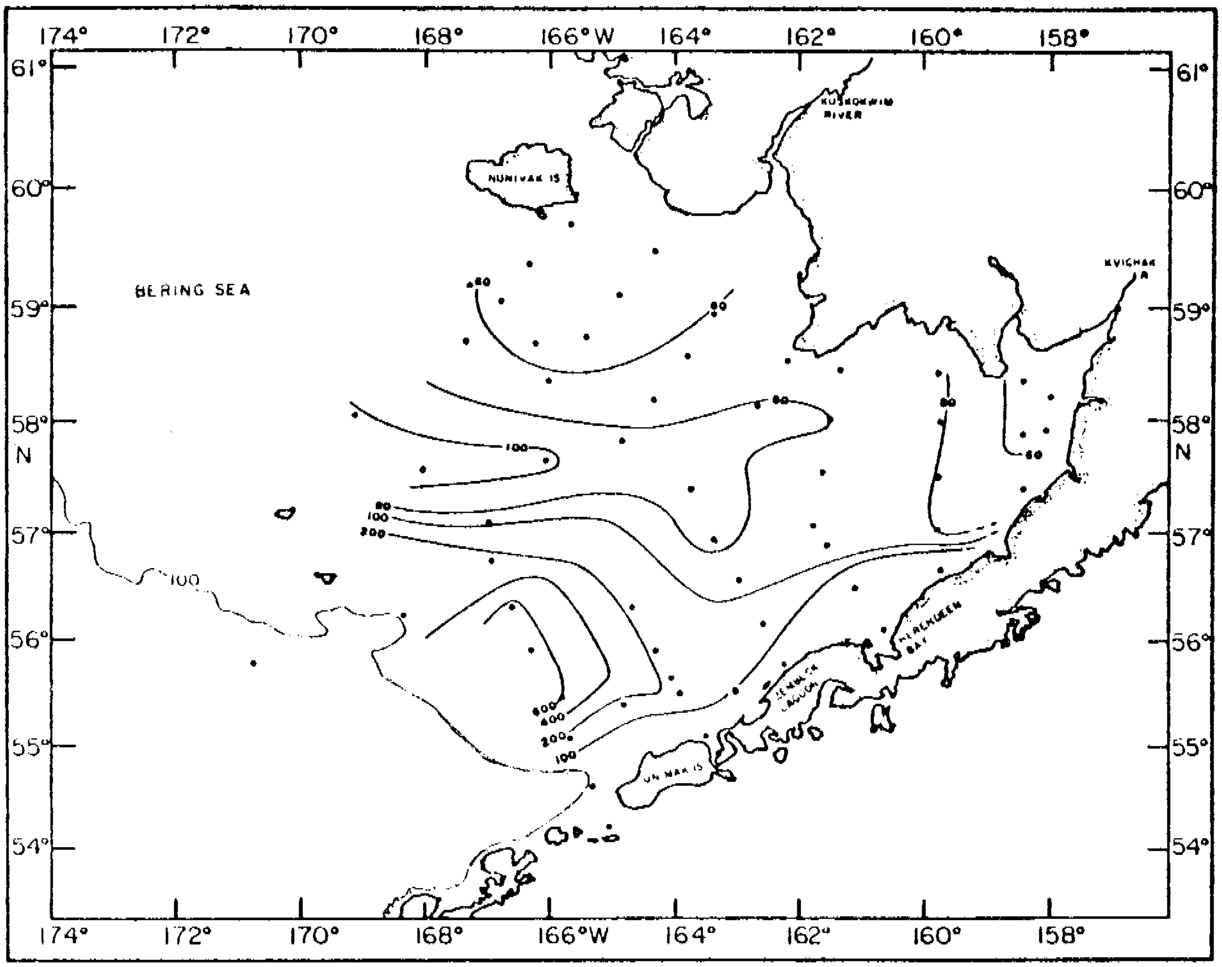

Figure 4-18. Areal distribution of methane 5 m from the bottom during Sept.-Oct. 1975. Concentrations are expressed in nℓ/ℓ (STP).

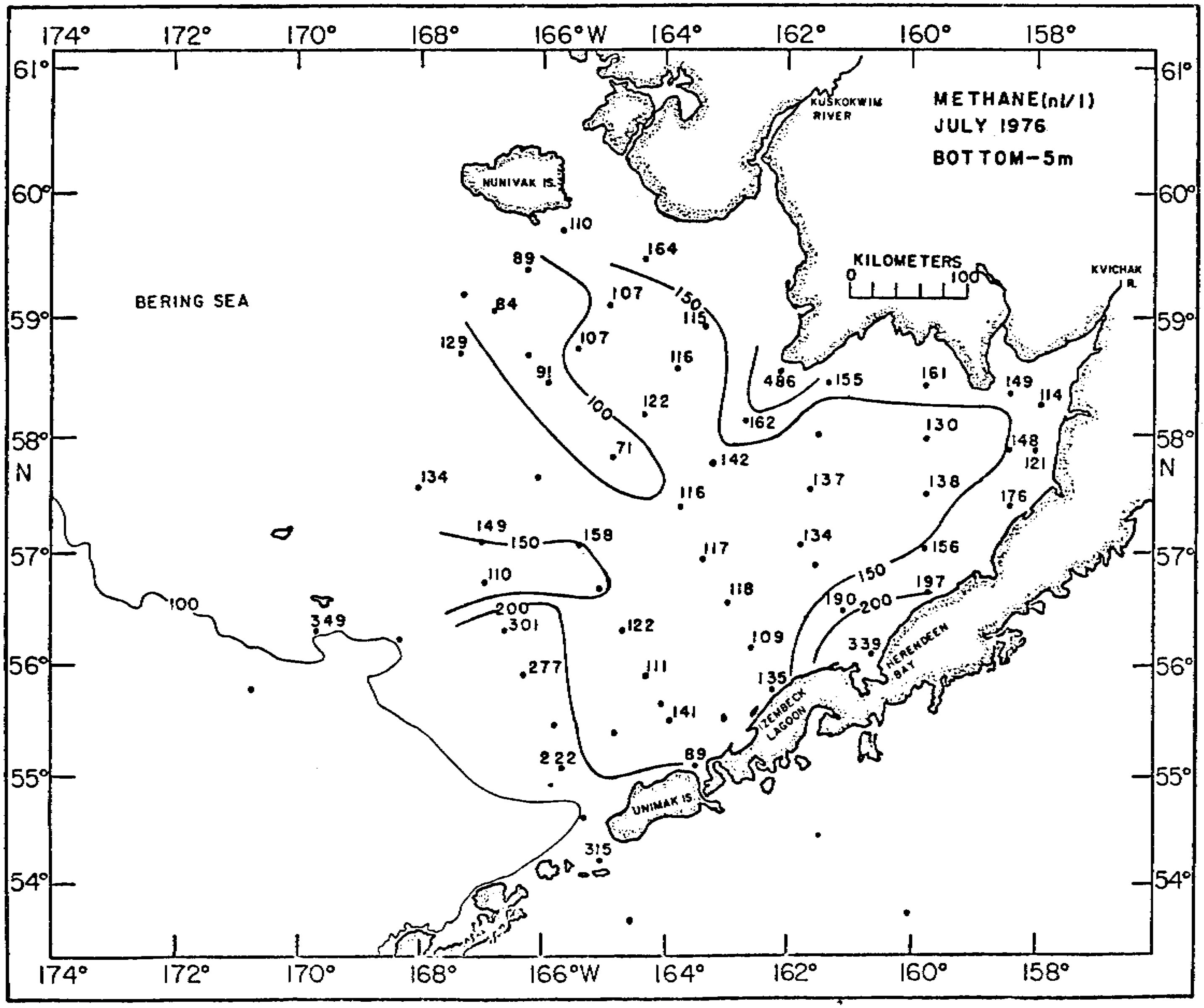

Figure 4-19. Areal distribution of methane within 5 m of the bottom in June-July 1976. Concentrations are expressed in nℓ/ℓ (STP).

seasonal source in the Golden Triangle region north of Unimak Pass. We assume that this methane is predominantly of biogenic origin, since it is not supported by higher concentrations of ethane and propane, and may arise from the biochemical reduction of organic matter or carbon dioxide in the sediment column (Claypool, 1974; Reeburgh and Heggie, 1977). This does not preclude the fact that methane production might proceed at the sediment-water interface and be susceptible to seasonal fluxes of organic carbon. Similarily, methane production from micro-environments in the water column, such as fecal matter, also may contribute to the seasonal differences in the distribution of methane (Scranton and Brewer, 1977).

4.42 Ethane and Ethene

During the fall of 1975, the concentration of ethane varied little spatially, ranging from 0.4 to 0.6 nℓ/ℓ (Cline and Feely, 1976). In summer, the range in surface concentrations was 0.3 to 2.9 nℓ/ℓ. The highest values were recorded in eastern Bristol Bay and along the wastline of the Alaskan Peninsula with lesser amounts found in the central basin (Figure 4-20). Little difference between the surface layers and the near-bottom waters was observed in fall, but in summer, the near-bottom concentrations were significantly higher (see Figure 4-21). It is suggested that this occurrence is related to greater vertical stability in the water column allowing ethane to accumulate below the thermocline (Figure 4-22).

The distribution of ethene for surface and near-bottom waters during July 1976 is shown in Figures 4-23 and 4-24. Surface concentrations ranged from 2 nℓ/ℓ in the central basin to values in excess of 5 nℓ/ℓ toward the east. At the time of these measurements, elevated biological activity was evident in the surface waters because of the deep green color and the enormous quantities of feeding birds. We associate the high concentrations of ethene to biological

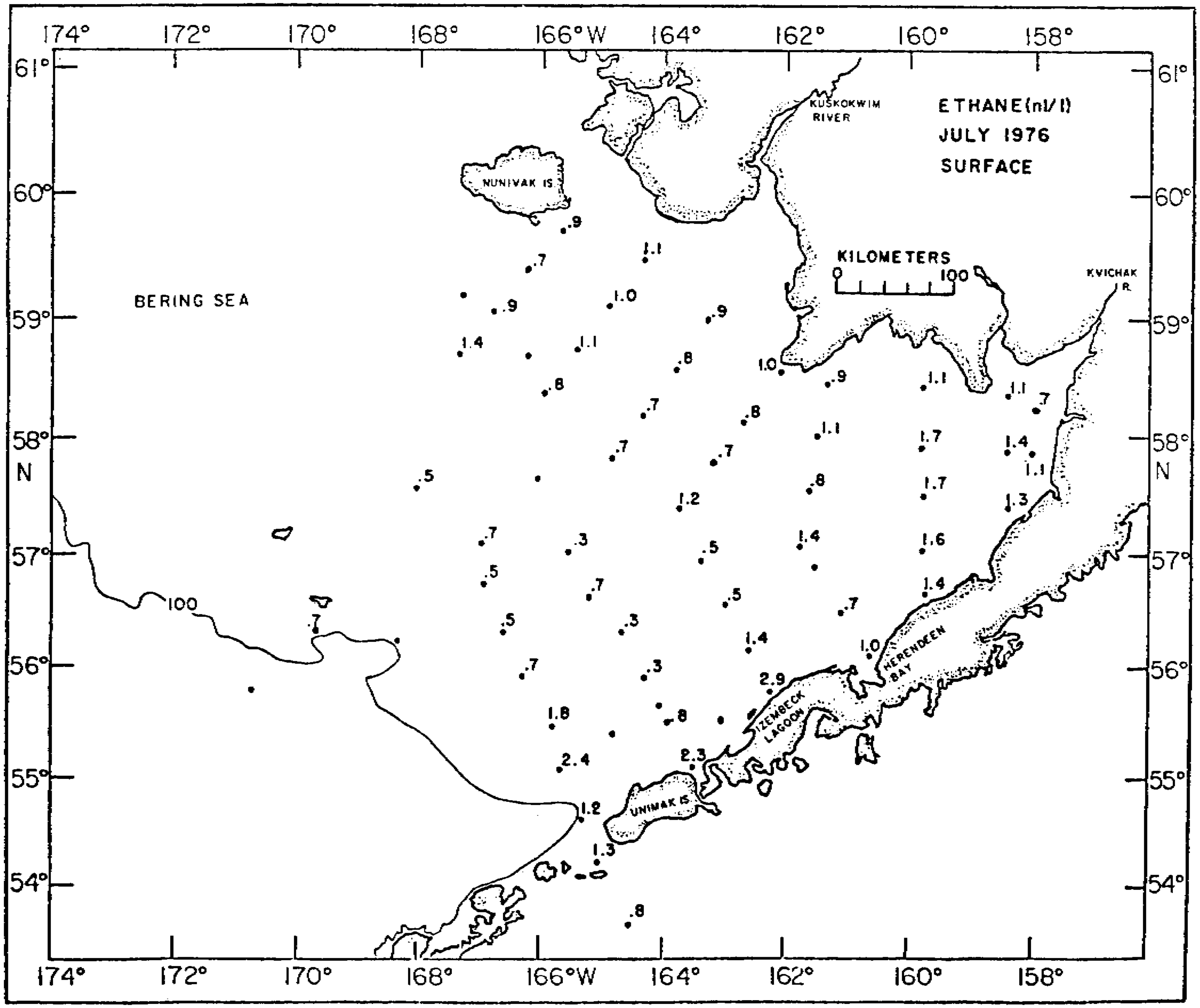

Figure 4-20. Areal distribution of ethane in surface waters during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

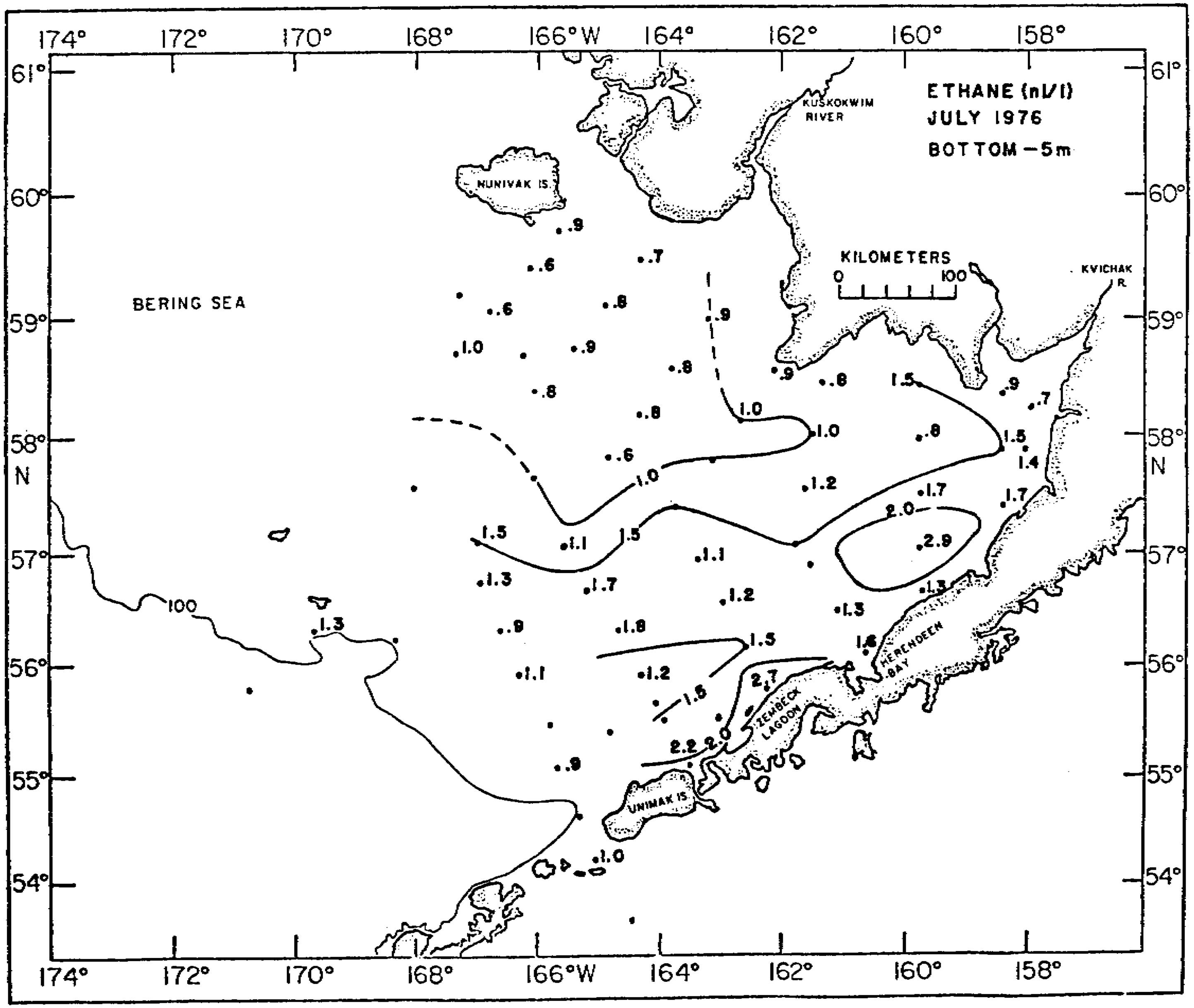

Figure 4-21. Areal distribution of ethane within 5 m of the bottom in July 1976. Concentrations are expressed in nℓ/ℓ (STP).

production. Similarily, the previously noted high concentrations of ethane near the Alaskan Peninsula are probably biological in origin as well; being related chemically or biochemically to the production of ethene (J. Brooks, Texas A & M University personal communication).

The near-bottom distribution of ethene is similar to that of temperature (Figure 4-22). The well pronounced tongue of ethene-deficient water lies along the central axis of the basin and correlates well with the low temperature water. This water was thought to be derived from the Gulf of Anadyr in the northern Bering Sea, but now is believed to represent relict water formed during the previous winter (Schumacher and Coachman, 1977). Mean flow within this water mass is sluggish with cyclonic flow predominately around the perifery. Concentrations within the core of the plume are generally less than 2 nℓ/ℓ, increasing to concentrations in excess of 5 nℓ/ℓ toward the east (Figure 4-24). Due to the shallow nature of the inner basin, the coastal water (7 < 50 m) is well mixed vertically, thus the concentration of ethene is rather uniform with depth (Figures 4-23 and 4-24).

Our observations would suggest that ethane and ethene in surface waters should range from 0.5 to 3 nℓ/ℓ and 0.5 to 5 nℓ/ℓ respectively, the higher values being indicative of increased biological activity. However the ratio of ethane to ethene remains generally less than unity, except when the concentrations of both components are very small (e.g., < 0.2 nℓ/ℓ).

4.43 Propane and Propene

The distribution of propane shows little variation of Bristol Bay, either seasonally or spatially. Near-surface concentrations of propane plus propene in fall of 1975 were uniformly near 0.5 nℓ/ℓ, increasing slightly to 0.6 to 0.8 nℓ/ℓ in the near-bottom waters (Cline and Feely, 1976). Measurements taken

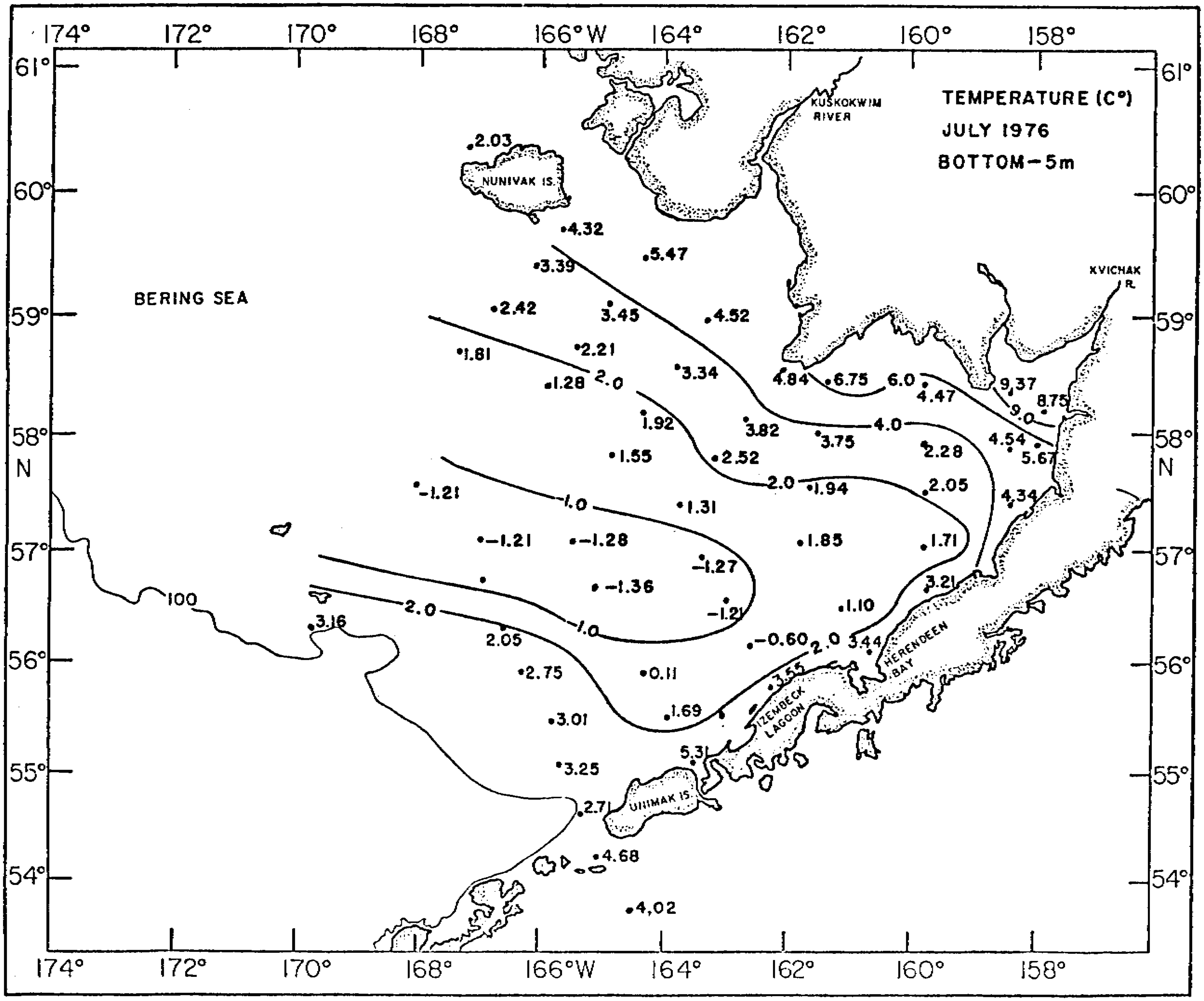

Figure 4-22. Distribution of temperature (°C) in the near-bottom waters of Bristol Bay in July 1976.

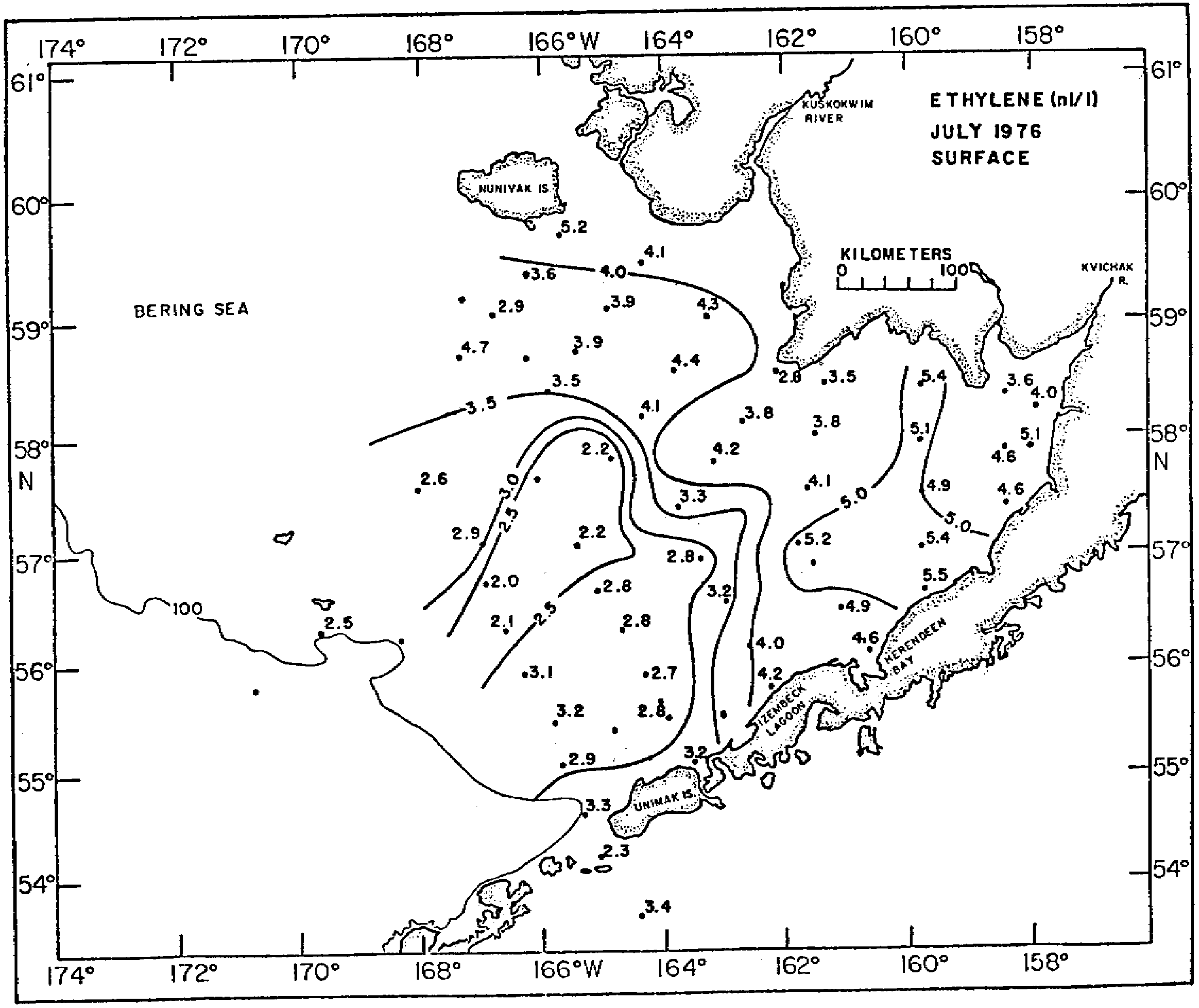

Figure 4-23. Areal distribution of ethene in surface waters during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

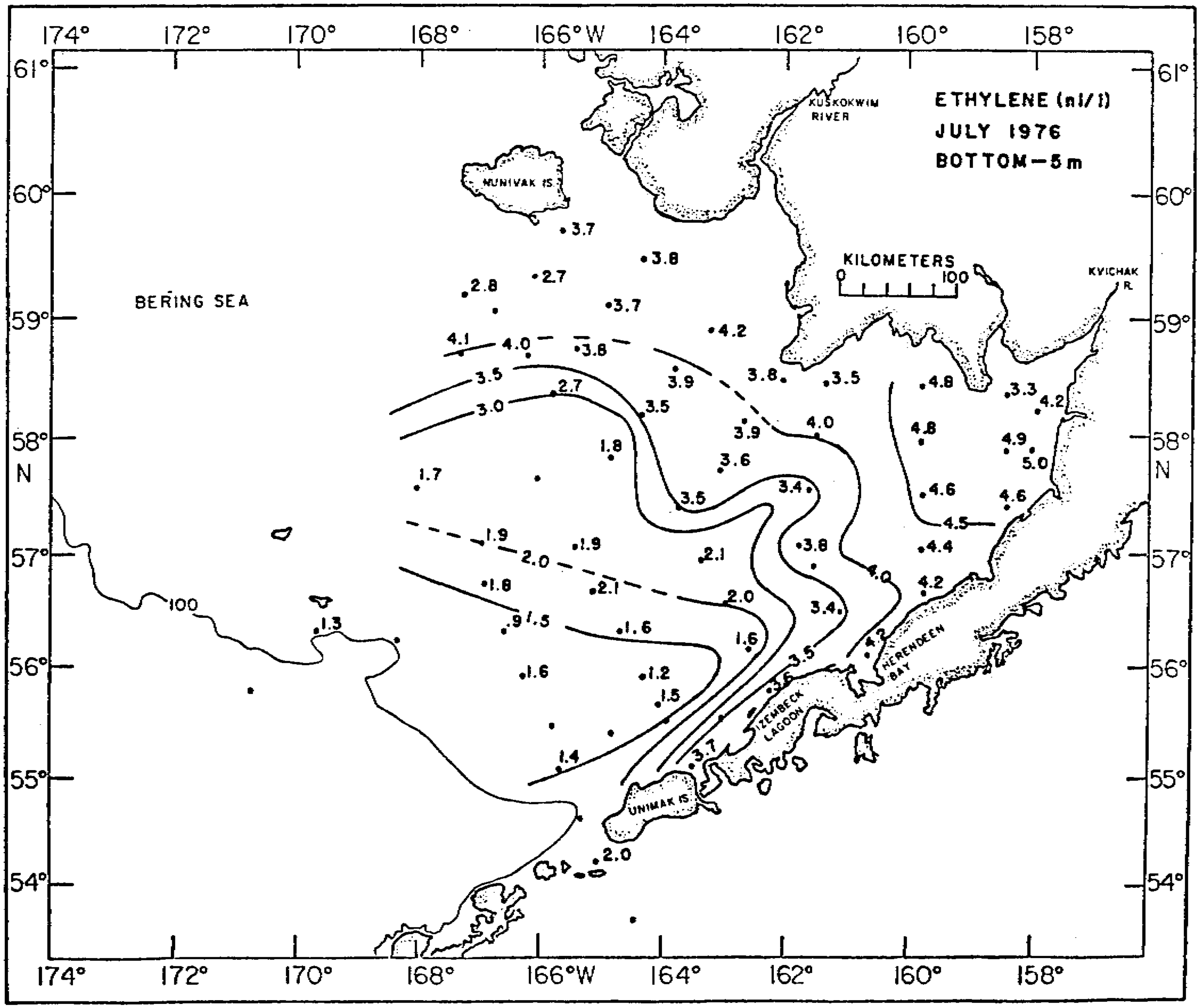

Figure 4-24. Areal distribution of ethene within 5 m of the bottom during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

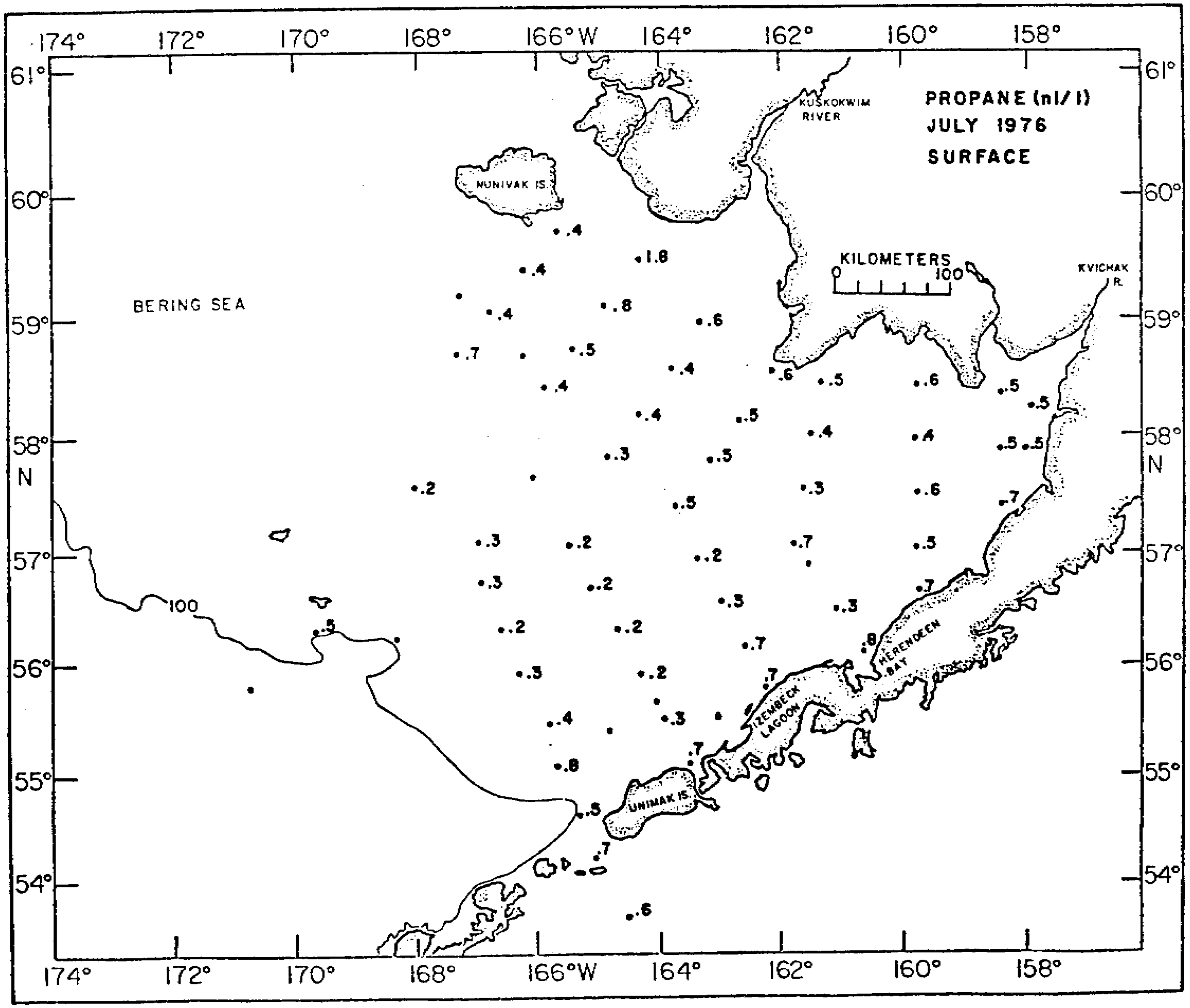

Figure 4-25. Areal distribution of propane in surface waters during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

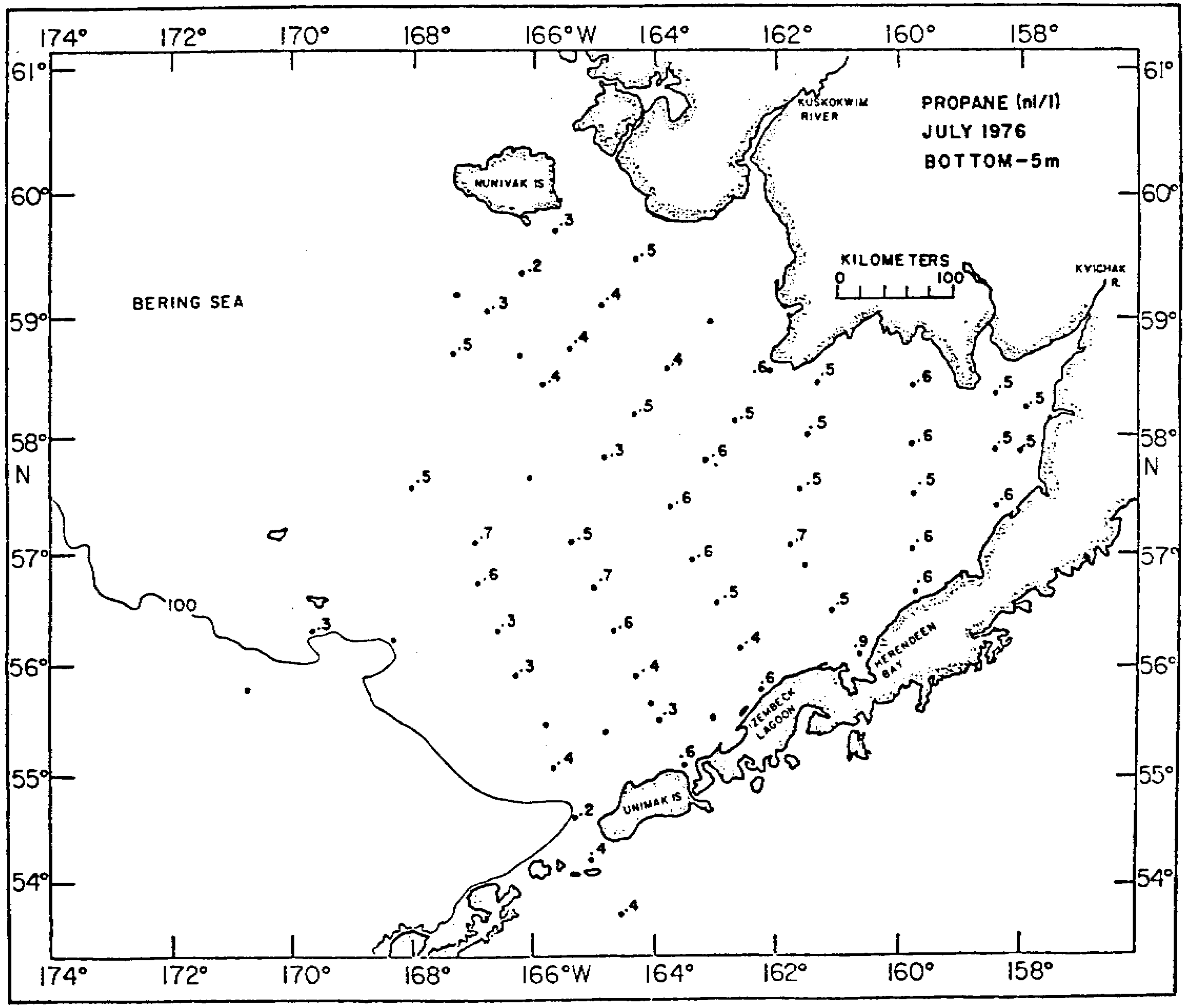

Figure 4-26. Areal distribution of propane within 5 m of the bottom during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

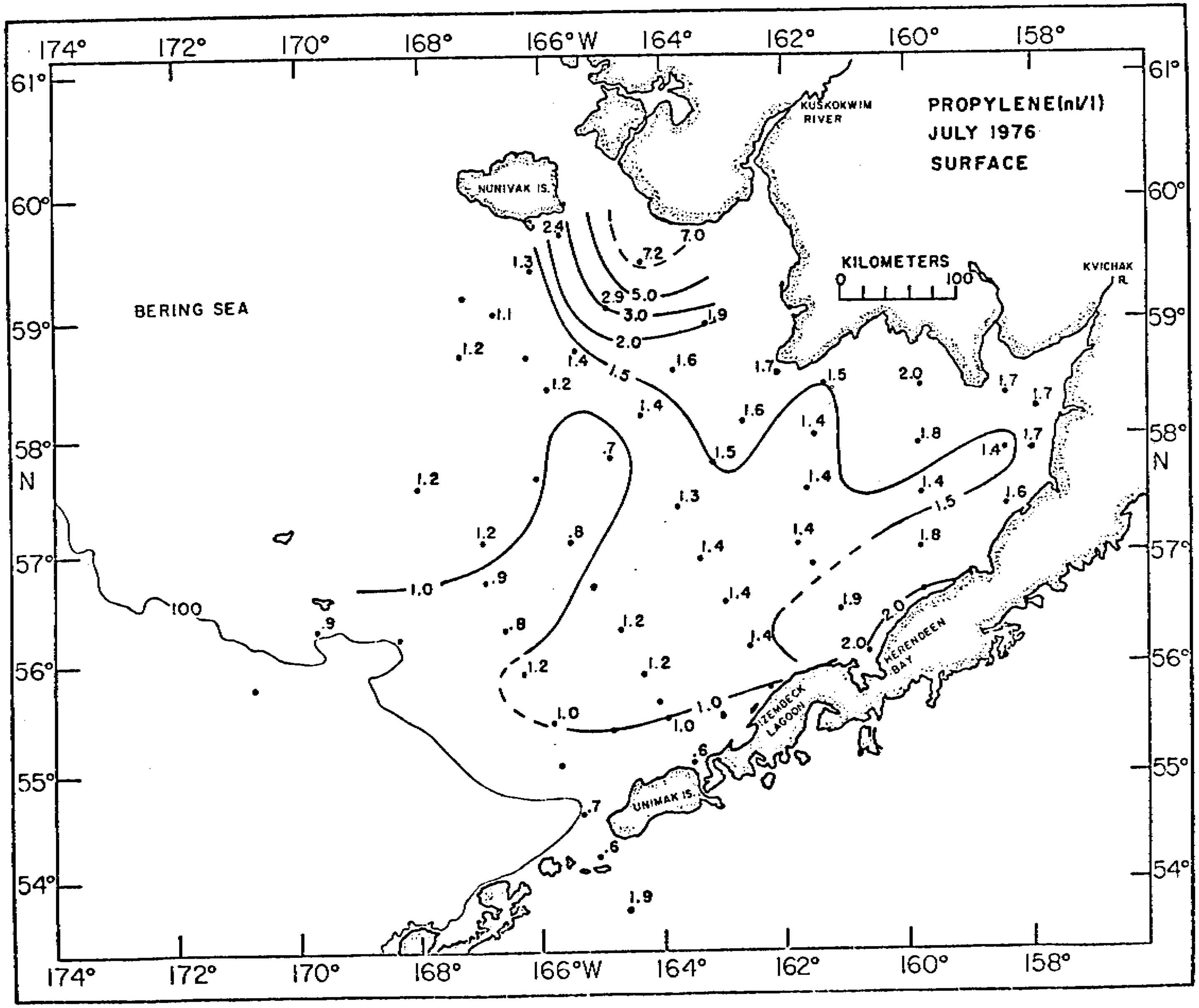

Figure 4-27. Areal surface distribution of propene in Bristol Bay in July 1976. Concentrations are given in nℓ/ℓ.

July of 1976 were of better quality and indicated that propane varied from 0.2 nℓ/ℓ to a high value of 1.8 nℓ/ℓ near the Kuskokwim River (Figure 4-25). The near-shore areas were characterized by propane concentrations in excess of 0.5 nℓ/ℓ (Figure 4-25).

Near-bottom concentrations varied little from those observed in the surface layers (Figure 4-26). The range of values was 0.2 nℓ/ℓ to 0.9 nℓ/ℓ, the latter observation taken near Herendeen Bay. No evidence was found for the introduction of petroleum or natural gas based on the abundance or distribution of propane.

The concentration of propene in the surface layers was significantly higher in summer compared to the preceeding fall. Concentrations in excess of 7 nℓ/ℓ were observed near the Kuskokwim River delta with values in excess of 1 nℓ/ℓ over most of the shallow near-shore areas (Figure 4-27). As was the case for ethene, propene appears to be produced during periods of elevated biological activity.

4.44 Iso-butane and n-Butane

Concentrations of iso- and n-butane were everywhere below 0.1 nℓ/ℓ. Because of inherent low-level contamination of water samples, the uncertainty in the concentration of butanes below 0.1 nℓ/ℓ is very large. In most cases, the concentration of the C_4 aliphatics, after correction for blanks, was below the detection limit of 0.05 nℓ/ℓ.

4.5 Norton Sound

A water column survey of low molecular weight hydrocarbons was conducted in Norton Sound in September of 1976. The sampling grid employed for the preliminary survey is shown in Figure 4-28. During the course of the investigation, a gas seep was discovered south of Nome Alaska and a more detailed grid was implemented to elucidate the size and distribution of the hydrocarbon plume. This grid is shown in Figure 4-29.

The preliminary results of this cruise are discussed elsewhere (Cline, 1976), but the salient features will be included here for completeness. A more detailed account of the Norton Sound gas seep has been published previously (Cline and Holmes, 1977).

4.51 Methane

Surface concentrations of methane in nℓ/ℓ are shown in Figure 4-30. The dominant feature is the large plume of methane-rich water emanating from Safety Sound due east of Cape Nome. The highest surface concentration of methane in this region was 600 nℓ/ℓ, representing approximately 11-fold supersaturation with respect to the atmosphere. We assumed a partial pressure of methane in the atmosphere of 1.4 ppmv. At the time of the observations, the surface temperature and salinity was 10°C and $25^{\circ}/oo$ respectively (Muench et al., 1978). The occurrence of methane-rich surface waters near lagoons is not uncommon as we have observed similar distributions in Bristol Bay.

There also appears to be a surface source of methane in the eastern extremity of Norton Sound. However, it is likely that this surface feature has resulted from a vertical flux of methane from below, where extremely high concentrations of methane were found.

The near-bottom distribution of methane is depicted in Figure 4-31. A strong bottom source of methane exists east of Stuart Island, where concentrations exceed 2000 nℓ/ℓ. The elevated concentrations of methane detected near the bottom are probably due to thermal stratification (Muench et al., 1978), or a strong production of methane from the bottom, or both. Without detailed knowledge of the strength of benthic methane sources, or at least the distribution of organic carbon in the surficial sediments, we can not evaluate the

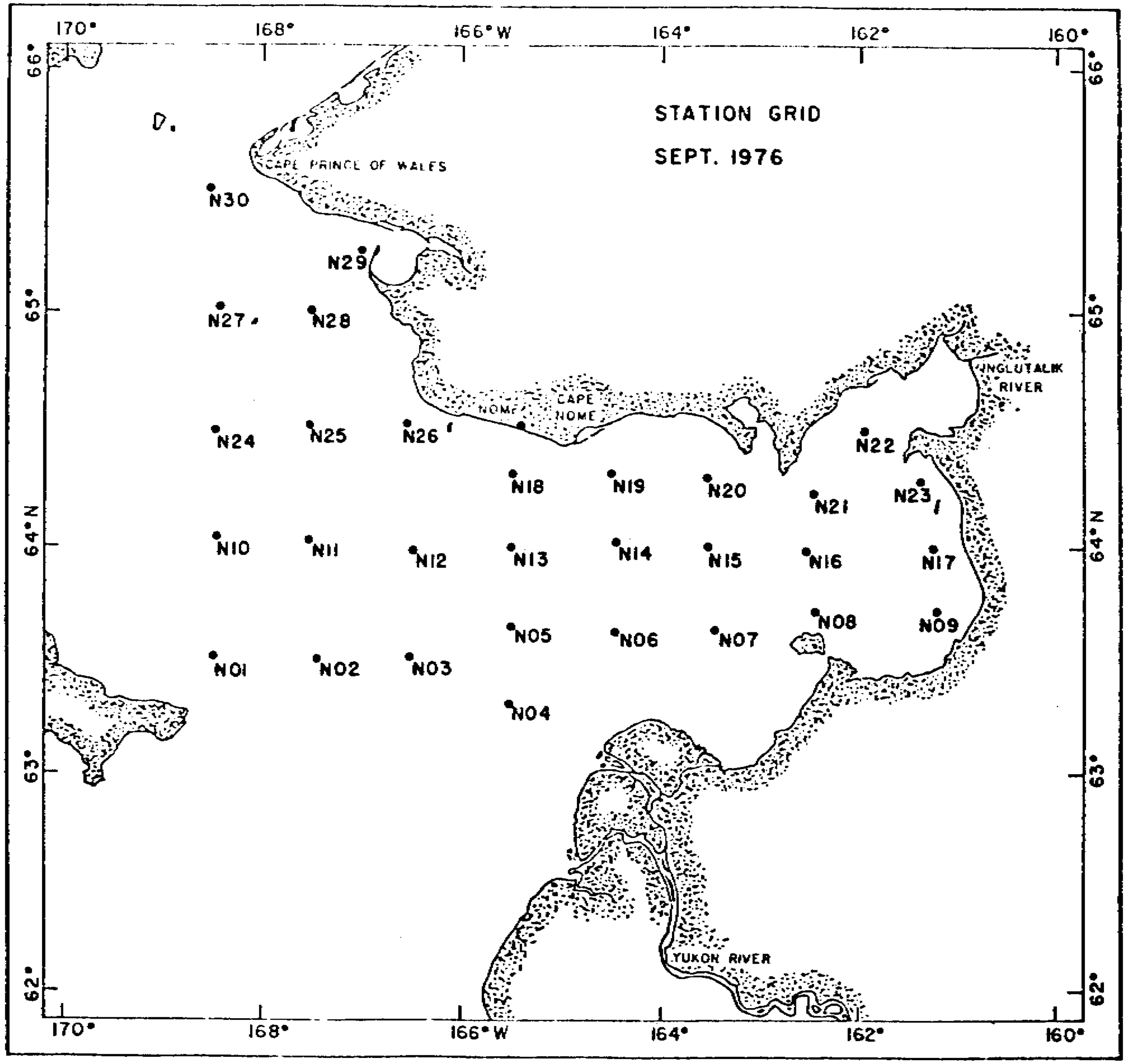

Figure 4-28. Station locations in Norton Sound.

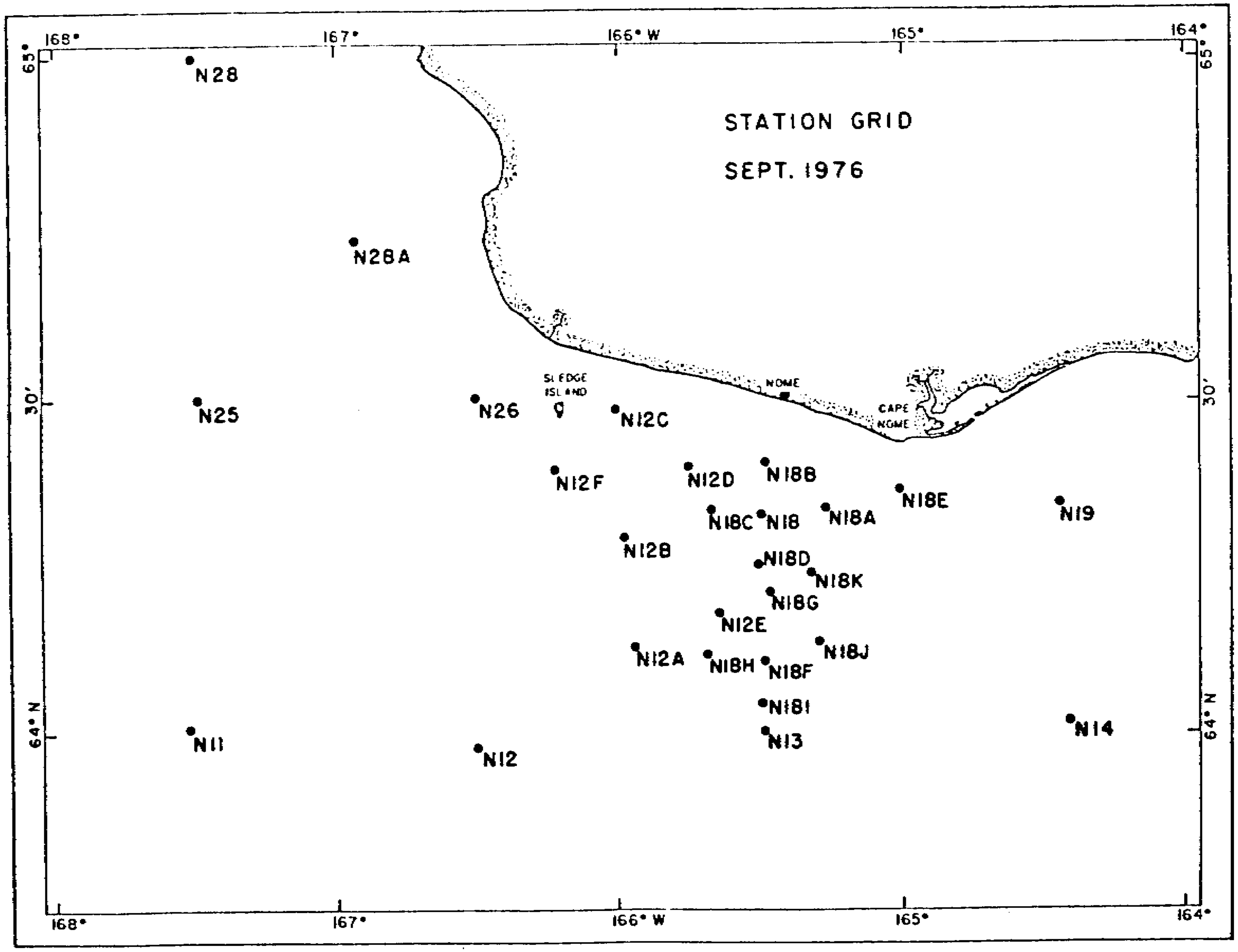

Figure 4-29. Station locations used for detailed survey of the gas seep.

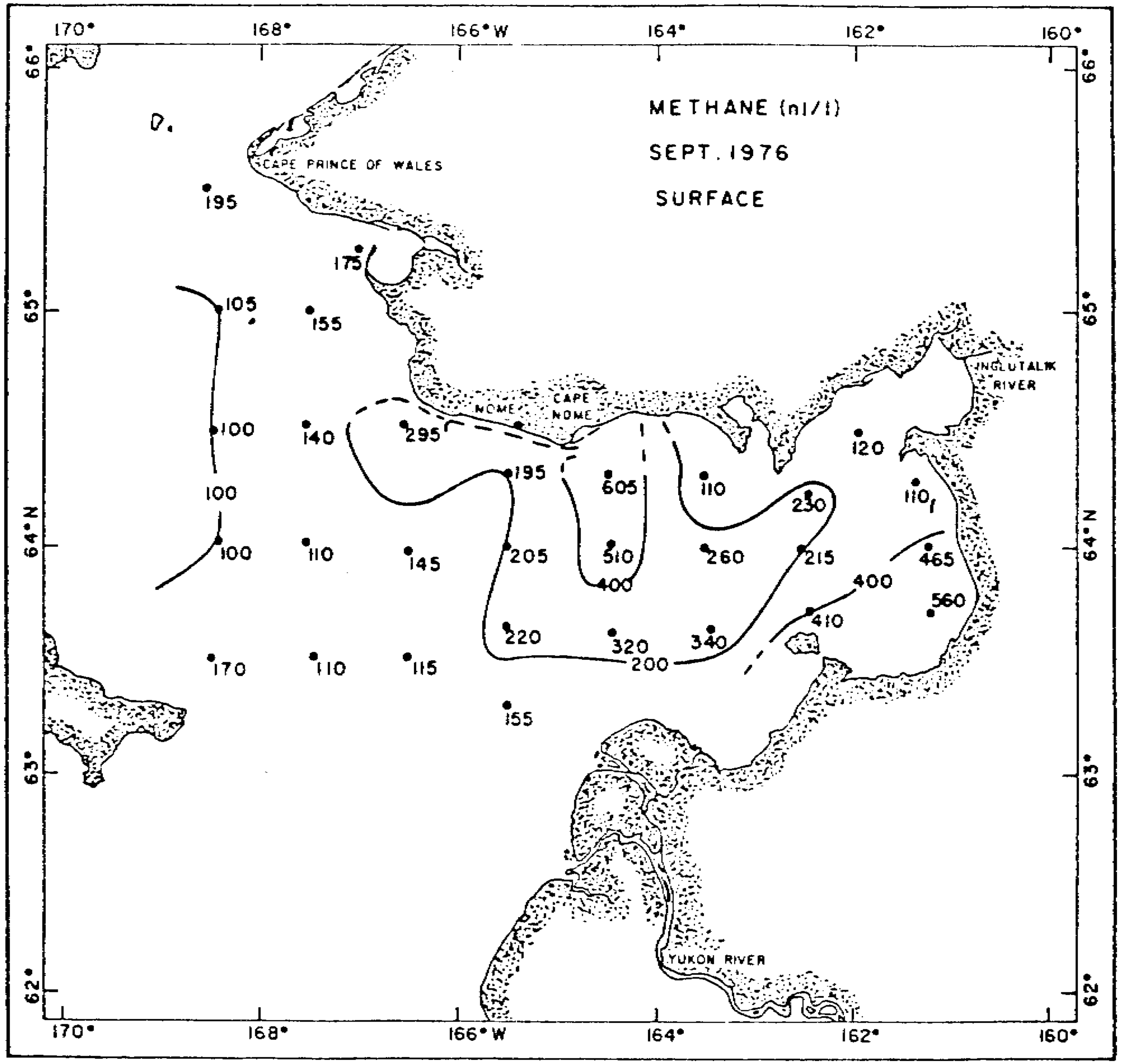

Figure 4-30. Areal surface distribution of methane in September 1976. Concentrations are expressed in nℓ/ℓ (STP).

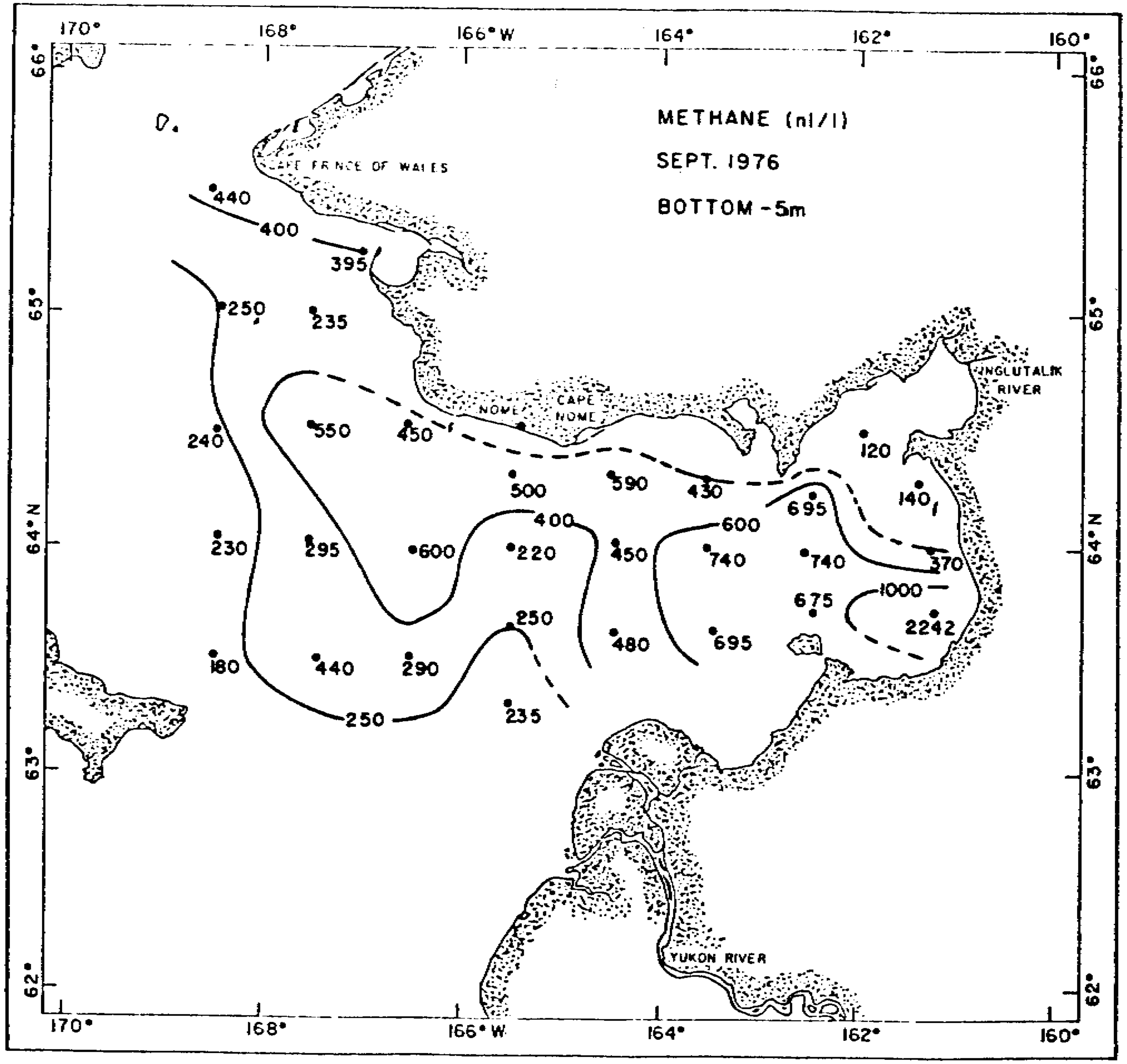

Figure 4-31. Areal distribution of methane within 5 m of the bottom during September 1976. Concentrations are expressed in nℓ/ℓ (STP).

relative merits of each process. Assuming that methane is quasi-conservative, the distribution of methane in the near-bottom waters suggests a diffusive flux from the eastern extremity of the basin to a point south of Nome. At that point the plume is intercepted by the methane-deficient coastal water moving north (Muench, et al., 1978).

Although the distribution of methane reveals strong localized sources, the average concentration in the surface and near-bottom waters is 230 ± 150 nℓ/ℓ and 410 ± 190 nℓ/ℓ. The near-bottom average was calculated neglecting the singularly high value of 2240 nℓ/ℓ observed east of Stuart Island.

4.52 Ethane and Ethene

The surface distributions of ethane and ethene are shown in Figures 4-32 and 4-33. Ethane is sporadically variable in the surface layers with no well-defined sources. A single high value (1.4 nℓ/ℓ) was observed near St. Lawrence Island with all other values less than 1 nℓ/ℓ. The average concentration of ethane in the surface layers is 0.5 ± 0.3 nℓ/ℓ, a value near that observed for the surface waters of the Chukchi Sea.

In contrast, the concentration of ethene in the surface waters is significantly higher and its distribution reveals localized sources (Figure 4-33). The strongest source of ethene appears northwest of Nome and presumably reflects local primary productivity. Concentrations of ethene in the core of the plume exceed 2 nℓ/ℓ. Average concentration of ethene is 1.3 ± 0.5 nℓ/ℓ. The mean ethane/ethene ratio in the surface layers is 0.4.

The near-bottom concentration of ethane is shown in Figure 4-34. The dominant feature of the region is the plume of ethane-rich water extending northwest along the coast. As is apparent in Figure 4-34, the plume extends north then west along the coast in accord with the general near-bottom circulation patterns. During this study, we were able to trace the plume for about 100 km.

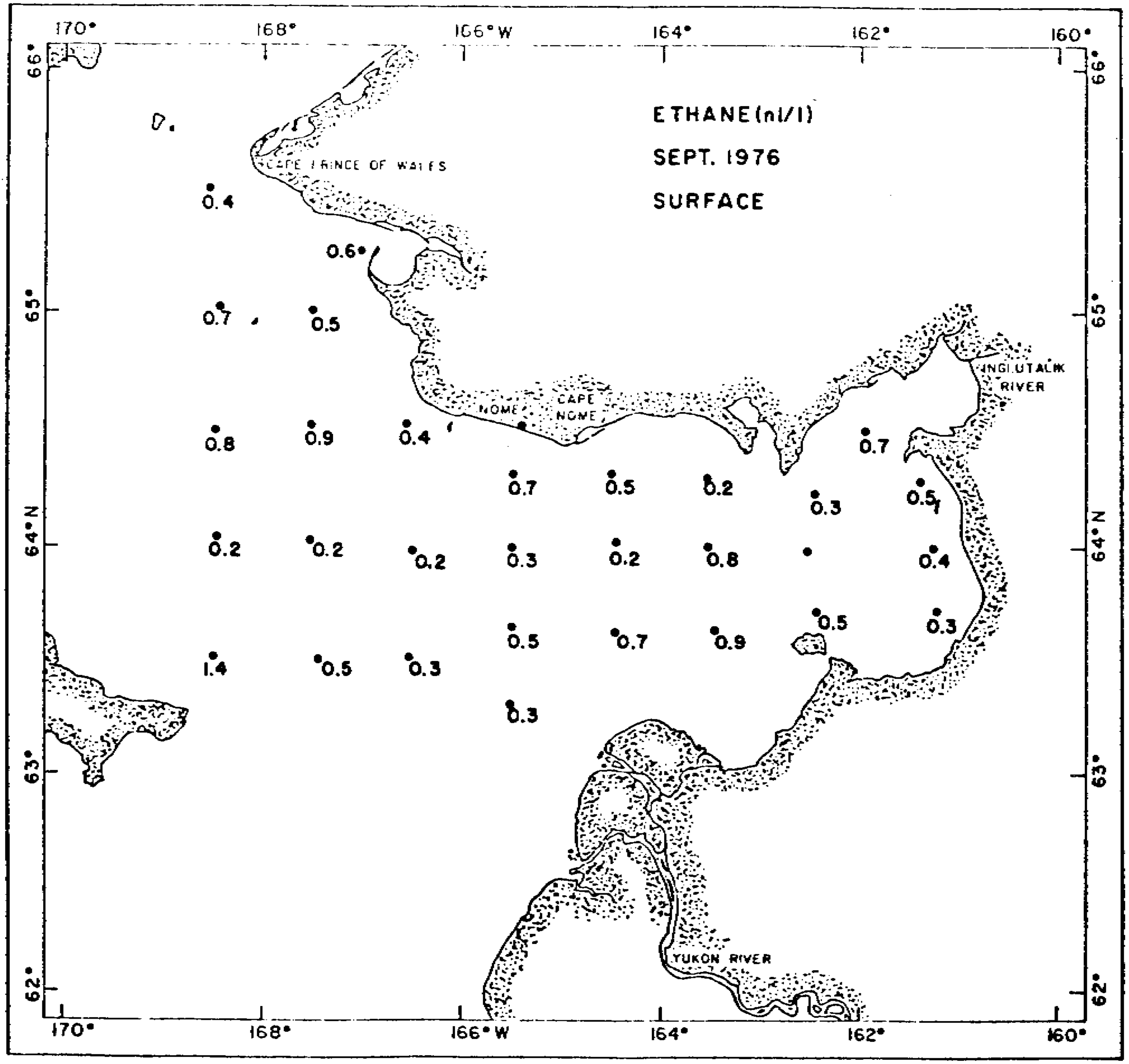

Figure 4-32. Areal surface distribution of ethane in Sept. 1976. Concentrations are expressed in nℓ/ℓ (STP).

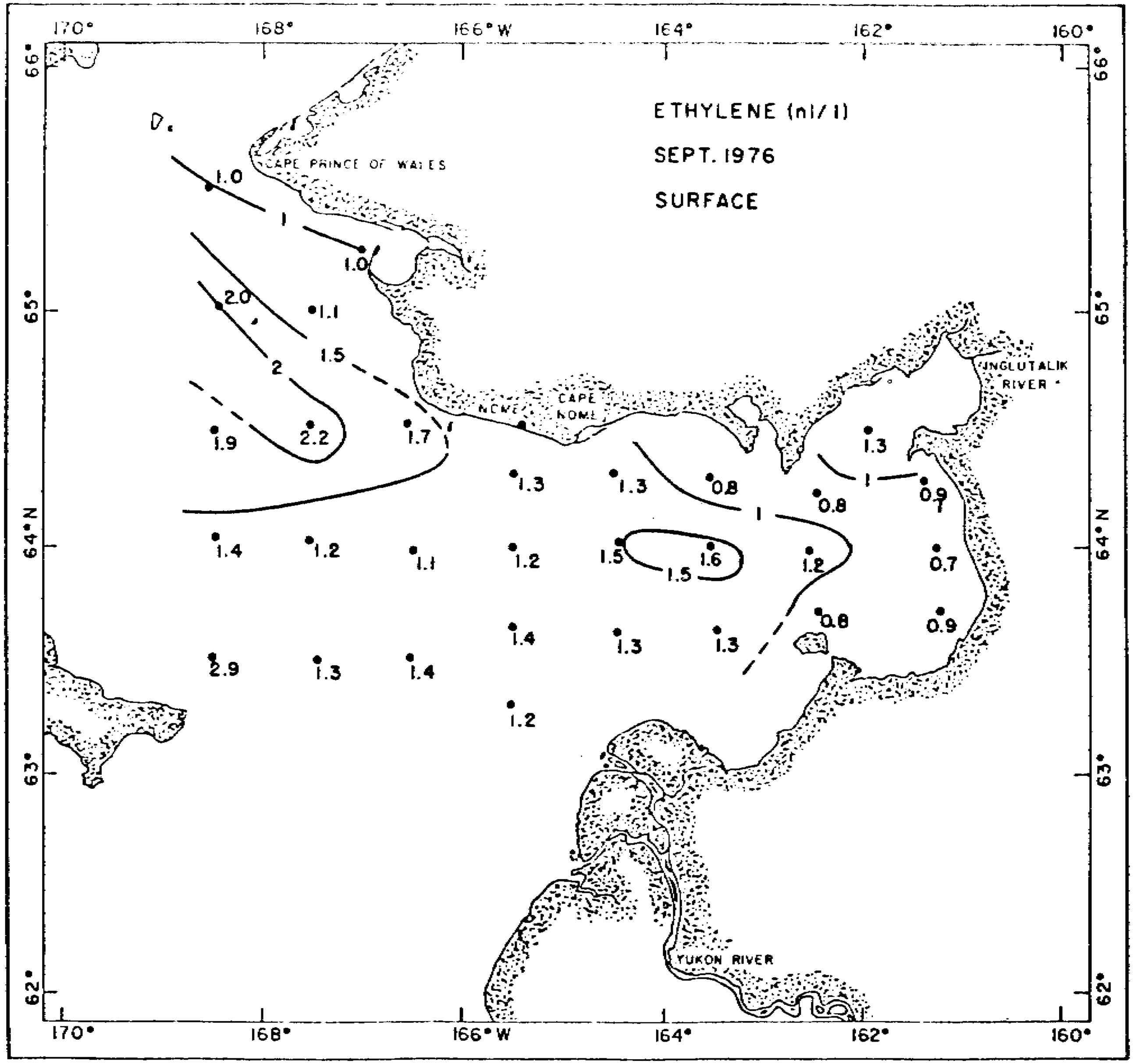

Figure 4-33. Areal surface distribution of ethene in Sept. 1976. Concentrations are expressed in nℓ/ℓ (STP).

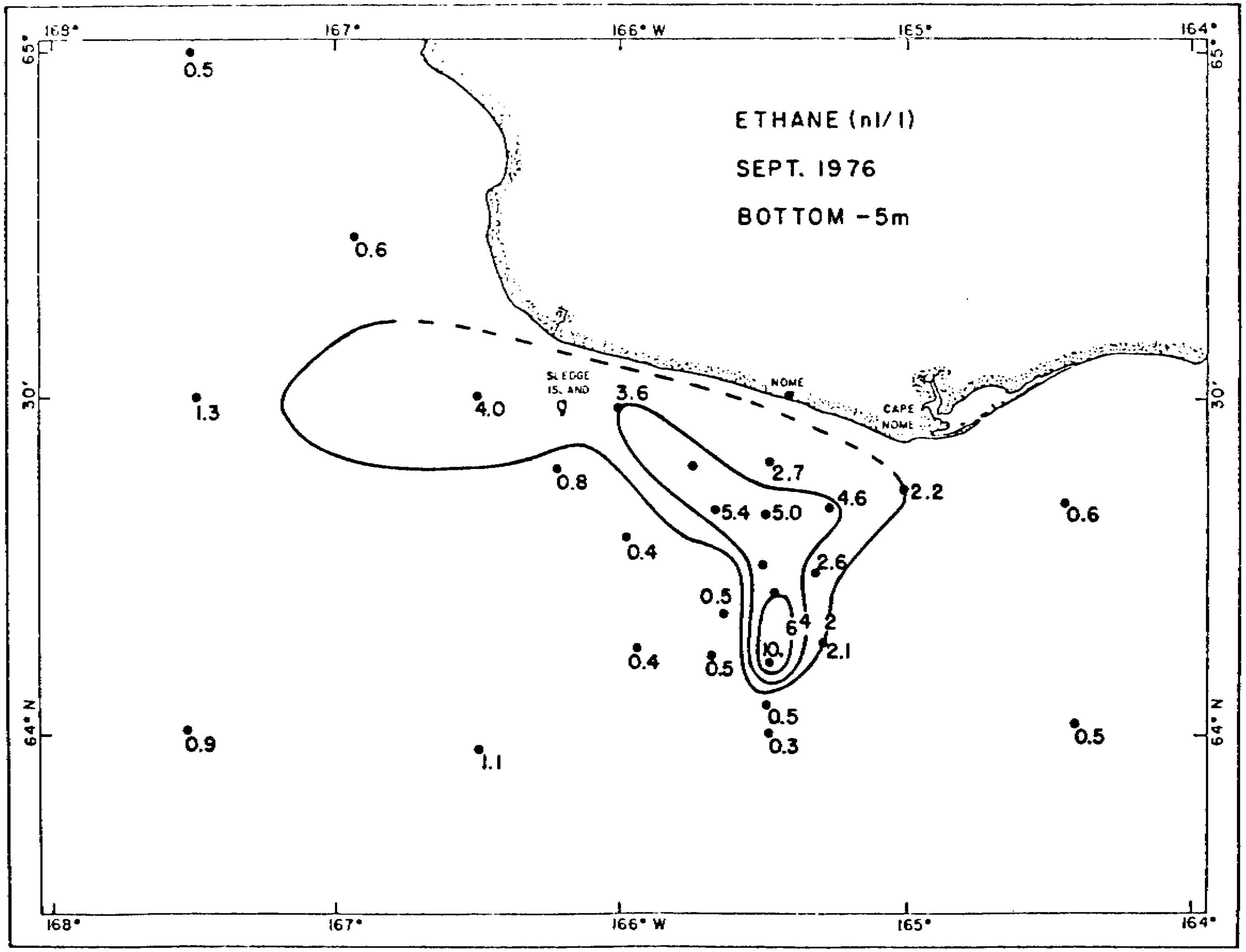

Figure 4-34. Areal distribution of ethane within 5 m of the bottom in the vicinity of the submarine gas seep. Concentrations are given in nℓ/ℓ (STP).

Comparison of Figure 4-34 indicates that the concentration of ethane in the core of the plume is approximately 20-fold above background. Unexpectedly, near-bottom methane concentrations in the region are not indicative of the seep (see Figure 4-31). Additional discussion on the nature of the gas seep may be found in the paper by Cline and Holmes (1977).

The mean concentration of ethane to the east and south of the seep area is 0.5 ± 0.3 nℓ/ℓ. To the west of the seep area, it is not possible to distinguish clearly the ambient levels of ethane from those brought about by the influence of the seep itself, although it is likely not to differ significantly from that observed to the east.

The concentration of ethene in the bottom waters is significantly higher than in the overlying surface waters (Cline, 1976). Concentrations of ethene increase toward the west along the axis of Norton Sound and generally correlates with the distribution of salinity and temperature (Cline, 1976). The range in concentrations of ethene is from 4 nℓ/ℓ near St. Lawrence Island to less than 1 nℓ/ℓ north of Stuart Island at the eastern extremity of Norton Sound and negatively correlates with the near-bottom distribution of methane (see Figure 4-31).

4.53 Propane and Propene

The concentration of propane within 5 m of the bottom is shown in Figure 4-35. As was evident from the near-bottom distribution of ethane, the concentration of propane also is anomalously high in the presumed seep area south of Nome. Maximum concentration observed was 2.5 nℓ/ℓ, a value approximately 12-fold above the ambient levels observed toward the south 0.2 nℓ/ℓ). The "puff" nature of the dispersion plume may represent multiple sources or the episodic nature of the seep itself. Because the sampling was not synoptic in time, we

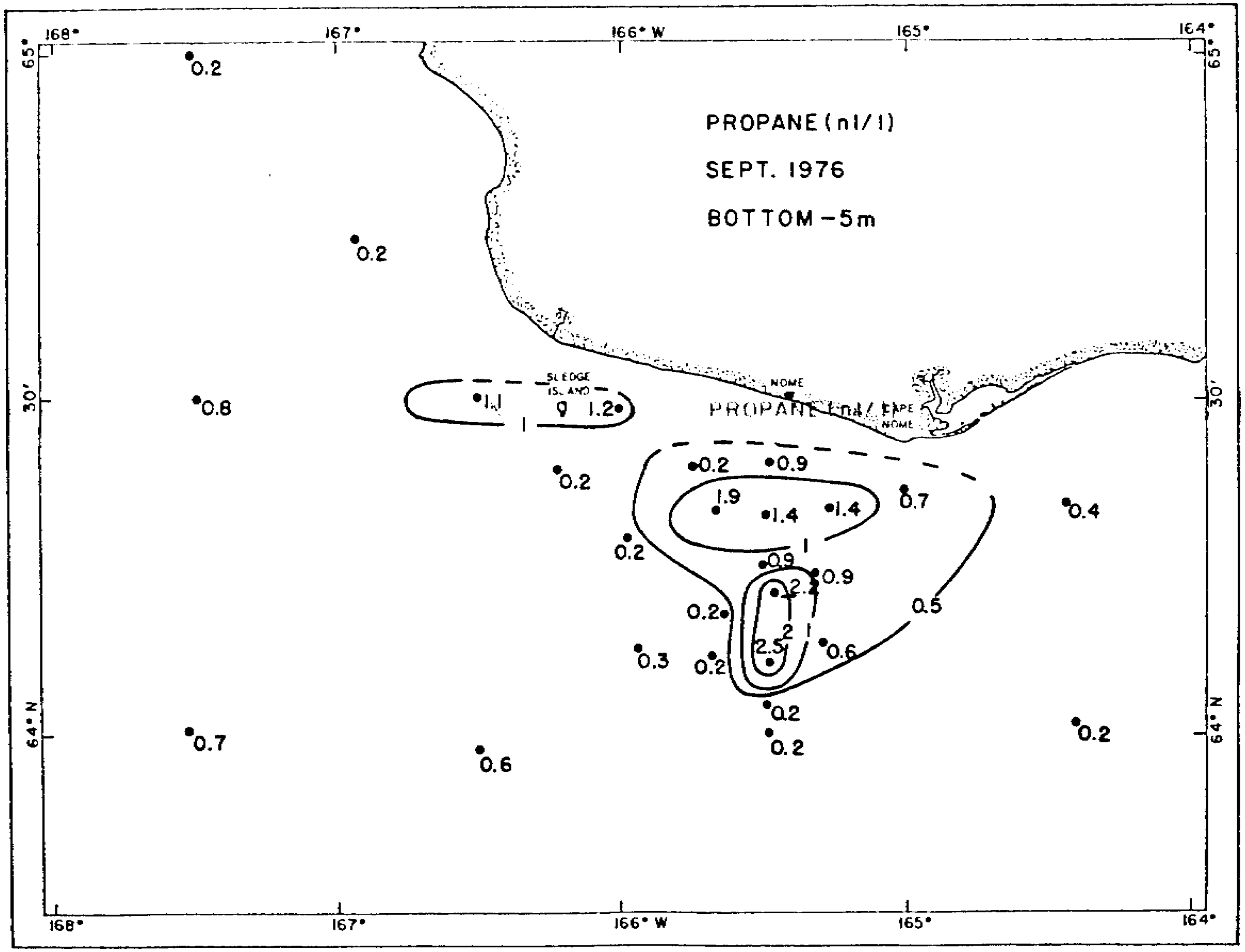

Figure 4-35. Areal distribution of propane within 5 m of the bottom in the vicinity of the submarine gas seep. Concentrations are expressed in nℓ/ℓ (STP).

can not be sure of the reason for the plume characteristics. The drift of the plume is in accord with general circulation of the region.

The surface distributions of propane and propene were uniform spatially, averaging 0.2 ± 0.1 nℓ/ℓ and 0.5 ± 0.2 nℓ/ℓ respectively. As is normally observed, the concentration of propene exceeds that of propane.

4.54 Butanes and Higher Homologs

The concentrations of iso- and n-butanes over most of the region were at or below the detection limit (.05 nℓ/ℓ), except in the region of the seep. In this location, both butanes reached maximum concentrations of 0.5 nℓ/ℓ at the point where maxima also were observed in the concentrations of ethane and propane. The distribution of the plume is identical to that observed for the aforementioned hydrocarbons. The ratio of iso-butane to n-butane is approximately 1 in the plume.

There was also evidence of C_5 hydrocarbons in the seep area. Several of the chromatograms were allowed to "run" beyond the normal elution time of the C_4's to scrutinize for the presence of higher molecular weight hydrocarbons (i.e., pentanes, hexanes, and possibly low molecular weight aromatics). At two stations where evidence indicated the presence of unusually high concentrations of ethane and propane, a complex, partially unresolved mixture was evident on the chromatogram at the retention times of the C_5's. These results were not quantified as neither the extraction procedure nor the chromatographic analysis is quantitative for the heavier hydrocarbons.

4.6 Southeastern Chukchi Sea

A survey of the distributions of low molecular weight hydrocarbons was carried out in September of 1976. The sampling grid is shown in Figure 4-36.

The results of this cruise have been discussed elsewhere (Cline, 1976), but the salient features will be included here for completeness.

4.61 Methane

The areal distributions of methane in nℓ/ℓ (STP) are shown for the surface layers (Figure 4-37) and 5 meters from the bottom (Figure 5-18). Surface concentrations of methane (excluding Kotzebue Sound proper) are rather uniform, ranging from a low of 100 nℓ/ℓ at the northern extremity of the survey grid to a high of 215 nℓ/ℓ near the coast northwest of Kotzebue. The average concentration was 130 ± 25 nℓ/ℓ, or a factor 2.5 above equilibrium saturation. In contrast, surface concentrations within inner Kotzebue Sound are significantly higher (338 ± 110 nℓ/ℓ), primarily due to vertical mixing of methane-rich water from below.

The distribution of methane in the near-bottom waters is highly variable, reflecting both localized and advective sources. An example of the former is shown in Kotzebue Sound where the concentration of methane exceeds 3000 nℓ/ℓ. At the time of these observations, the water column in Kotzebue Sound was highly stratified with warm low salinity water at the surface ($S = 25^{o}/oo$, $T = 9^{o}C$) and cold, relatively high salinity water at the bottom ($S = 28^{o}/oo$, $T < 1^{o}C$). Methane released from reducing bottom sediments was apparently trapped below the resulting pycnocline. It will be shown in subsequent sections that these elevated concentrations of methane were not supported by similarily high levels of other LMWH (e.g., ethane, ethene, etc.), suggesting a biogenic origin.

The plume of methane-rich water emerging from the western Chikchi Sea appears to be an artifact of circulation. It correlates well with the intrusion of relatively cold water (< $4^{o}C$) from the Siberian Shelf (Cline, 1976).

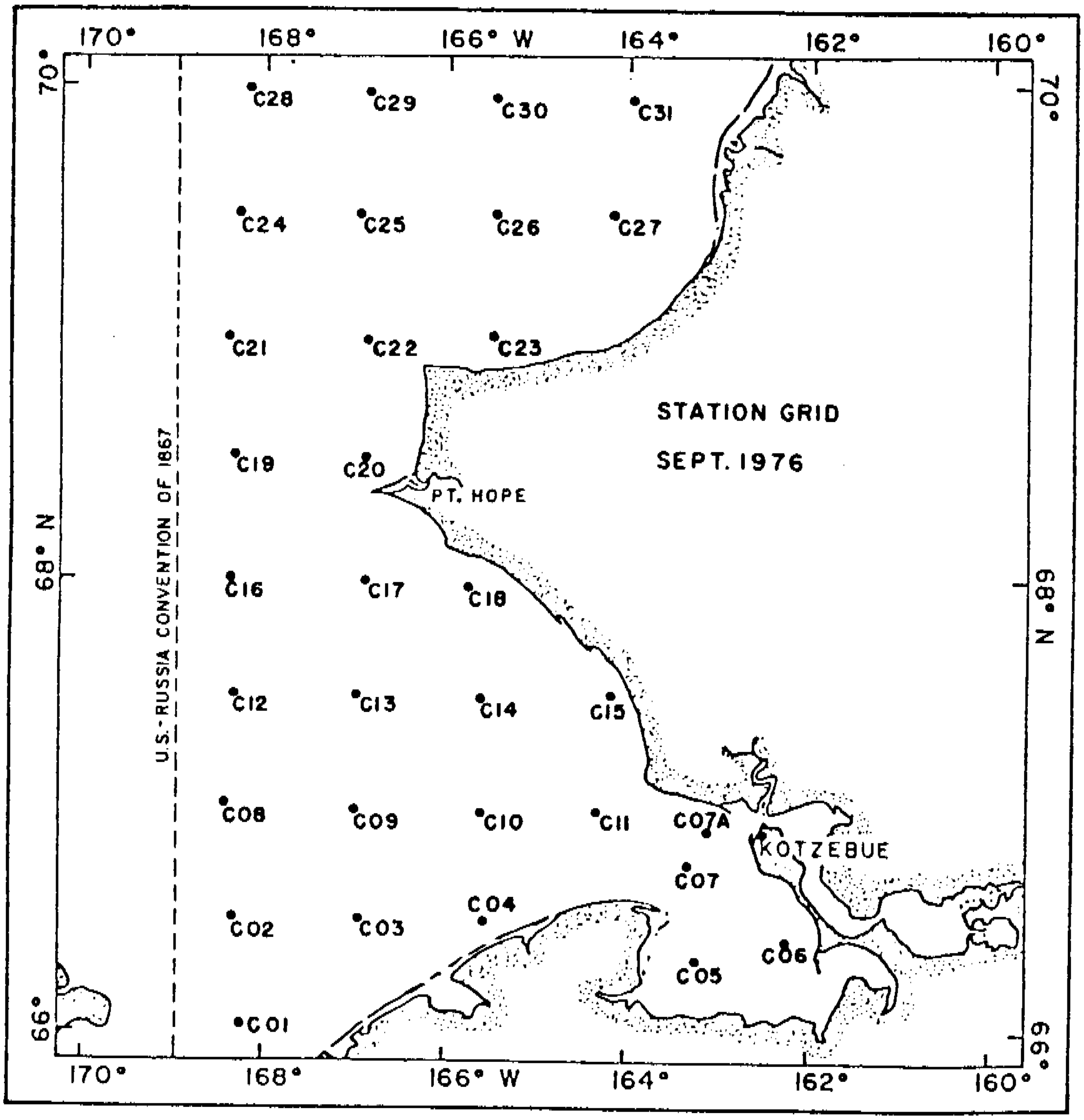

Figure 4-36. Station locations in southeastern Chukchi Sea, including Kotzebue Sound.

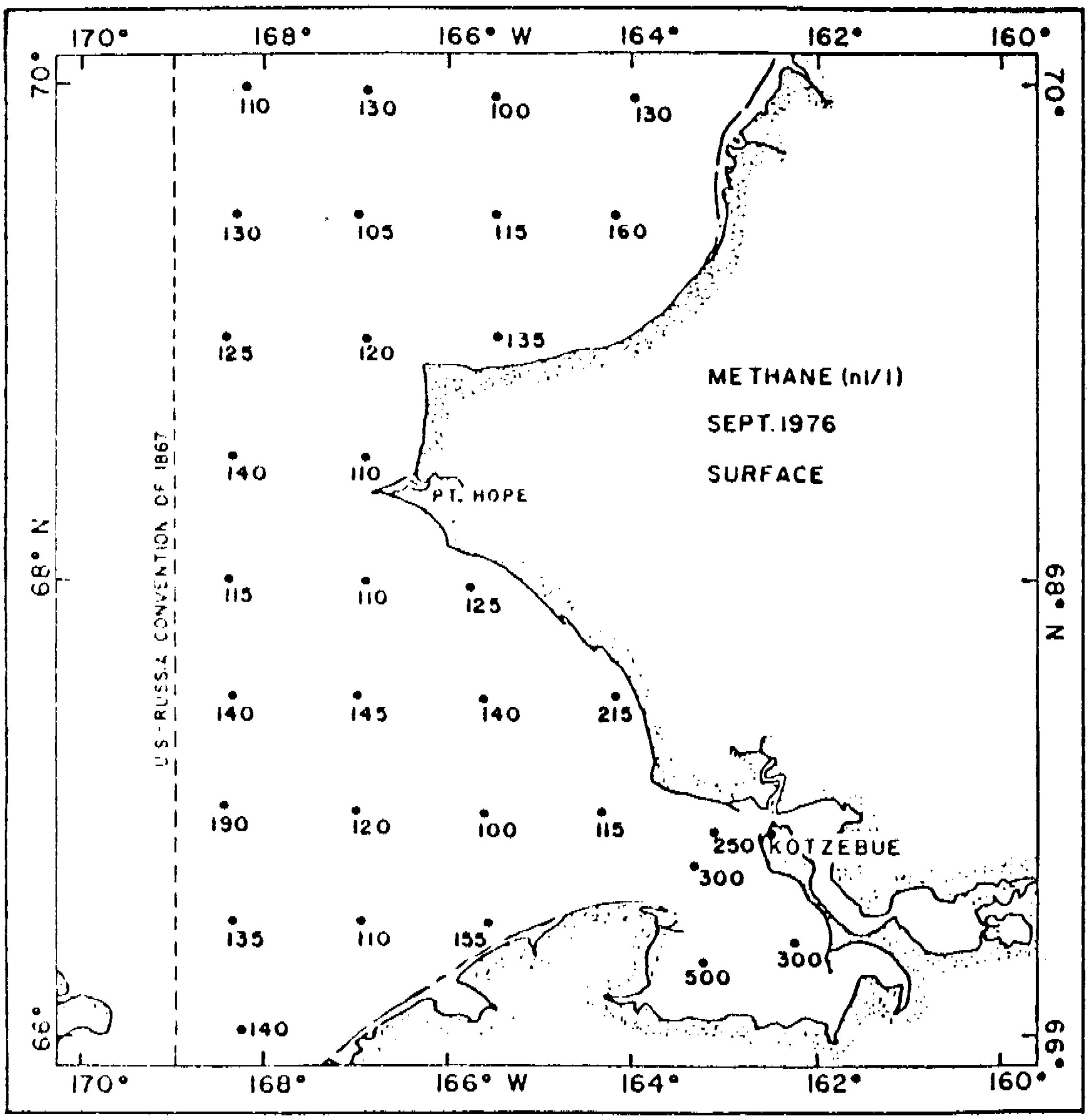

Figure 4-37. Areal surface distribution of methane in Sept. 1976. Concentrations are expressed in nℓ/ℓ (STP).

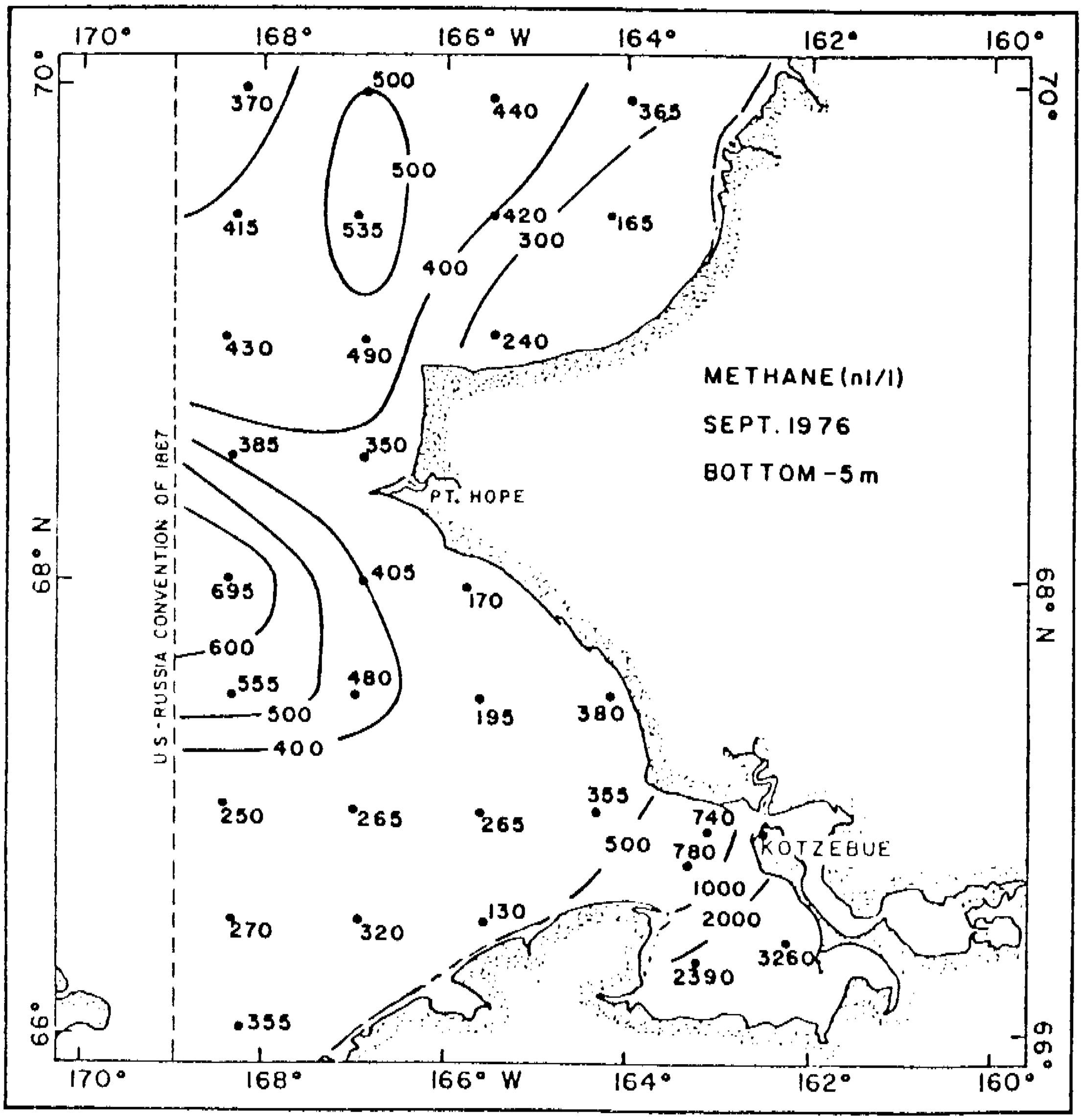

Figure 4-38. Areal distribution of methane within 5 m of the bottom in Sept. 1976. Concentrations are expressed in nℓ/ℓ (STP).

The average near-bottom concentration of methane (excluding Kotzebue Sound) is 360 ± 130 nℓ/ℓ. These levels of methane are rather typical for shelf waters over the OCS of Alaska based on our previous measurements.

4.62 Ethane and Ethene

The surface distributions of ethane and ethene are shown in Figures 4-39 and 4-40. Both components reveal little spatial variability, suggesting the absence of well-defined localized sources or sinks. The average ethane concentration in the surface layers is 0.6 ± 0.2 nℓ/ℓ and compares favorably with our observations in Bristol Bay and NEGOA.

Surface concentrations of ethene are systematically higher than those of ethane, reflecting modest biological activity. The average is 1.2 ± 0.4 nℓ/ℓ, or a factor of two above the average concentration of ethane.

Near-bottom concentrations of ethane and ethene are shown in Figures 4-41 and 4-42. Both of these components correlate strongly with the near-bottom temperature and salinity distributions, suggesting that circulation is the dominant factor.

Inspection of Figures 4-41 and 4-42 reveals that the ethane/ethene ratio approaches 1 near the western boundary of the grid. Although no definitive statement can be made about the origin of these hydrocarbons, the anomalous ethane/ethene ratio suggests a petrogenic contribution. If this speculation is true, the source exists to the west along the northern coast of Siberia. Normal dilution with ethane-deficient waters in the survey area would bias the ethane/ethene ratio to lower values.

An alternate explanation is that the ethane-rich water is also deficient in oxygen. The assemblage of hydrocarbons produced biogenically under oxygen deficient conditions is not well understood, but unlike the situation in

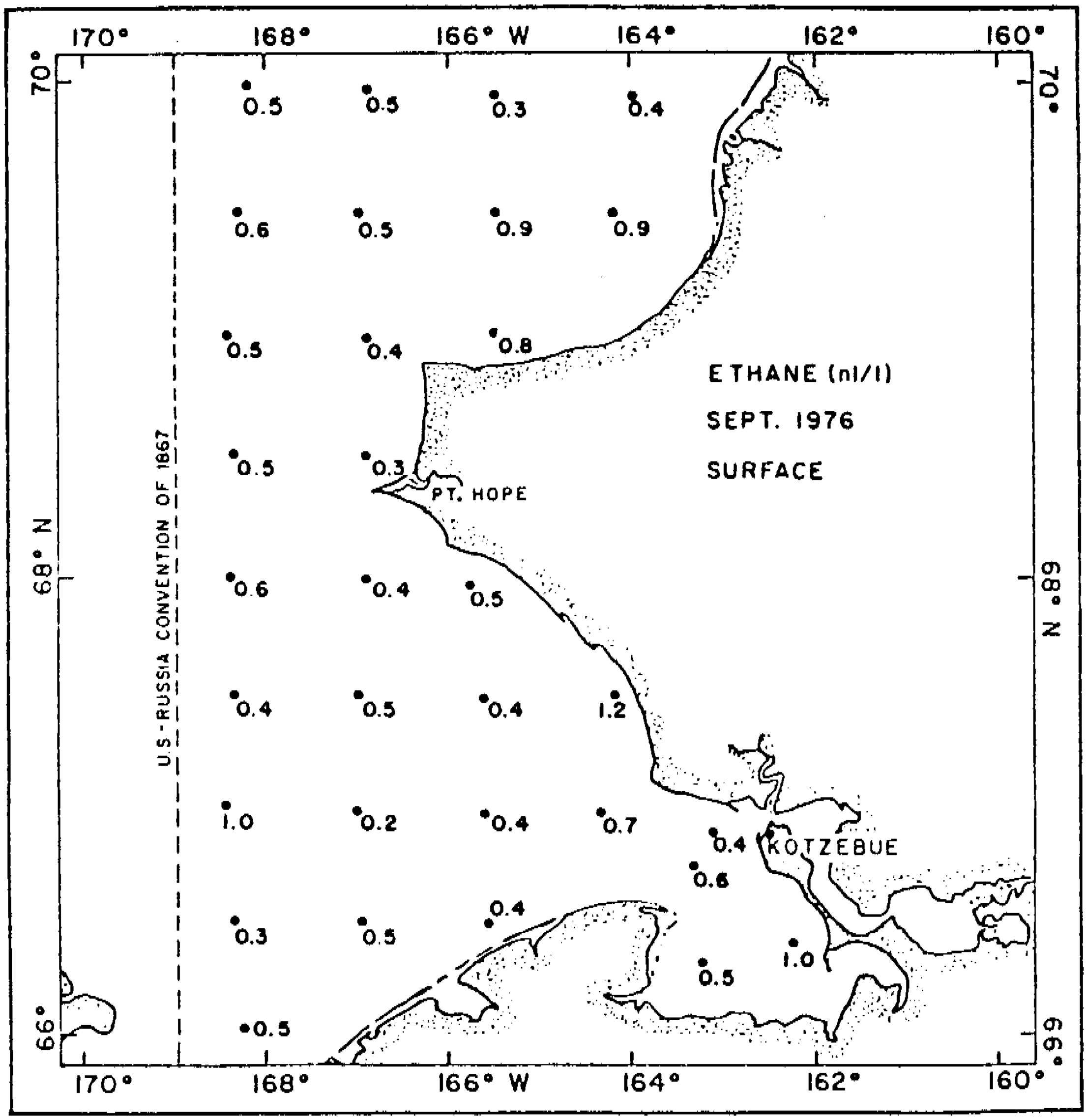

Figure 4-39. Areal surface distribution of ethane in Sept. 1976. Concentrations are expressed in nℓ/ℓ (STP).

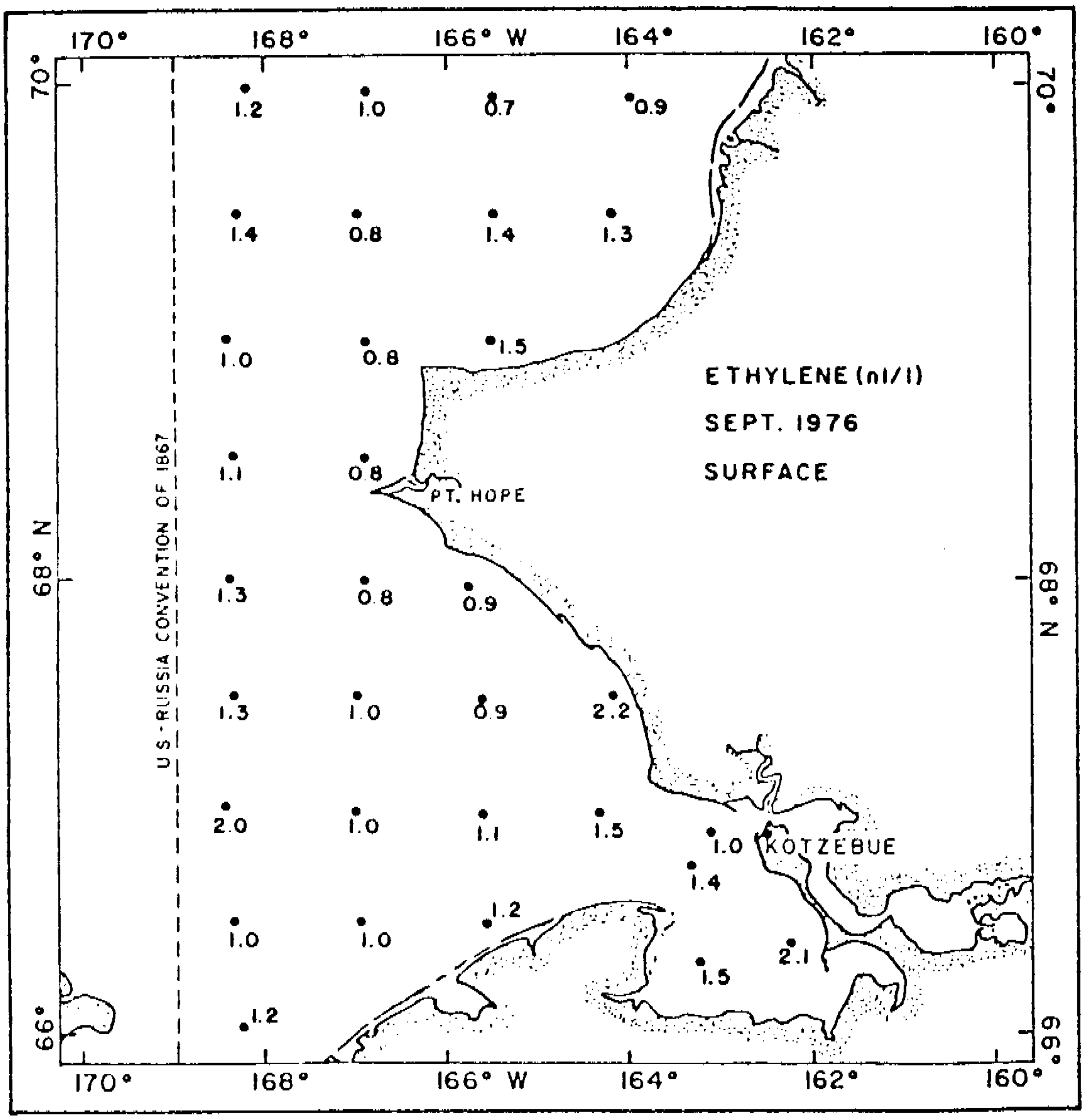

Figure 4-40. Areal surface distribution of ethene in Sept. 1976. Concentrations are given in nℓ/ℓ (STP).

well-aerated waters, ethane may be produced in abundance under low oxygen tensions. In a study of the distributions of LMWH in recent sediments taken from the Black Sea, an anoxic basin, Weber and Maximov (1976) found the concentration of ethane to exceed that of ethene in the pore waters. In those samples where a measurable quantity of ethene was found, the ethane/ethene ratio varied between 3 and 8. It has been suggested that small localized basins in the Siberian Shelf go anoxic seasonally (K. Aogaard, University of Washington, personal communication), thus the anomalously high concentrations of ethane shown in Figure 4-41 may have arisen biologically. More information is required on the distribution and abundances of the low molecular weight hydrocarbons produced biologically under reducing conditions.

The average near-bottom concentration of ethane and ethene is 1.1 ± 0.6 $n\ell/\ell$ and 2.6 ± 1 $n\ell/\ell$. On the average, the concentration of ethene exceeds that of ethane by a factor of 2.6. This is in excellent agreement with our findings in both the Gulf of Alaska and southeastern Bering Sea, where the factor ranges from 2 to 3. These results are biased in that the plume of C_2-rich water at 68^oN is characterized by unusually high concentrations of ethane relative to ethene.

4.63 Propane and Propene

The surface distribution of propane and propene is depicted in Figures 4-43 and 4-44. As was the case with the surface distributions of the C_2 aliphatics, no localized sources or sinks were observed. The average surface concentrations of ethane and ethene are 0.2 ± 0.1 $n\ell/\ell$ and 0.4 ± 0.2 $n\ell/\ell$. Concentrations of propene less than .05 $n\ell/\ell$ are reflected as zero (Figure 4-44). Propane, not unlike that of ethane and ethene, was correlated with near-bottom circulation. Average near-bottom concentrations of propane and propene were 0.6 ± 0.3 $n\ell/\ell$ and 0.6 ± 0.2 $n\ell/\ell$, respectively. These average values are

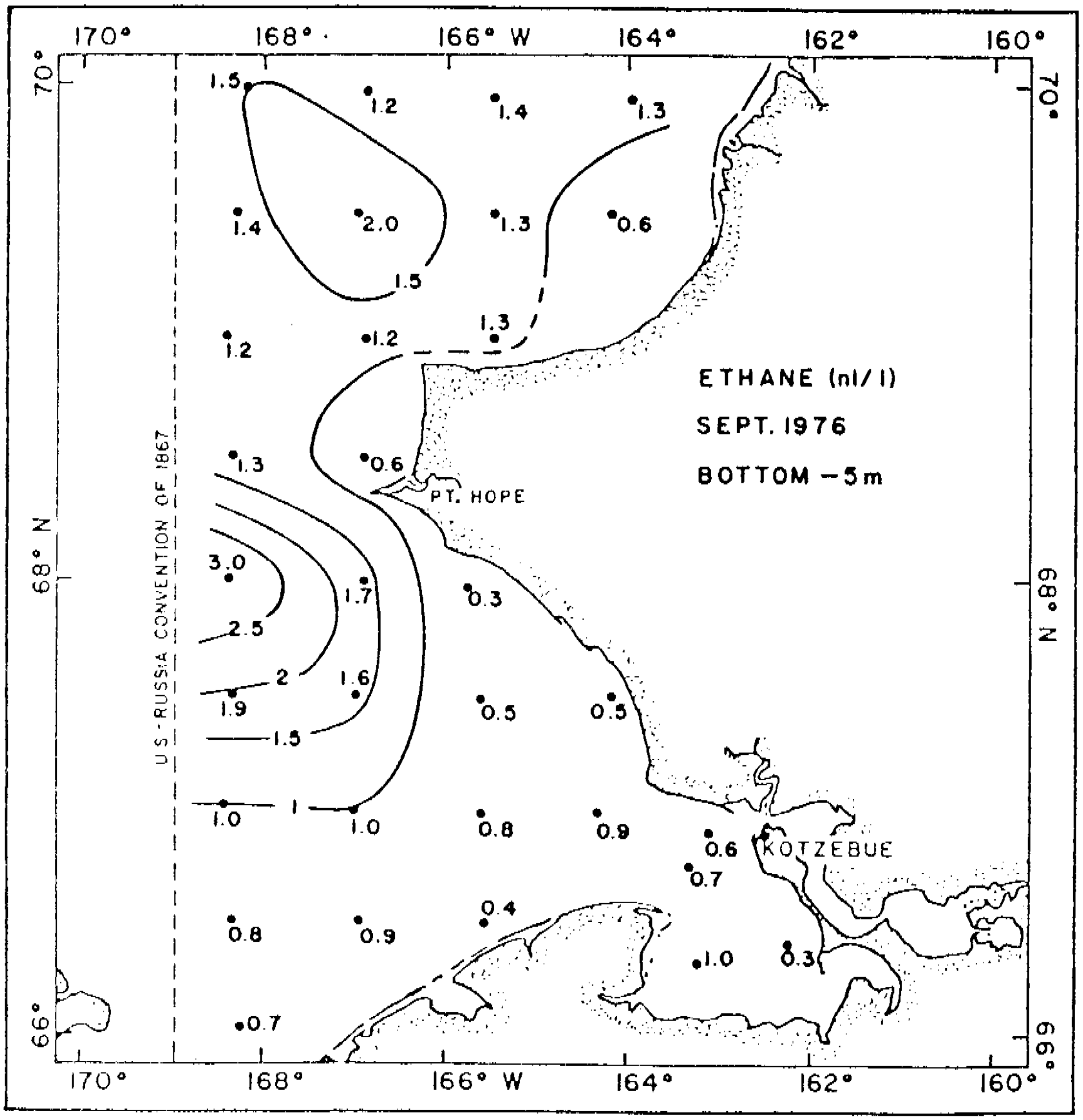

Figure 4-41. Areal distribution of ethane within 5 m of the bottom in Sept. 1976. Concentrations are expressed in nℓ/ℓ (STP).

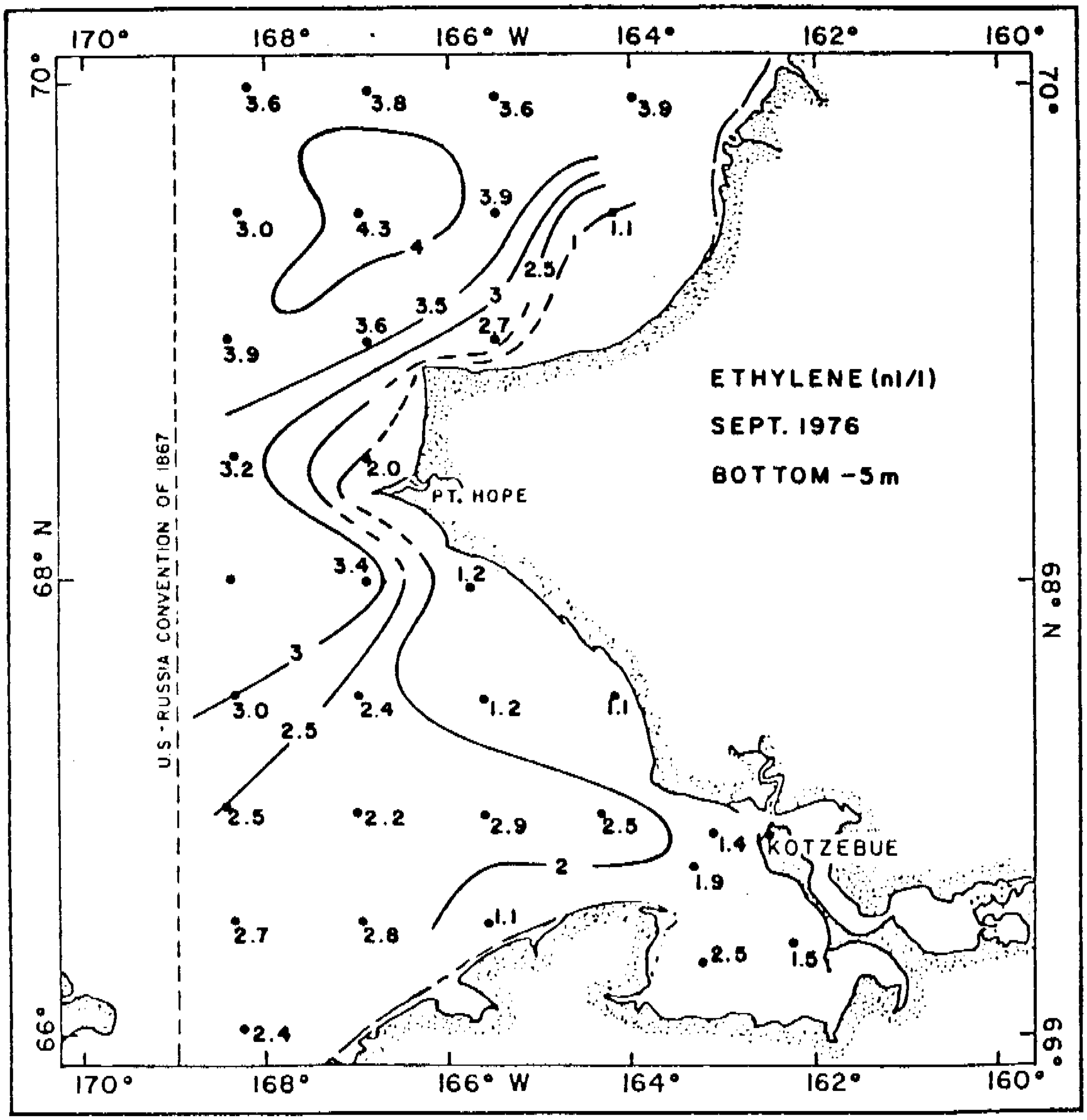

Figure 4-42. Areal distribution of ethene within 5 m of the bottom in Sept. 1976. Concentrations are expressed in nℓ/ℓ (STP).

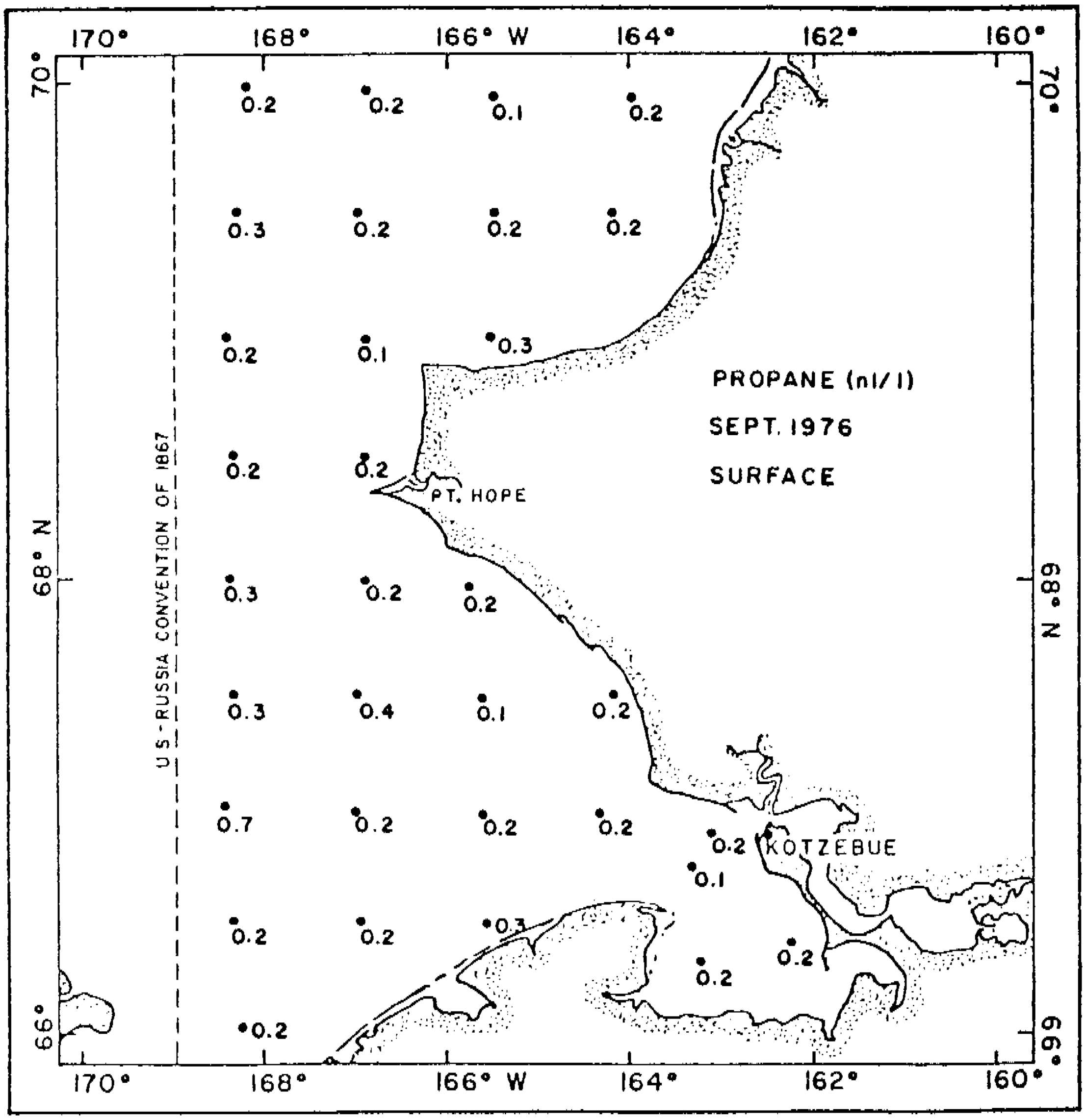

Figure 4-43. Areal surface distribution of propane in Sept. 1976. Concentrations are expressed in nℓ/ℓ (STP).

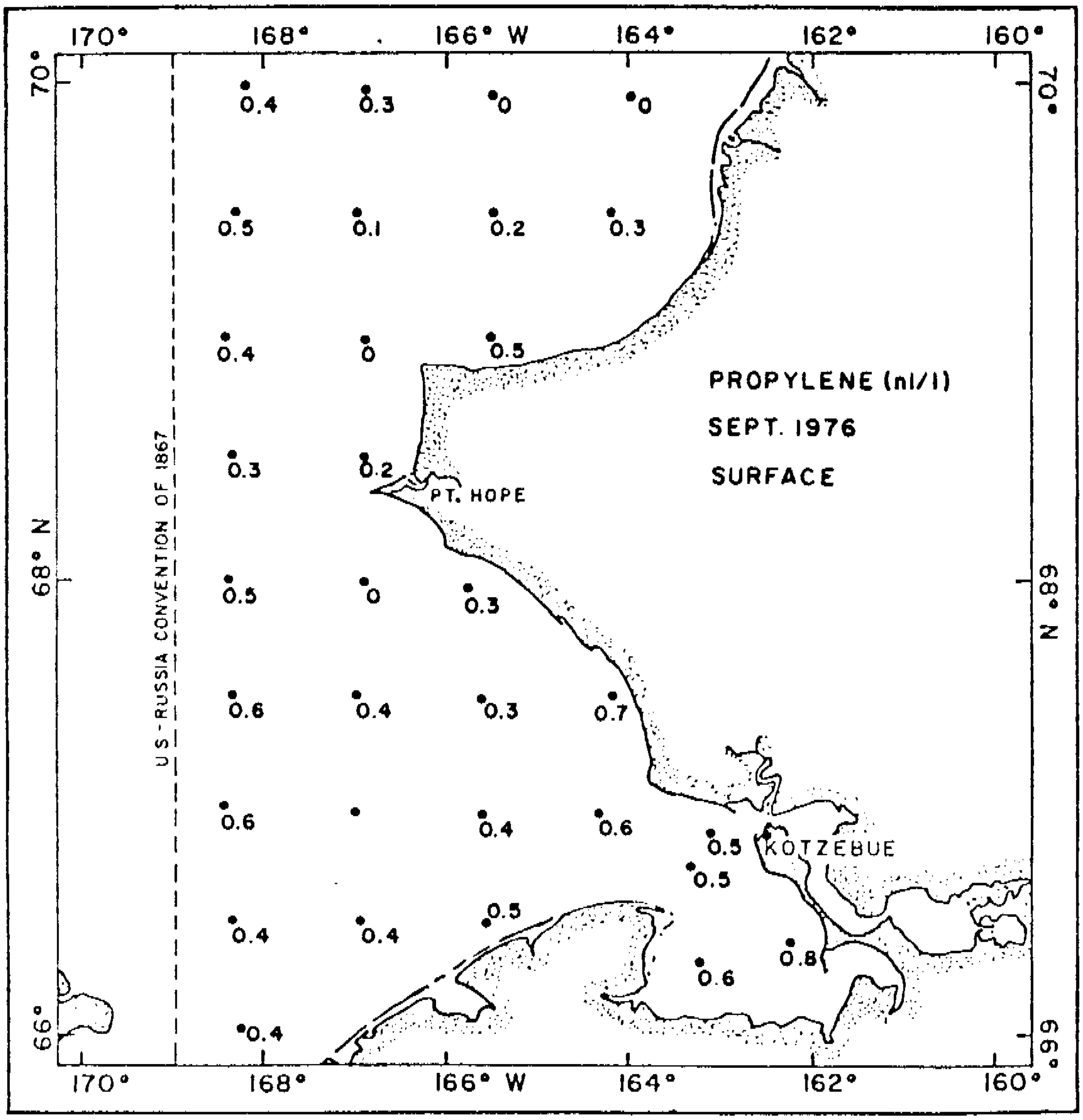

Figure 4-44. Areal surface distribution of propene in Sept. 1976. Concentrations are expressed in nℓ/ℓ (STP).

rather typical for near-bottom Alaskan shelf waters with the exception of the plume of propane-rich water emerging from the western Chukchi Sea (Cline, 1976). In this water mass the concentration of propane exceeded propene by a factor of two, quite anomalous compared to other regions studied (see section 4.62).

4.64 Butanes

The concentrations of iso- and n-butanes were uniformly below 0.1 nℓ/ℓ. Because of inherent low-level contamination of water samples, the uncertainty in the concentrations of butane below the 0.1 nℓ/ℓ level is very large. In most cases, the concentration of C_4 aliphatics, after correction for the carrier blank, was below the detection limit of 0.05 nℓ/ℓ.

4.7 Kodiak Island Shelf

A survey of the distribution of low molecular weight hydrocarbons was carried out in July of 1977 in conjunction with the summer visit to Cook Inlet (see section 4.2). The observational program was conducted aboard the R/V ACONA; some of the stations were dropped because of inclement weather. The four stations lost were at the southern extremity of the sampling grid. The survey grid is shown in Figure 4-45.

4.71 Methane

Surface concentrations were the highest along the southern coast (200-300 nℓ/ℓ) with an elongate distribution extending northward. This feature may be related to biological activity or the result of a countercurrent along the inner shelf. Range of values encountered was approximately 100 to 350 nℓ, lowest values found over Portlock Bank.

The distribution of methane near the bottom is illustrated in Figure 4-46. As was the case in the surface layers the highest concentrations were found

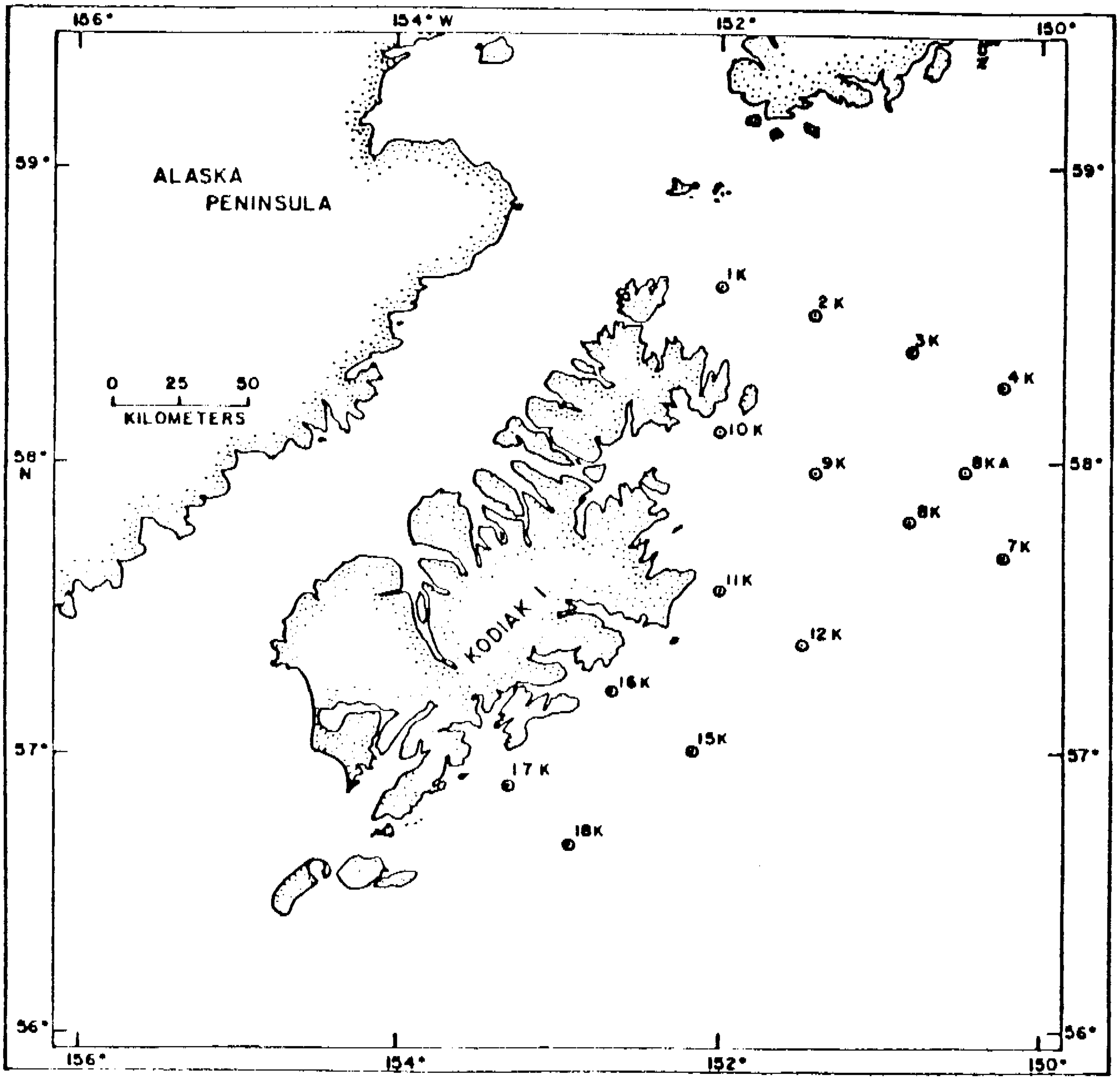

Figure 4-45. Station locations occupied on the Kodiak Shelf in July 1977. Station 8KA was located near a test drilling platform.

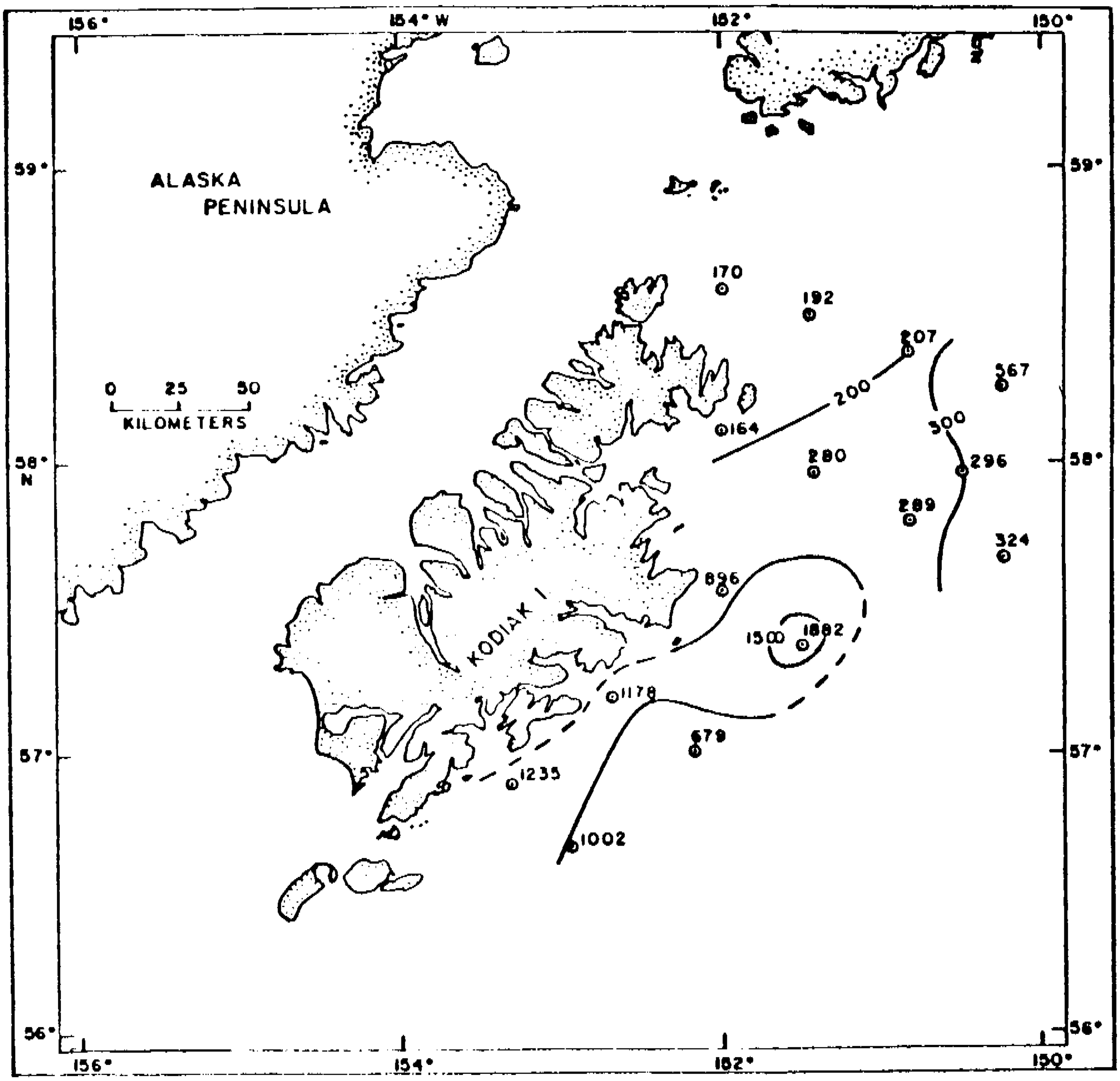

Figure 4-46. Areal distribution of methane within 5 m of the bottom in July 1977. Concentrations are expressed in nℓ/ℓ (STP).

along the southern coast, forming an elongate distribution toward the north. The highest value (1880 nℓ/ℓ) was observed at station 12 located over the Chinick Trough. The sediment texture is apparently sand-silt (75%/25%) at this location. Concentrations of methane at this level over a high energy shelf environment are unusual and presumably represent strong biological activity. The high concentrations observed farther to the south occur over Kiliuda Trough, whose sediments are characterized by a relatively high concentration of clay-size material. In general, the finer-grained material would be expected to contain higher concentrations of organic matter to support microbial methane production. As noted above, the lowest methane concentrations (150-300 nℓ/ℓ) were found in the region of Portlock Bank, where coarse sands and gravels prevail. Minimal methane production would be expected under these conditions.

4.72 Ethane and Ethene

The surface distribution of ethane is shown in Figure 4-47. The pattern in the surface layers is similar to that observed for methane, although the range is much smaller. Concentrations of ethane in the waters along the southern coast reach a maximum of 0.9 nℓ/ℓ. These relatively large values are probably related to the concomitant release of ethene (see below). Lowest values occur in the north, where minimum concentrations observed were 0.4 nℓ/ℓ.

Near the bottom the ethane concentration varied from 0.2 nℓ/ℓ to 0.8 nℓ/ℓ, the average was 0.5 ± 0.2 nℓ/ℓ. Again the highest concentrations are observed near the coast (0.6-0.8 nℓ/ℓ) with a general decrease offshore. The concentration range for the deeper shelf waters is 0.2-0.8 nℓ/ℓ. At station 12, the concentration of ethane near the botoom was only 0.7 nℓ/ℓ. This suggests that the high methane value observed at this station was of biogenic origin.(Figure 4-46).

The concentration of ethene was uniformly high in the surface shelf waters as indicated in Figure 4-48. Ethene concentrations ranged from lows of 3.2 nℓ/ℓ

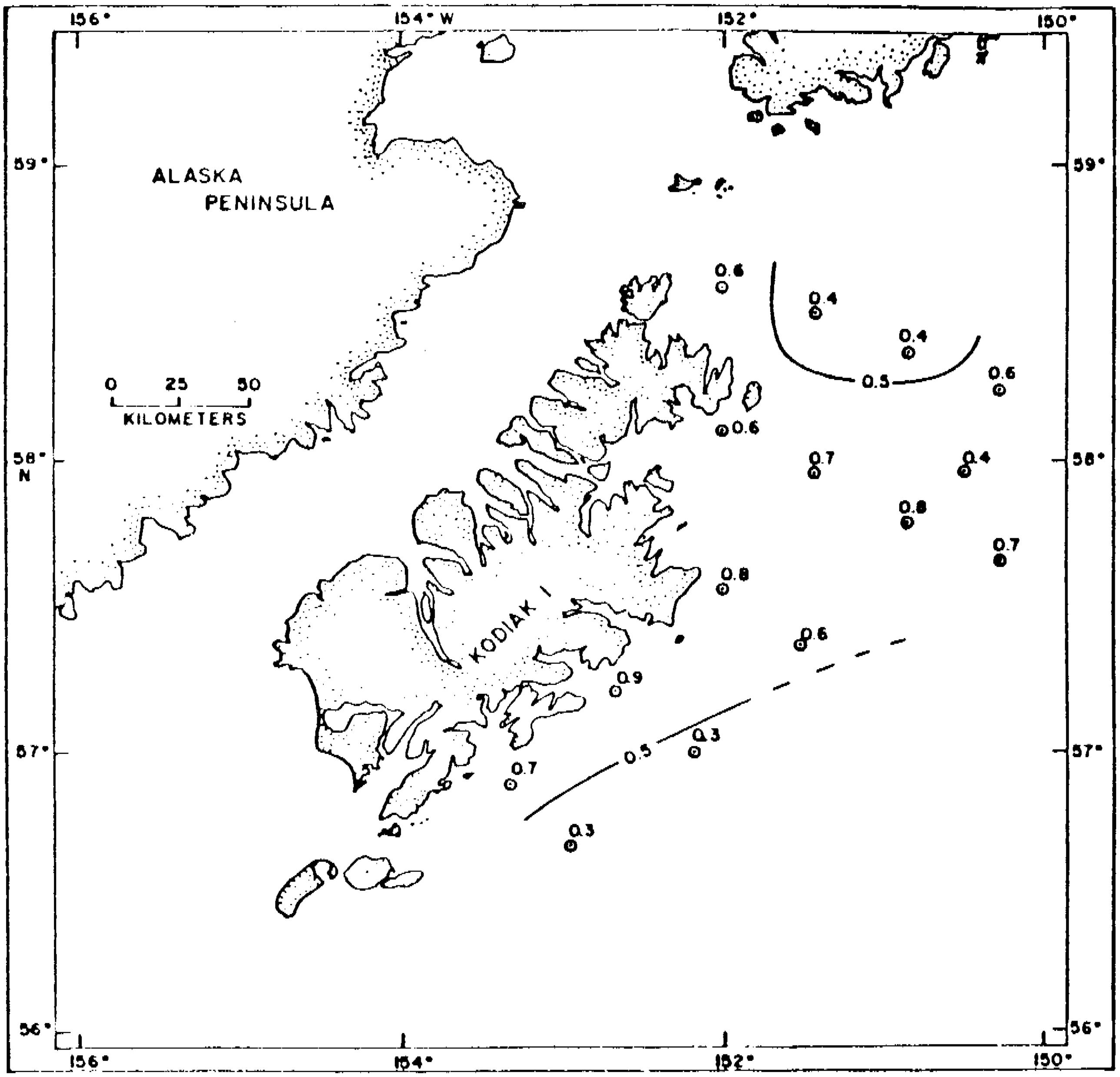

Figure 4-47. Areal surface distribution of ethane in July 1977. Concentrations are expressed in nℓ/ℓ (STP).

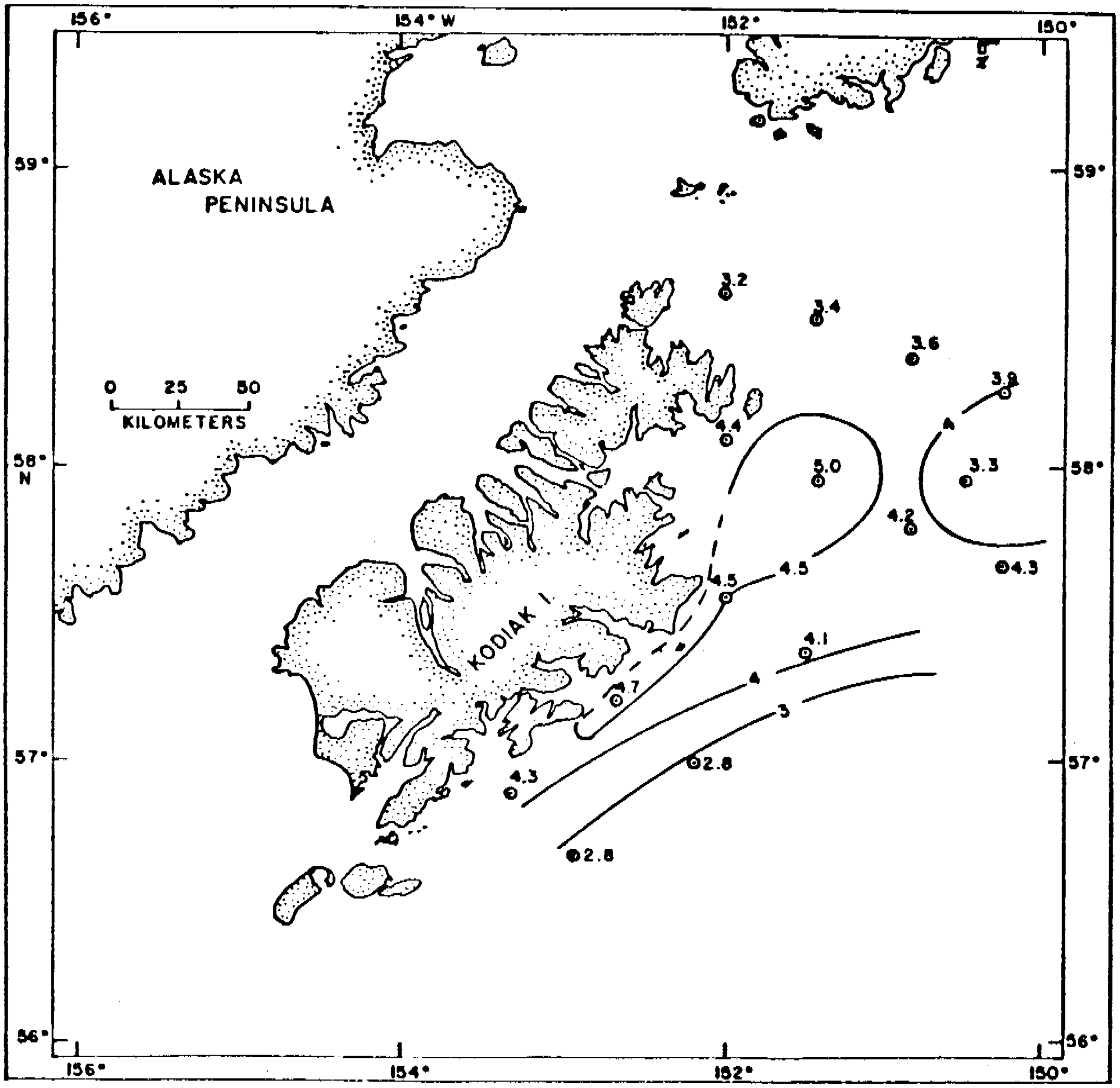

Figure 4-48. Areal surface distribution of ethene in July 1977. Concentrations are expressed in nℓ/ℓ (STP).

in the north to a high of 5 nℓ/ℓ off Marmot Bay. As shown earlier, the high concentrations extend south along the coast of Sitkalidak Island. The distribution of ethene appears to be controlled by primary productivity of processes related to it. The aforementioned elevated concentrations of ethane observed in the surface layers near the coast are presumably related oxidatively to the production rate of ethene. This has yet to be shown however.

The highest concentration of ethane observed near the bottom was 3.4 nℓ/ℓ found over Portlock Bank (Cline, 1976). High concentrations were also found near the coast (2.0-2.4 nℓ/ℓ) with lesser values observed offshore (< 1.5 nℓ/ℓ).

4.73 Propane and Propene

The surface distribution of propane is reflected in Figure 4-49. Near-shore values range from 0.5 to 0.8 nℓ/ℓ; offshore they typically vary between 0.3 to 0.5 nℓ/ℓ. The average surface concentration was 0.5 ± 0.2 nℓ/ℓ.

Less horizontal structure in the distribution of propane was evident in the near-bottom waters. Concentrations north of Afognak Island were 0.1 to 0.3 nℓ/ℓ; along the coast toward the south the maximum concentration of propane observed was 0.5 nℓ/ℓ.(Cline, 1976).

Distributions of propene are not shown because they are quite similar to those found for ethene. This is not surprising since presumably they are generically related. Surface concentrations ranged form 2 nℓ/ℓ to a low of 0.8 nℓ/ℓ. Near-bottom concentrations were significantly lower, ranging from trace amounts (< .05 nℓ/ℓ) to levels near 1 nℓ/ℓ.

4.74 Butanes

The concentration of iso- and n-butane was everywhere equal to or less than the detection limit of 0.05 nℓ/ℓ.

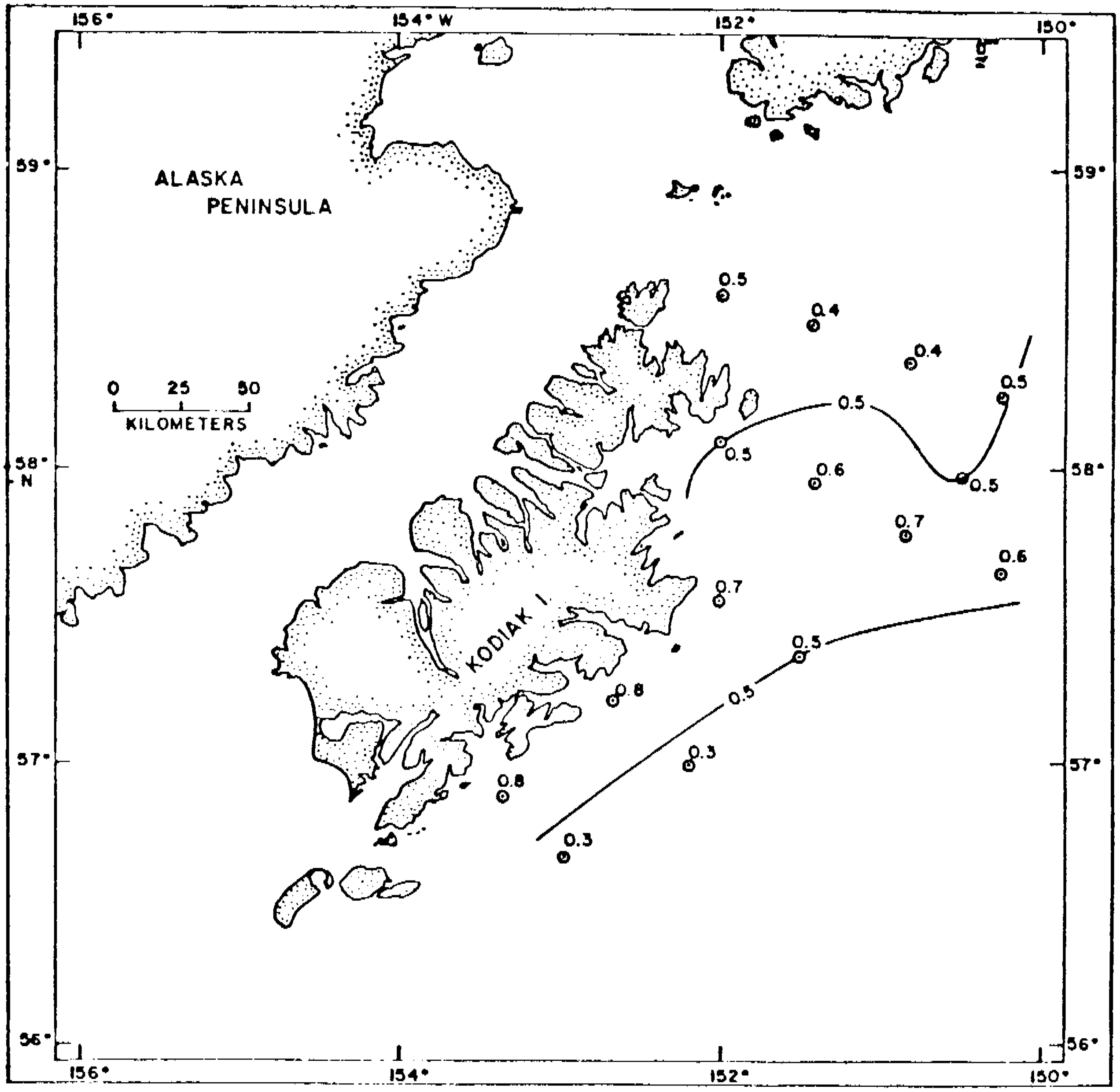

Figure 4-49. Areal surface distribution of propane in July 1977. Concentrations are expressed in nℓ/ℓ (STP).

5. DISCUSSION

5.1 Average Conditions

The seasonal and spatial distributions of the low molecular weight aliphatics methane, ethane, ethene, propane, propene, iso- and n-butanes have been evaluated in several potential lease areas of the Alaskan Shelf. Typical concentration ranges observed in near-bottom waters are shown in Table 5-1. The table is biased in that it does not contain seasonal information for all areas, although a cursory examination of Table 5-1 shows remarkable similarity between various areas, regardless of season. The most severe discrepencies may occur in areas such as Norton Sound and Chukchi Sea where total ice cover is prevalent during winter. In the near absence of primary production and attendant low light levels, the abundance of ethene and propene could deviate radically from the average values shown here. Ice cover also would radically reduce air-sea exchange, affecting the ethane/ethene ratio.

The information provided in Table 5-1 reflects the expected ambient concentrations of the low molecular weight hydrocarbons in the various OCS areas studied to date. In the event of a spill, well blowout, or chronic leakage, these abundances and ratios provide a useful measure of typical ambient conditions. Expected trends and departures from these conditions based on previous studies in Norton Sound and Cook Inlet will be discussed in section 5.3 below. Before preceeding with a discussion of useful petrogenic indicators as gleaned from our Alaskan studies, a brief comparison of these data with other marine areas will be made.

5.2 Oceanic Distributions of LMWH.

In the early years of this decade, considerable interest was generated into the distribution and abundance of the low molecular weight aliphatics,

Table 5-1 Typical seasonal range of hydrocarbon concentrations observed in the near-bottom waters of the OCS areas investigated. Unusually high concentrations occurring singly have not been included in the ranges. Number of observation 1 periods in each survey area is given in parentheses.

Region	NEGOA (3)	LCI[2] (2)	Bristol Bay (2)	Norton Sound[1] (1)	Chukchi Sea (1)	Kodiak Shelf (1)
Component	nℓ/ℓ (STP)					
Methane	100-1500	100-900	60-600	200-2000[3]	200-3000[3]	150-2000
Ethane	0.2-1.0	0.3-0.8	0.5-2.0	0.3-1.3	0.3-3.0	0.2-0.8
Ethene	0.5-3.0	0.5-5.0	0.5-5.0	0.3-4.0	1-4.0	0.5-3.5
Propane	0.2-0.6	0.1-0.6	0.2-0.7	0.2-0.5	0.2-1.3	0.1-0.5
Propene	0.2-0.6	0.2-0.8	0.2-2.0	0.2-0.9	0.3-0.8	0.8-2.0
Isobutane	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05
n-butane	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05
$C_{2:0}/C_{2:1}$	< 0.5	≤ 0.5	< 1	< 0.5	< 1	< 0.5

[1] The range does not include observations from region of gas seep.

[2] The range does not include observations from the region north of Kalgin Island.

[3] The upper value is the result of strong thermal stratification that existed at the time of the measurements (see text).

methane being the predominant component of focus (Linnenbom and Swinnerton, 1970; Frank et al., 1970; Lamontagne et al., 1971; Lamontagne et al., 1973; Brooks and Sachett, 1973; and the references cited in these publications). Much of this work was facilitated by the rapid gas extraction and GC analyses that was developed and perfected by Swinnerton and Linnenbom (1967).

In late 1972, Lamontagne et al. (1973) analyzed surface ocean samples between Long Beach California and McMurdo Station, Antarctica. Surface concentrations of methane varied between 40-70 nℓ/ℓ; the highest values were found at high latitudes in the southern ocean. Concurrent with these measurements, the atmospheric partial pressure of methane was also determined (1.36-1.43 ppmv). If we assume a mean surface salinity of 34°/oo, the equilibrium concentration of methane at 25°C, 10°, and 0°C would be 35 nℓ/ℓ, 48 nℓ/ℓ, and 63 nℓ/ℓ respectively, assuming a mean mixing ratio of 1.4 ppmv (Yamamoto et al., 1976). Since the aforementioned values overlap extensively with the solubility estimates, we conclude that the open Pacific Ocean is very near saturation with respect to methane. Data reported from other oceanic areas reflects the same situation, that is, open oceanic surface waters are generally near saturations with respect to the partial pressure of methane in the atmosphere (Swinnerton and Lamontagne, 1974).

With the exception of the northeast Gulf of Alaska, our studies have been confined to the shallow shelf waters. The lowest concentrations of methane were observed off the shelf, where minimum surface values of 70 nℓ/ℓ were common (Cline, 1977b). Given a mean surface temperature and salinity of 10°C and 32°/oo, the equilbrium concentration would be 50 nℓ/ℓ, representing approximately 40% supersaturation (Yamamoto et al., 1976). It should be borne in mind that these waters are in close proximity to the shelf and would be influenced by it.

Ethane and propane concentrations at the surface in the open Pacific averaged 0.2 nℓ/ℓ and 0.3 nℓ/ℓ (Lamontagne et al., 1973), rather similar to the lower range of concentrations we observed in Alaskan shelf waters (see Table 5-1). In most of the areas investigated, the concentration of ethane in surface waters exceeded that of propane in contrast to the oceanic conditions.

The concentration of ethene in the open Pacific was highly variable in response to regional biological activity. Concentrations ranged from 3-6 nℓ/ℓ (Lamontagne et al., 1973). In view of the fact that these measurements were made between 30°N and 80°S latitude during November and December, the high levels of ethene correspond to the upper concentration ranges we have observed in the Alaskan OCS during the summer months (see Table 5-1). In sharp contrast to these conditions, concentrations of ethene in excess 20 nℓ/ℓ were found in the eastern Strait of Juan de Fuca during August of 1977 (Baker et al., 1978). These high concentrations are apparently the result of high incident radiation and late summer phytoplankton bloom (see Figure 5-1). Only modicum amounts of ethane were found (< 1 nℓ/ℓ).

In the near-shore continental shelf regions, the concentrations of the low molecular weight hydrocarbons are generally higher than those found offshore (Swinnerton and Lamontagne, 1974). This situation may be the result of elevated biological activity or from petrogenic sources, either natural seeps or anthropogenic sources, (Brooks and Sackett, 1973). In numerous surveys of the shelf areas of the Gulf of Mexico, investigators from Texas A & M University have documented the unusual abundance of the higher homologs of methane (see Frank et al., 1970; Brooks and Sackett, 1973; Sackett, 1977; and references contained therein), particularily near production platforms, shipping lanes, points of transfer, and probable subsurface seep structures.

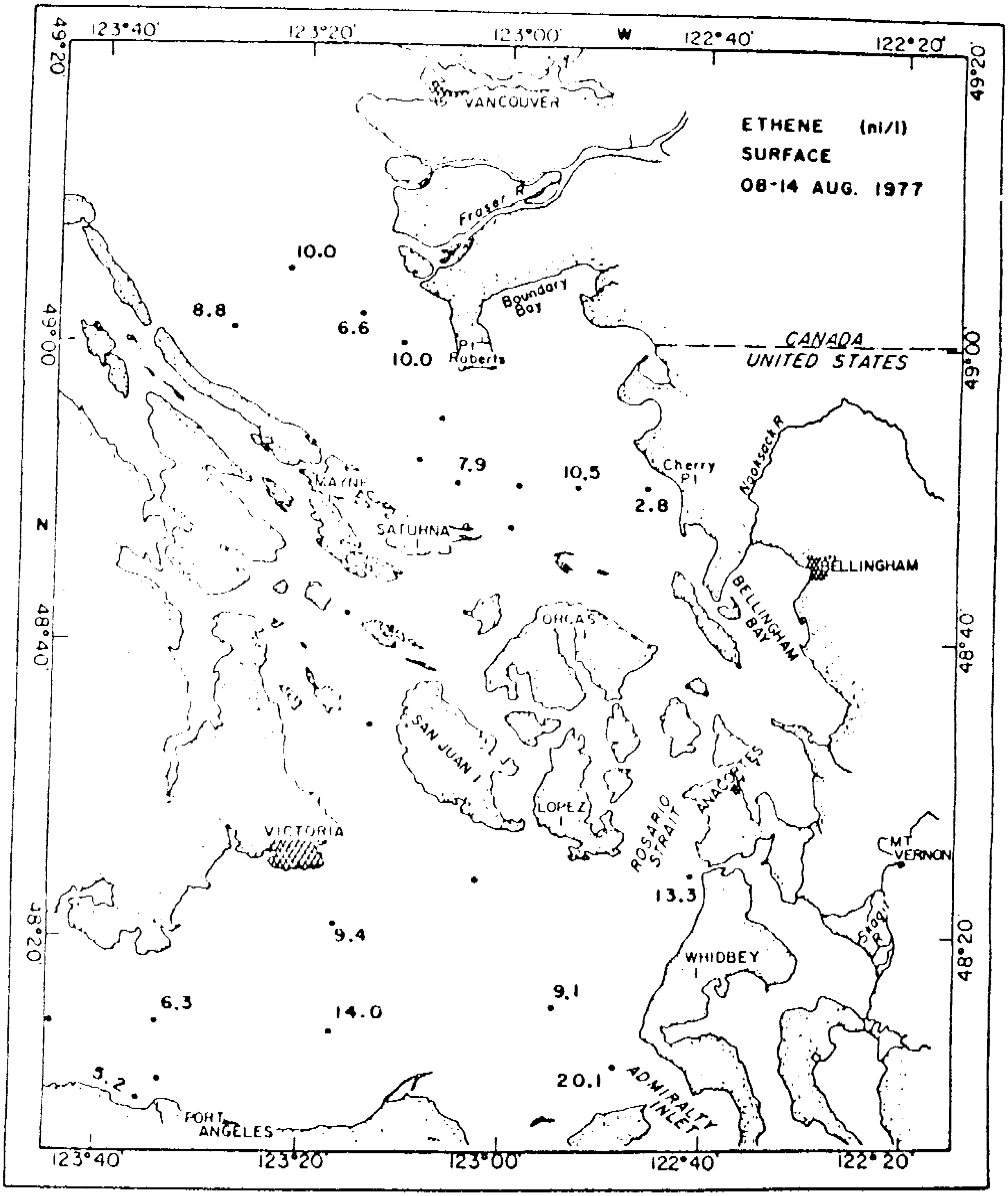

Figure 5-1. Selected surface concentrations of ethene in the waters of northern Puget Sound during early August 1977. Concentrations are expressed in nℓ/ℓ (STP).

Methane concentrations along Louisiana-Texas shelf ranged from 50 nℓ/ℓ to over 2000 nℓ/ℓ (Brooks and Sackett, 1973). More typical values were in the neighborhood of 150-200 nℓ/ℓ, not unlike surface concentrations found in most of the Alaskan OCS areas. Systematically high values were found (~2000 nℓ/ℓ) in Mississippi River estuary, decreasing to near saturation levels offshore (Brooks and Sackett, 1973). Much of the methane observed in the Mississippi River estuary is believed to arise from anacrolic methanogenesis in the organic-rich sediments (Brooks and Sackett, 1973).

Although the surface concentration of methane over the Louisiana and Texas shelf is not unusual relative to Alaskan shelf waters, it is unusually high when compared to the Florida and Mississippi shelves (Brooks and Sackett, 1977). Similarily, the concentrations of ethane, propane, and butanes were found to be unusually high. For example, concentrations of ethane and propane over the Texas shelf were 4 nℓ/ℓ and 6 nℓ/ℓ respectively, whereas butanes locally exceeded 10 nℓ/ℓ. With the exception of the Norton Sound gas seep and the region of Upper Cook Inlet, the concentration of butanes never exceeded 0.05 nℓ/ℓ. Similarily we may assume that the concentration of ethane and propane in pristane Alaskan surface waters never exceeds 2 nℓ/ℓ, and is usually less than 1 nℓ/ℓ. Other "so-called" pristine areas, such as the Caribbean Sea, show surface ethane and propane concentrations to vary between trace quantities and 0.4 nℓ and 1 nℓ/ℓ respectively. Again these ranges closely parallel our results in the Alaskan OCS. Our conclusions are that the higher homologs of methane are generally low in Alaskan shelf waters and compare favorably with some of the lowest values measured anywhere in the world (Swinnerton and Lamontagne, 1974).

5.3 Source Indicators of Hydrocarbons

The principal objective during the early phases of this program was to determine the temporal distributions of the low molecular weight aliphatics.

In view of the fact that no offshore production wells are in operation, except those in Upper Cook Inlet, these measurements led to an assessment of the ambient levels of LMWH sustained by natural processes. In addition to this objective, our aim also was to identify unique compositional characteristics of petrogenic hydrocarbons, if they could be found, and contrast them with "normal" abundance derived from biogenic sources or direct solution from the atmosphere. These identification parameters would be highly useful in a monitoring strategy directed toward chronic petroleum pollution of a catastrophic spill.

Our extensive survey work over the Alaskan OCS has led to the discovery of two areas believed to be receiving petrogenic hydrocarbons. They are Norton Sound and Upper Cook Inlet. In the first case the hydrocarbons are believed to be associated with a gas seep of thermogenic origin (Cline and Holmes, 1977). In the latter, the source is unknown but is believed to be associated with oil and gas production in the McArthur oil field in Trading Bay (Blasko, 1974) or possible submarine seepage in that same area. Higher molecular weight hydrocarbon analyses have not been performed to confirm these speculations.

Prior to this investigation, several parameters were used to distinguish anthropogenic hydrocarbons from those of natural origin. One of these procedures distinguishes contaminated ocean water from pristane waters on the basis of the contamination index (Swinnerton and Lamontagne, 1974):

$$CI = 1/3\ (C_1/C_1^* + C_2/C_2^* + C_3/C_3^*), \qquad (1)$$

where C_i^* represents the concentration of the i^{th} alkane hydrocarbon in presumably clean seawater. We decided to apply this test to Cook Inlet, where petroleum contamination is believed to occur (Cline, 1977a). The baseline levels of hydrocarbons for Upper Cook Inlet is not well established, but if we assume $C_1^* = 600$ nℓ/ℓ; $C_2^* = 0.3$ nℓ/ℓ and $C_3^* = 0.2$ nℓ/ℓ, all derived from early spring measurements in LCI, the contamination index would be approximately 11. The largest uncertainty is the baseline concentration of methane, because the biogenic contribution of the upper inlet is not known. It is presumably not much above 800 nℓ/ℓ, which is the maximum concentration observed north of the Forelands. A similar calculation performed in the lower inlet (adjacent to Kachemak Bay) indicates a value of 1.7, significantly below the value of 5 given as the threshold level for contaminated waters.

Another useful parameter for distinguishing hydrocarbons of petrogenic origin is the methane to ethane plus propane ratio (Frank et al., 1970). The diagnostic feature of this ratio is predicated on the relative abundance of methane. Biogenic hydrocarbons show an abundance of methane relative to ethane and propane, whereas most natural gases and crude oils are enriched in the higher homologs of methane (Clark and Brown, 1977). Although the concentrations of methane, ethane and propane may vary considerably in a crude oil, depending on the source material, maturation processes, and migrational pathways, it is generally concluded that $C_1/C_2 + C_3$ ratios in excess of 1000 are indicative of biogenic sources (Bernard et al., 1976). This ratio must be used with caution as some natural gases (dry gas) are nearly exclusively methane (Moore et al., 1966).

A case in point is reflected in Figure 5-2, where the $C_1/C_2 + C_3$ ratio for the near-bottom waters of Bristol Bay is illustrated. Most of the values are less 100 and would suggest some input of hydrocarbons from thermal processes. These measurements were made at a time of high biological activity, resulting in large accumulations of ethene in the water column (see Figures 4-21 thru 4-24). As we have observed elsewhere, the concentration of ethane usually increases in proportion to the amount of ethene present. An extreme example of this is illustrated in Figure 5-3, where the vertical distributions of various

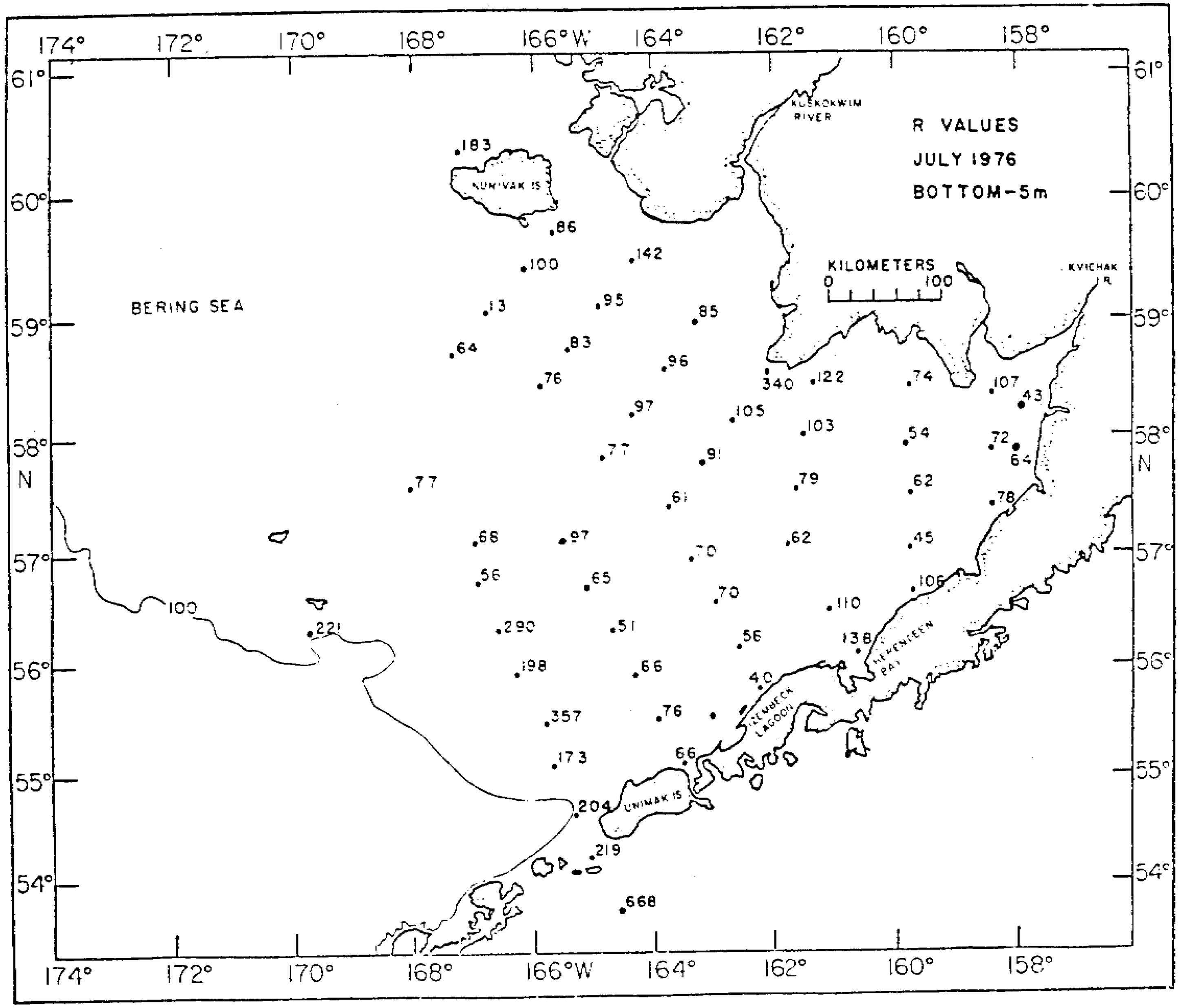

Figure 5-2. The ratio of the concentrations of methane to ethane plus propane ($C_1/C_2 + C_3$) within 5 m of the bottom in Bristol Bay in July 1976.

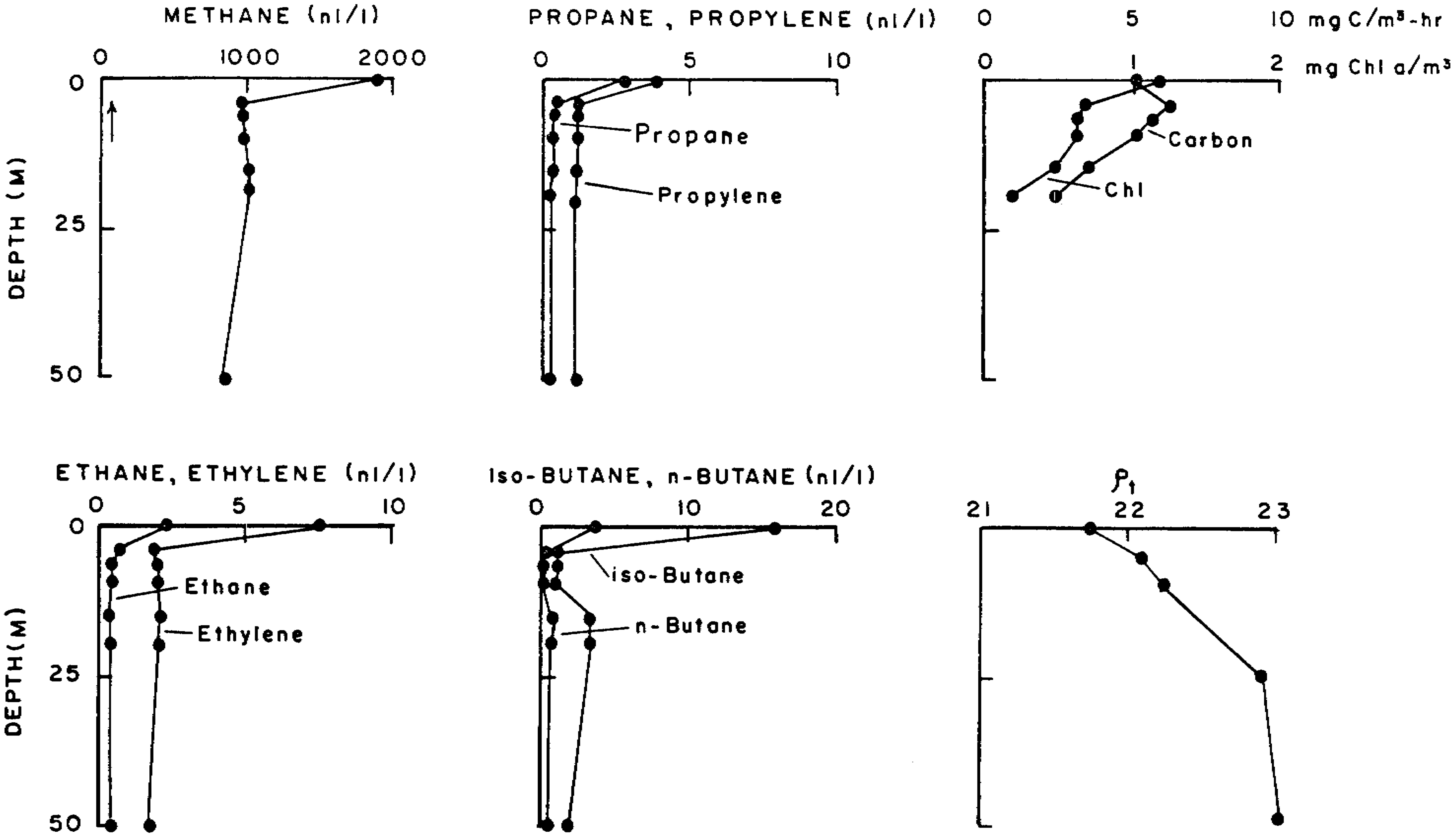

Figure 5-3. Vertical distributions of methane (a) ethane and ethene (b) propane and propene and iso-butane and n-butane (d) at a station in the central basin of Puget Sound. Also shown are profiles of carbon fixation and chlorophyll a (e) and σ_t (f).

hydrocarbons are shown for a station in Puget Sound. The highest concentrations of all low molecular weight hydrocarbons occurs at the surface as does the concentrations of chlorophyll and the maximum rate of photosynthesis. In each case, the concentrations of ethene and propene exceed that of ethane and propane respectively. Of the higher homologs of methane, i-butane was observed to be in the highest concentration. Although surface petroleum contamination can not be ruled out in this case, the data certainly suggest that the hydrocarbon assemblage is due to biological or photosynthetic effects, rather than anthropogenic input. The $C_1/C_2 + C_3$ ratio is approximately 330 and would suggest a large biogenic component. It is interesting to note that both n- and i-butanes also showed the largest relative increases over the Texas and Louisiana shelves (Brooks and Sackett, 1973).

In contrast, the $C_1/C_2 + C_3$ ratio in the near-bottom waters of NEGOA shelf was generally above 400, some values exceeding 2000 in the Hinchinbrook Sea Valley (Figure 5-4). This hydrocarbon assemblage is more typically "biogenic" in character.

Two areas identified in the Alaskan OCS as probable sources of petroleum hydrocarbons are Norton Sound (Cline and Holmes, 1977) and Cook Inlet (Cline, 1977b). The $C_1/C_2 + C_3$ ratio in the near-bottom waters south of Nome Alaska is illustrated in Fugure 5-5. In the immediate vicinity of the seep, the ratio decreases to a value near 50. To the east the ratio increases to values in excess of 500. Preliminary estimates have been made of the composition of the gas seep, based on the molar ratios observed in the water column (Cline and Holmes, 1978). These calculations suggest that the gas phase would yield a $C_1/C_2 + C_3$ ratio near 10, or approximately a factor of 5 less than that observed in the water column. Obviously, dilution of petrogenic gas with biogenic alkanes has altered the ratio upward.

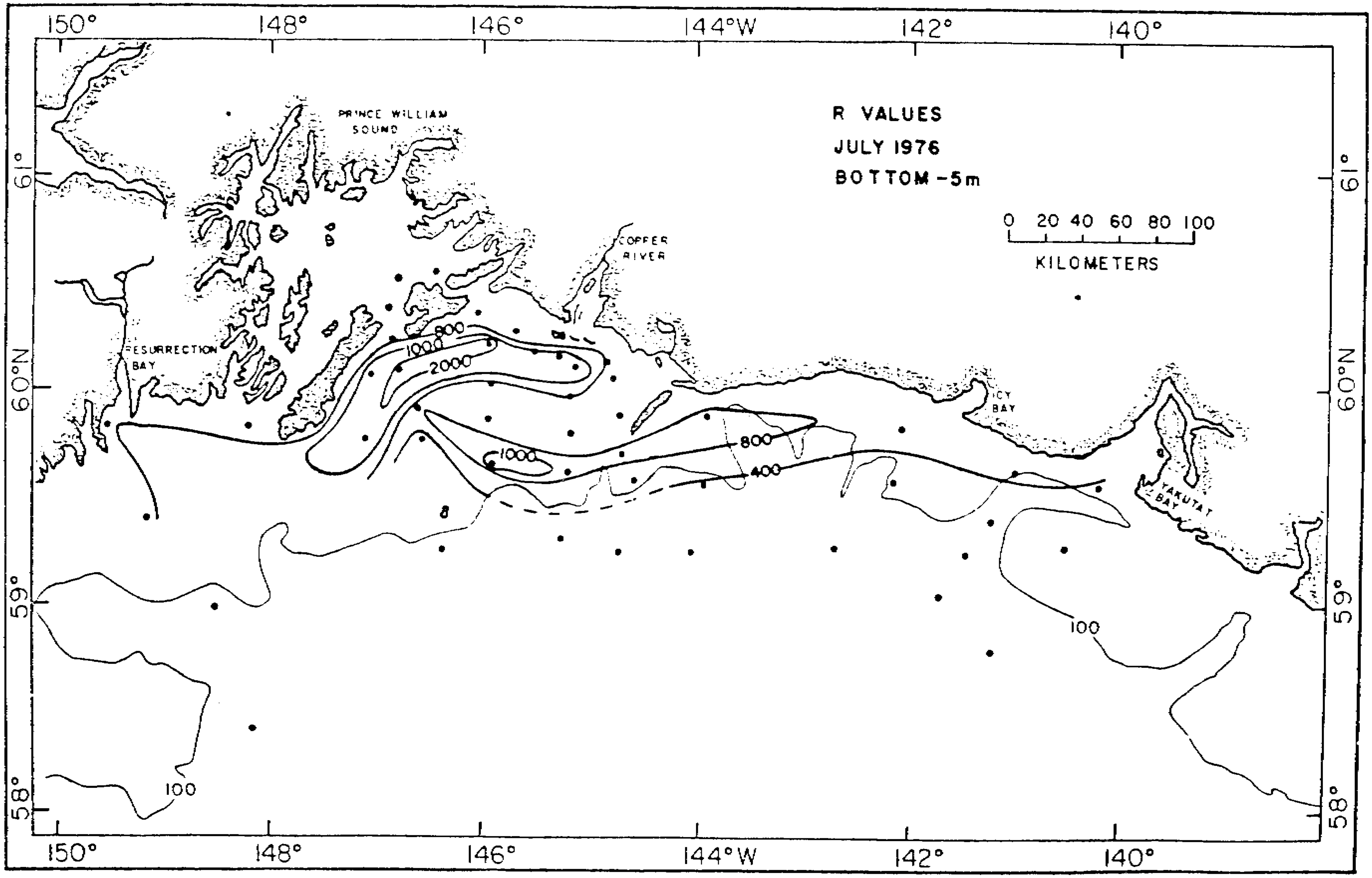

Figure 5-4. The near-bottom $C_1/C_2 + C_3$ ratio observed in the northeast Gulf of Alaska during July 1976. Values in excess of 1000 are generally believed to represent biological compositions.

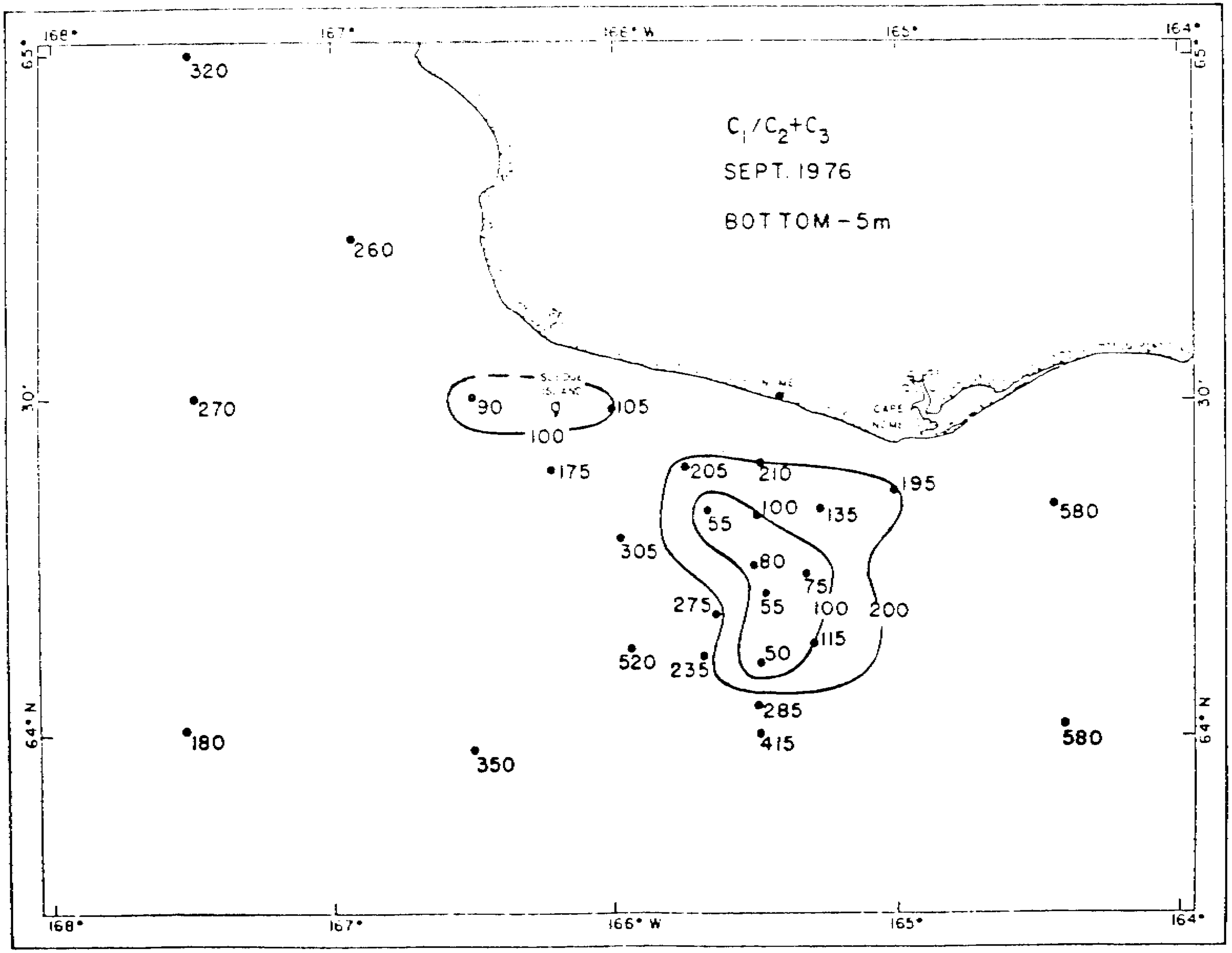

Figure 5-5. The alkane ratio, $C_1/C_2 + C_3$, in the vicinity of the gas seep in Norton Sound. Observations were made in Sept. 1976.

As previously mentioned, there appears to be petrogenic gas source in Upper Cook Inlet. Because the water column is well mixed, we have averaged the surface concentrations of methane, ethane, propane to calculate a $C_1/C_2 + C_3$ ratio. The value thus obtained is 84. It is suspected that the higher homologs of methane have been diluted with biogenic methane, although many of the producing gas wells in Upper Cook Inlet are high in methane relative to ethane and propane (Kelly, 1968).

While the $C_1/C_2 + C_3$ alkane ratio is satisfactory for delineating petroleum input when ample seasonal HC data are available, the ratio involves the concentration of methane, which may be highly variable, both spatially and seasonally. The parameter is not highly useful for diffuse sources in the presence of high background levels of methane. In an attempt to identify reliable and unique compositional parameters involving low molecualr weight hydrocarbons, emphasis in this work has been placed on the higher homologs of methane, in particular the ethane/ethene ratio. The former compound is not produced in abundance by organisms, whereas the latter is not present in crude oils. Examples of the usefulness of this particular parameter are shown for Norton Sound and Cook Inlet (Figures 5-6 and 5-7). The normal ethane-ethene relationship for Norton Sound bottom waters is shown as solid circles (Figure 5-6). The slope of the line is approximately 0.3, not unlike that found for the northeast Gulf of Alaska. Solid triangles above the 45° line represent values obtained in and adjacent to the seep. The apparent lack of a trend in the seep samples simply refects the fact that the ethane rich-waters are mixing laterally with both ethene-rich and ethene-impoverished waters. The bulk of the samples show an ethane/ethene ratio in excess of 4, compared to ratios less than 1 elsewhere.

A similar situation exists in Upper Cook Inlet (Figure 5-7). Samples taken from the upper inlet (solid symbols) show $C_{2:0}/C_{2:1}$ ratios in excess 1, reaching a maximum near 8. The ambient ratio derived from Lower Cook Inlet was 0.1, a value somewhat lower than observed elsewhere in the Alaskan OCS. The reason for this was the abundance of ethene being produced biologically at the time of measurements.

Cook Inlet represents a striking example of the utility of the ethane-ethene ratio for distinguishing petrogenic hydrocarbon sources. Both the petrogenic source and the biological components form nearly orthogonal relationships; a situation representing maximum delineation. In contrast to observations in Norton Sound, the hydrocarbon gases form a well-behaved distribution, mixing with a single source in the lower inlet. The sharp decrease in the concentration of ethane longitudinally down the inlet is due to mixing and gas exchange across the sea surface.

For comparitive purposes, a typical ethane-ethene relationship for NEGOA is depicted in Figure 5-8. These data represent both surface and near-bottom measurements for the fall of 1975. The slope of the line is 0.45 with all values falling below the 45° line. It appears that under normal circumstances, the ethane/ethene ratio is less than 0.5 for all waters and may be much less, depending on the degree of biological activity. The exception to this rule is when the concentrations of ethane and ethene fall to rather low levels (< 0.5 nℓ/ℓ). Under these circumstances, the ratio may be near unity or slightly greater.

The low molecular weight hydrocarbon studies conducted to date in Alaskan shelf waters have illustrated that several compositional parameters are useful in distinguishing thermogenic gases from their biogenic counterparts. The $C_1/C_2 + C_3$ alkane ratio is useful in supporting data such $8^{13}C$ compositions of

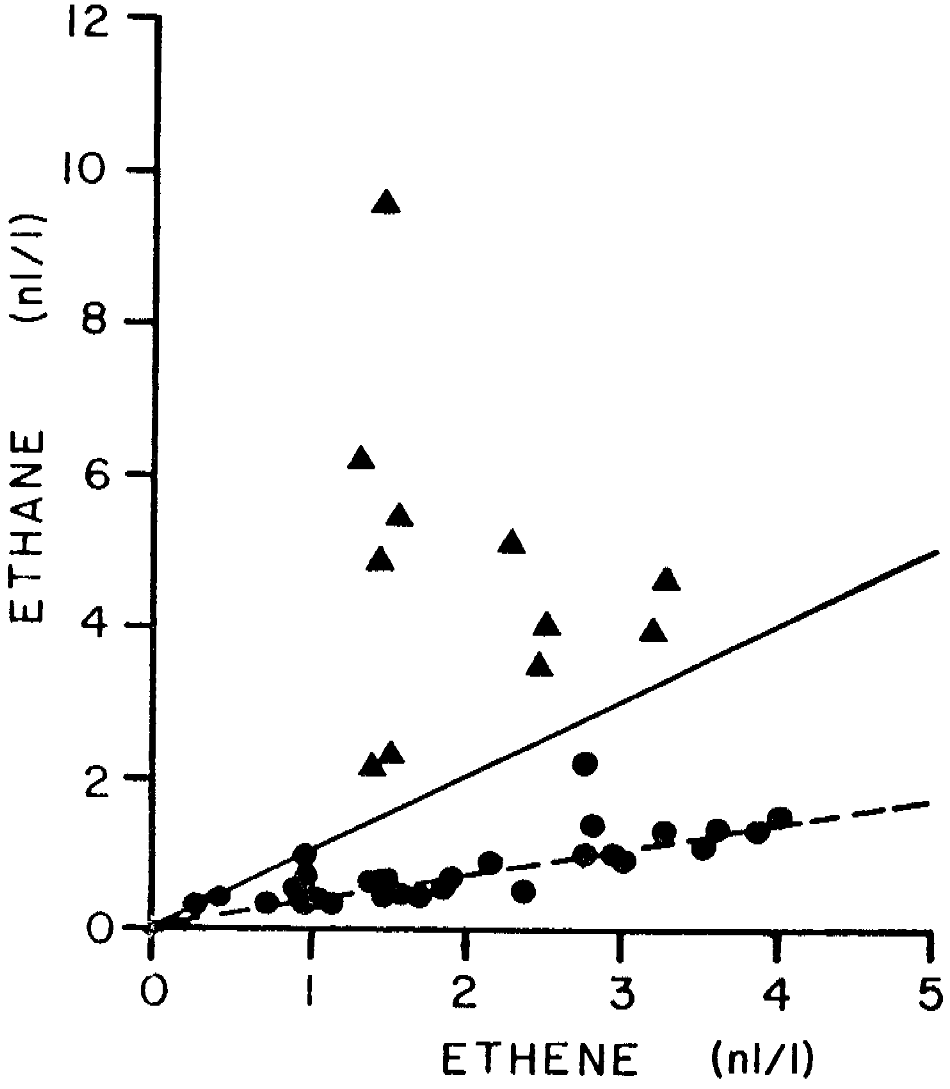

Figure 5-6. The relationship between ethane and ethene in the near-bottom waters of Norton Sound. Solid circles represent samples taken to the east and south (upstream) of the gas seep. Solid triangles represent samples taken in the hydrocarbon plume and are distinguished from the ambient concentrations by the solid line ($C_{2:0}/C_{2:1} = 1$).

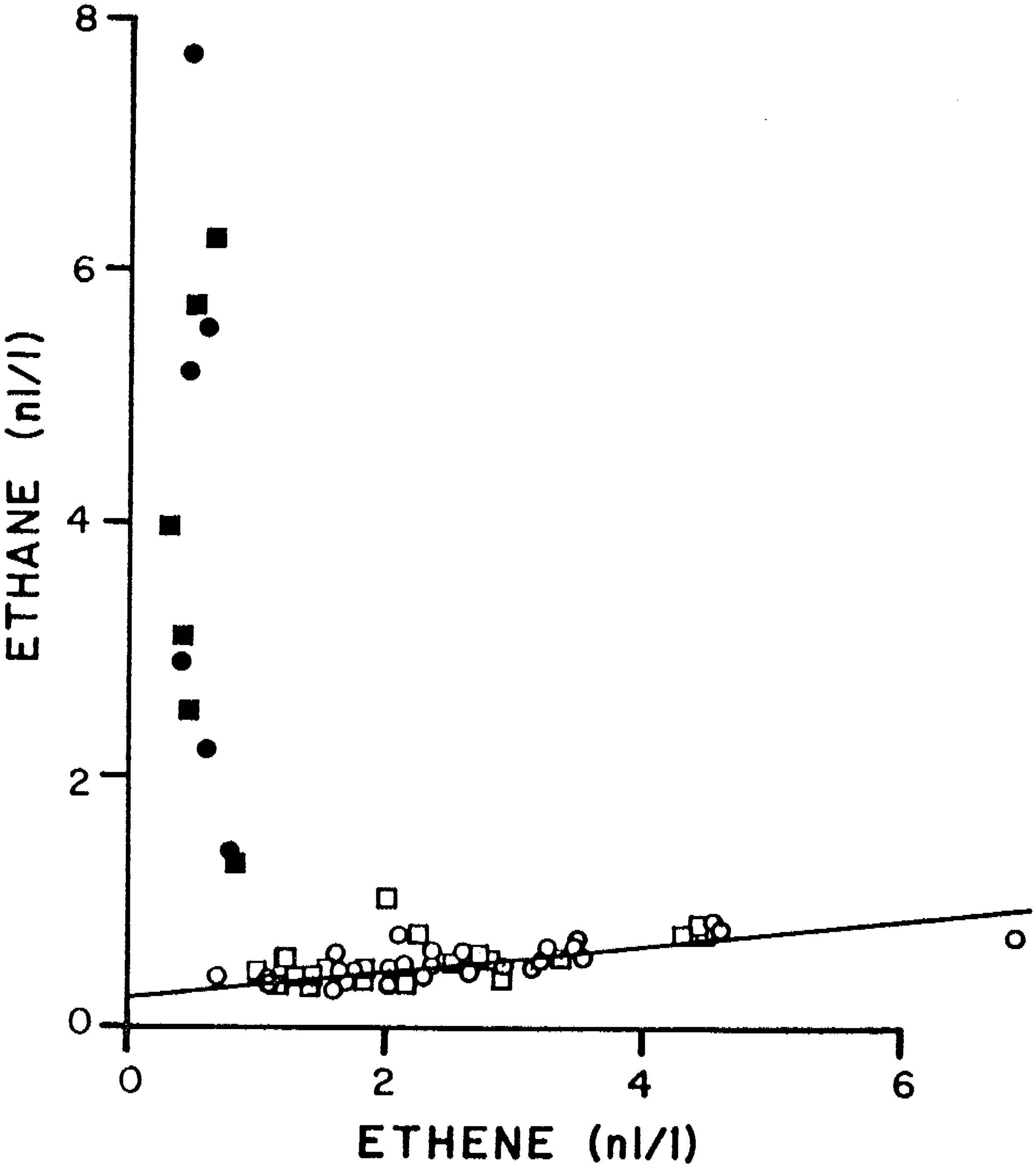

Figure 5-7. The relationship between ethane and ethene in the surface (o) near-bottom waters (■) of Cook Inlet in July 1977. Solid symbols indicate the relationship north of Kalgin Island. The linear dependence of ethane upon ethene for all samples south of Kalgin Island is $C_{2:0} = 0.11\ C_{2:1} + 0.23$ (n = 100). Only a fraction of actual data used in regression is shown in the figure.

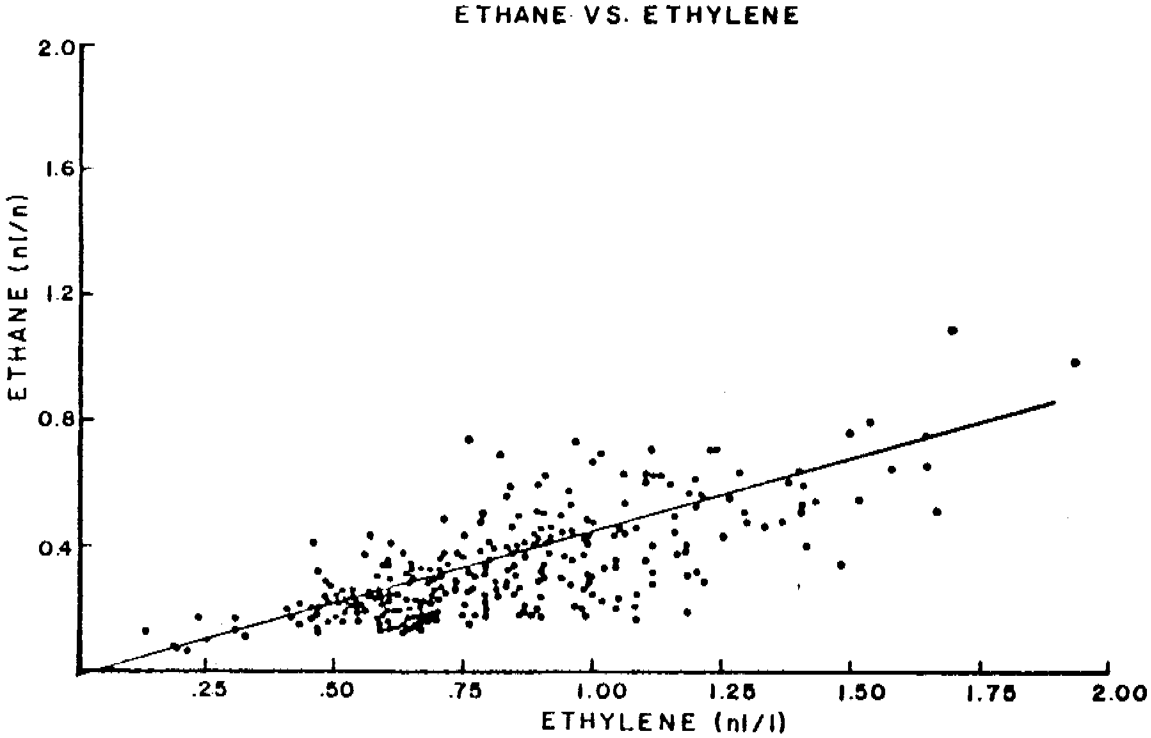

Figure 5-8. The relationship between ethane and ethene for surface and near-bottom waters in the fall of 1975. The slope of the line ($C_{2:0}/C_{2:1}$) is 0.45.

the methane are available. Except in the cases where copious quantities of gas are present, isotopic analysis of the methane would be difficult to achieve because of the quantities of gas available for measurement. The normally high variability in the concentration of methane also clouds the utility of this parameter.

Using the $C_{2:0}/C_{2:1}$ and/or $C_{3:0}/C_{3:1}$ ratios as diagnostic parameters appears to hold more promise, particularily when the hydrocarbon concentrations are in excess of 0.5 $n\ell/\ell$. A rather conclusive test for petrogenic hydrocarbons might be, based on the compositional character of the low molecular weight fraction,

$$\left.\begin{array}{l} C_{2:0}/C_{2:1} > 1 \\ C_{3:0}/C_{3:1} > 1 \end{array}\right\} \text{ for all } C_{2:0},\ C_{2:1},\ C_{3:0}, \text{ and } C_{3:1} > 1\ n\ell/\ell$$

If isotopic characterization of the methane were obtainable, this, in conjunction with the above ratios, would indeed be highly diagnostic.

6. CONCLUSIONS

Baseline surveys have been completed in the northeast Gulf of Alaska, Cook Inlet, southeastern Bering Sea, Norton Sound, and southeastern Chukchi Sea. Not all the areas were visited seasonally, but the data obtained to date are probably sufficient to delineate the background levels of the low molecular weight aliphatic hydrocarbons to be expected in a future monitoring activity. In addition useful diagnostic components of the LMWH suite have been identified by which the presence of petrogenic hydrocarbons might be elucidated.

6.1 Cook Inlet

The horizontal and vertical distributions of the dissolved low molecular weight hydrocarbons, methane, ethane, ethene, propene, propane, iso- and n-butanes, have been determined in Lower Cook Inlet for the periods April and July 1977. The purpose of this investigation is to identify the seasonal abundances and distributions of these hydrocarbons as indicators of petroleum input.

Seasonal measurements conducted reveal a strong biogenic input if LMWH, particularly in LCI. In the Kamishak-Kachemak Bay area, methane concentrations were in the range of 100-150 nℓ/ℓ during April, increasing significantly to above 200 nℓ/ℓ during July. The increases in the concentrations of methane are largely due to microbial degradation of organic matter, either in the surficial sediments or from the overlying water column. Ethane, a good indicator of gas or oil input, was generally less than 0.5 nℓ/ℓ in the lower portion of the inlet. This fact, together with the strong seasonal dependence on concentrations of ethene and propene, would indicate a predominant biological source. For example, ethene concentrations in the surface layers ranged from an April mean of 0.5 nℓ/ℓ to values greater than 2 nℓ/ℓ in July. Concordant with this noted increase in ethene was a modest elevation in the concentrations of ethane; presumably they are either chemically or biologically related.

In Upper Cook Inlet, north of the Forelands, the concentration of alkenes was small with a strong predominance of alkanes, notably ethane and propane. This fact alone would suggest a thermogenic rather than a biogenic source. Chromatographic evidence indicates that higher alkanes also were present, including butanes and unresolved pentanes. Maximum concentrations of ethane and propane observed were 7.7 nℓ/ℓ and 4.4 nℓ/ℓ, respectively. Corresponding levels of ethene and propene were less than 0.5 nℓ/ℓ. Throughout the region north of Kalgin Island, the $C_{2:0}/C_{2:1}$ was greater than 1 and generally less than 0.2 elsewhere in the inlet. Preliminary analysis of the probable gas phase, using a dynamic bubble model, suggests that the $C_{2:0}/C_{3:0}$ ratio is near 1. This would imply that the original source is petroleum and not dry gas. The highest concentrations of ethane and propane were noted above the Forelands on the west side of the inlet. This area encompasses the McArthur oil field. Precise source of the hydrocarbons is as yet undetermined.

These studies have shown that the concentrations of the low molecular weight alkanes are extremely low throughout most of Cook Inlet and even small increases in the input rate would by easily detected. Also, the ratio of ethane to ethene is a reliable parameter by which thermogenic and biogenic hydrocarbon sources may be distinguished. Our studies have also shown that this particular test parameter will be useful in other OCS areas as well.

6.2 Northeast Gulf of Alaska

Three field programs have been initiated and completed in the northeast Gulf of Alaska during late 1975, spring and summer of 1976. Results obtained from these field studies have served to document the seasonal ambient levels of the LMWH, their distributions and probable sources. No large or significant submarine sources were identified as the result of these measurements, even though an intensive study was made of the Kayak Island fault system. Ranges of expected hydrocarbon concentrations to be expected in NEGOA are shown in Table 5-1.

The waters of the northesat Gulf of Alaska are characterized by highly variable levels of the C_1 and C_2 components, depending on seasonal and geographical parameters. The bottom sediments in the vicinity of Tarr Bank are silty-muds, and thus appear to be vigorous source of methane gas. Methane found in the bottom waters of this region was not supported by the higher homologs, thus biogenic rather than thermogenic processes are believed operative. Although the geological setting would suggest the probability of submarine seeps in the Katalla-Kayak Island region, we observed none as the result of this program.

The single anomalous feature in the northeast ulf that has been observed to date is the unusually high concentrations of ethane and propane observed at the entrance to Yakutat Bay. Maximum ethane and propane concentrations observed were 11.4 nℓ/ℓ and 4.6 nℓ/ℓ, respectively. These concentrations are the highest observed to date in the OCS of Alaska. The high surface concentrations were not observed at depth where one might expect the greatest concentration to occur if they were associated with petroleum seepage (Cline and Holmes, 1977). However, if the seep was located within Yakutat Bay, normal estuarine circulation would have suppressed the bottom signature. There still exists the likelihood that the alkanes arose via biological mechanisms. This mechanism will be explored in detailed studies to be conducted this year in Cook Inlet.

6.3 Southeastern Bering Sea (Bristol Bay)

A total of two field programs were conducted in Bristol Bay; the first in September-October of 1975, the second in July of 1976. The results of these field exercises documented the ambient levels of hydrocarbons, their distributions, and their probable sources. No sources of petroleum-related hydrocarbons were definitively identified. In the event of future petroleum development activities in the southeastern Bering Sea, the benchmark data shown in Table 5-1 should provide the necessary background information vital to the documentation of petroleum or natural gas introduction into this environment.

The natural levels of the C_1-C_4 hydrocarbons in the southeastern Bering Sea were relatively low and generally reflect minimal biological input or petroleum pollution. Significant seasonal effects were seen only in the abundances and distributions of the olefinic components ethene and propene and presumably were due to elevated levels of primary production noted in summer. Methane concentrations were highly variable in both time and space, but no more so than observed in other OCS areas of Alaska. The rivers emptying into Bristol Bay are low in methane; waters derived from the lagoon systems on the Alaskan Peninsula are rich in methane. We assume that these enriched waters were derived from bacterial methane production associated with the eel grass communities. The concentrations of ethane and propane were everywhere near or below 1 $n\ell/\ell$, the higher values being observed near the bottom. Surface concentrations of these hydrocarbons are largely controlled by air-sea exchange rate and the benthic production rate. Some of the ethane and propane found in the surface layers also may have arisen from the chemical or biochemical reduction of ethene and propene. However, no information is available on the merits of this mechanism at the present time.

6.4 Norton Sound

A survey for LMWH was conducted in Norton Sound in September of 1976. The most significant discovery was the presence of a gas seep in a highly localized region south of Nome, Alaska. Analyses of these data have been amplified and form the basis of the report by Cline and Holmes (1977), which shall not be repeated here for the sake of brevity. Remarks will be confined to the general hydrocarbon distributions not influenced by seep activity.

At the time of the observations, strong sources of methane were observed at the eastern extremity of the basin and from the lagoon system to the east of Cape Nome (Cline, 1976). The former is the result of benthic microbial metabolism releasing large quantities of methane to the lower water column, whereas the latter appears to be associated with the surface waters presumably originating from the lagoon system. Distributions are the result of prevailing circulation during the observational period. Methane concentrations exceeded 2000 nℓ/ℓ at the eastern extremity of the embayment because of the high degree of thermal stratification in the region. In general, concentrations of methane decrease from east to west in the basin, both in the surface layers and at depth.

Concentrations of the higher homologs of methane are generally less than 1 nℓ/ℓ over all of Norton Sound, except the seep area. The olefinic C_2 and C_3 components are generally greater than 1 nℓ/ℓ with concentrations decreasing west to east in contrast to that observed for methane. These components are reflective of biological activity not associated with methanogenesis and would suggest that the outer region is more productive than the inner portion of the basin.

A plot of ethane versus ethene for all nonseep samples indicates a ratio less than 0.5 in agreement with other areas investigated.

6.5 Southeastern Chukchi Sea

The distribution and abundance of LMWH in the southeastern Chukchi Sea was surveyed in September 1976, during the second half of the Norton Sound cruise. A complete description of our findings can be obtained from the relevant Quarterly Report (Cline, 1976).

As was the case in other OCS areas, the abundance and distribution of methane reflected sources, circulation, and degree of vertical mixing. Kotzebue Sound, although very shallow (< 20 m), was highly stratified and large concentrations of methane accumulated below the thermocline (Table 5-1). Maximum concentrations of methane were in excess of 3000 nℓ/ℓ near the town of Kotzebue, but were not supported by elevated levels of the higher homologs. Ethane and propane were uniformly less than 1 nℓ/ℓ; however, somewhat higher concentrations of ethane were observed within the inner Sound (2.5 nℓ/ℓ).

Evident in the near-bottom waters west of Point Hope was a strong plume of methane, apparently originating to the west over the Siberian Shelf. In this case the occurrence of methane was supported by similarly high concentrations of ethane (3 nℓ/ℓ) and propane (1.3 nℓ/ℓ), but ethene concentrations were also significantly high (> 3.4 nℓ/ℓ). It has been suggested that this water mass, characterized primarily by its low temperature, arose to the west along the northern Siberian Shelf where the concentration of oxygen quite often falls to very low levels in late summer, allowing near-anoxic conditions to prevail in the near-bottom waters (Aagaard, University of Washinton, personal communication). If this is so, unusual ratios of ethane and ethene also might prevail as was the case with this water mass. Whereas ethene is more oxidized than ethane, a preponderance of ethane might occur normally in waters of low oxygen content. It is also possible that the high concentration of ethane was due to seep activity along the Siberian Shelf; but without confirming observations in the territorial waters of Russia, this proposal remains pure speculation at this point.

In other localized areas of the Chukchi Sea, hydrocarbon abundances were quite normal as compared to other OCS areas studied (Table 5-1).

6.6 Kodiak Shelf

During July of 1977, the vertical and horizontal concentrations of the LMWH were determined over the southeastern shelf of Kodiak Island. Hydrocarbon assemblages indicated biological sources rather than thermogenic.

Methane concentrations were highly variable, both in the surface layers (80-369 nℓ/ℓ) and at depth (160-1880 nℓ/ℓ). Variability is presumed related to biological activity in both the water column and underlying sediments.

Concentrations of ethane were everywhere less than 1 nℓ/ℓ, although these levels are considered to be significantly higher than those observed for this season in other OCS areas. Ethene concentrations in the surface layers were relatively high (3-5 nℓ/ℓ), reflecting significant levels of biological activity. It is assumed that the aforementioned levels of ethane are related to these concentrations of ethane. Ethane/ethene ratios have been calculated (although not shown) for the Kodiak Shelf. Values are everywhere less than 0.5 nℓ/ℓ, indicating a predominant biogenic hydrocarbon source.

The concentrations of propane, both in the surface layers and at depth, never exceeded 0.8 nℓ/ℓ. The range in the surface layers was 0.3 nℓ/ℓ to 0.8 nℓ/ℓ; at depth it was 0.1 nℓ/ℓ.to 0.5 nℓ/ℓ. Again, the source is believed to be biogenic rather than thermogenic.

7. FUTURE ENDEAVORS

The past research activity centered on the seasonal and spatial variations in low molecular weight hydrocarbons with some attention being given to significant source regions. The field observational program in the Bering Sea, Norton Sound, Chukchi Sea and the northeast Gulf of Alaska has, for the most part, satisfied our commitment to the establishment of baseline levels of LMWH in these areas. Some of the geographical areas have been visited three times, others only once, thus seasonal information will be limited in scope in some areas, altogether absent in others. It would be desirable from a scientific point of view to continue our studies on the distributions, sources and ultimate fate of natural marine hydrocarbons, but we recognize that all of these goals may not be in the best interest or within the capabilities and jurisdiction of the OCS program. For these reasons, we feel that future research activities concerning LMWH should be redirected toward local source areas.

Future research activities should concentrate on known hydrocarbon inputs, whether they be natural or man-made. Included in these categories would be: a) anomalous hydrocarbon sources, b) natural gas and oil seeps, and c) existing petroleum platforms and producing wells. The aim of these studies would be to ascertain the sources and composition of the hydrocarbons, their input rates, and their usefulness as tracers of soluble and emulsified hydrocarbons. Where inputs are identified, plume trajectories and space scales should be elucidated in conjunction with current velocities and directions.

As the result of our observations made in September 1976 in Norton Sound, a major gas seep was identified, which may include associated petroleum. If this is so, then a field effort should be mounted to elucidate its composition, plume dimension, and possible influence on the indigenous biological community.

Low molecular weight hydrocarbon (aliphatics and aromatics) should be sampled in the water and sediment columns, supplemented with observations of the heavier fractions in sediments (suspended and bottom), organisms, and water. The seep in Norton Sound is located in shallow water (approx. 20 m) and would be accessible for sampling via SCUBA. Planning is currently underway to implement a major survey of the seep area in summer 1979.

Lastly, we feel that the current production of petroleum in Upper Cook Inlet should be examined in terms of LMWH. Detailed observations will be conducted this spring and summer into the sources of LMWH (including aromatics), with particular emphasis on the region north of the Forelands. Specific studies involving petrogenic components of petroleum will be supplemented with interdisciplinary studies involving the biogenic production of LMWH. This will be conducted in LCI in cooperation with biological oceanographers from PMEL. Depending on the outcome of these process studies, future work may be indicated in FY79.

Our findings in the Gulf of Alaska and the Bering Sea have shown interesting, but yet unexplained, relationships between ethane and ethene. If the latter two components arise from the sediment, as we believe the bulk of the methane does, what are the processes that result in the formation of ethane and ethene? Conceptually, we envision a biochemical origin for these gases, but the purely inorganic cracking of more complex organic molecules also may contribute significantly to their production. In the broadest context of the environmental assessment program, it seems that a knowledgeable understanding of the sources of natural hydrocarbons, the rates of input, and the ultimate fates are of paramount importance. Traditionally, it is the investigation of natural contaminants under natural environmental conditions that results in more reliable predictions concerning capacities, stress tolerances, and rates of recovery of a given system.

The production and escape of LMWH from sediments ought to be studied in the context of environmental and geochemical factors. Relationships between hydrocarbons and environmental characteristics, such as sediemnt type, size frequency, organic carbon content and origin, redox potential, sedimentation rates, pore water chemistry, and microbial populations, should be emphasized. Because the LMWH fraction is volatile, special coring apparatus must be constructed to eliminate exchange of gases with the atmosphere during sampling. As a first step, surficial hydrocarbon gradients and the loci of hydrocarbon production should be investigated in the upper 2 m of the sediment column. Depending on the outcome of these observations in promising localized areas, additional experiments should be developed to elucidate machanisms and environmental control parameters.

Acknowledgment

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We wish to take this opportunity to thank Charles Katz and Larry Keister for their assistance in analyses, data processing, and graphics. The captain and crew of the NOAA research ship DISCOVERER, from which most of these measurements were taken, are to be commended for their assistance and cooperation in the acquisition of samples.

8. RELEVANT PUBLICATIONS

The following papers and abstracts have been published or are in press.

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Holmes, M. L., J. D. Cline, and C. H. Nelson (1977). Acoustic anomalies and seeping gas in Norton Basin, Alaska. Geol. Soc. Amer., Seattle (Abstract).

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Holmes, M. L., J. D. Cline, and J. L. Johnson (1978). Geological setting of Norton Basin gas seep. Proc. Offshore Technol. Conf., OTC-3051.

Cline, J. D. and A. W. Young (1977). An improved interstitial water sampler for dissolved gases. Trans Am. Geophys. Union., 58: 1165 (Abstract).

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Natural Distribution and Environmental Background of Trace Heavy Metals in Alaskan Shelf and Estuarine Areas

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I. SUMMARY

During the current 1977-78 contract period we have completed all of the assigned baseline study work except for the Beaufort Sea and Cook Inlet. We have previously encountered severe logistical problems in attempting to obtain suitable samples from the open Beaufort Sea; another attempt will be made to characterize the natural heavy metal environment of a coastal lagoon this year. Baseline work in Cook Inlet has been expended this year but the major sampling cruises have not yet taken place.

In spite of the severely limited amount of suitable biological samples available for heavy metal analysis (a great deal of material has had to be discarded) we believe that sufficient baseline numbers are now available for the major lease areas. All of our data indicate that the sediments, water and indigenous biota of the Alaskan shelf and coastal waters have heavy metal contents which are as low or lower than those recorded elsewhere for similar unpolluted oceanographic environments in more temperate regions. The sediments contain concentrations of extractable trace metals which are a function of the grain size distribution, for example and, as would be expected, no unnatural enrichments have been recorded. Similarly, the means for the soluble contents of metals in the water column correspond to those recorded for open ocean areas anywhere. Because we have been looking at dynamic shelf regions we did not expect to observe depth differences that are a feature of deep oceanic areas. However, enhanced values adjacent to the bottom were commonly observed; this is here likely to be due to the incorporation of fine grained particulate and colloidal material rather than, say, regeneration of metals from biota debris but is, in either case, a natural feature. This near sediment enhancement is best seen from the very carefully obtained set of copper data obtained in the Bering Sea this past summer. One major objective of this cruise was to compare different collection methods. This study reinforced our concern about the integrity of water samples collected from the regular assigned NOAA vessels which made up the bulk of the baseline survey data. Our special methods of collection, handling and storage used for the estuarine "process studies" are described in this report.

As noted above, biota heavy metal contents have largely presented no surprises. Our most comprehensive set of data, however, are for marine mammals from the Bering Sea for which there are few comparison data available. We record in this report relatively enhanced values for toxic metals such as cadmium in kidney and liver samples and it would seem prudent that such meat should not comprise a major food source for the local inhabitants. The principal object of this sub-program was to look for patterns in the uptake of heavy metals by the various seal species which could be related to their own feeding habits (fish, benthos, etc.). Unfortunately, the project was terminated before sufficient statistical information could be obtained but some apparent trends are noted here.

The principal object of this year's program was to pursue several (fate-and-effects) process studies in selected estuarine areas adjacent to the shelf lease areas. The obvious need for long term research projects on the reactions and transport of heavy metals under "Alaskan" conditions, the rationale for choosing estuarine environments, and the emphasis on the sediment water boundary have all been discussed at length in previous reports and proposals. Although insufficient to obtain a complete picture, our three sampling trips to the Gulf of Alaska specific study site (Yakutat Bay) has indicated the basic water circulation patterns and the times of replacement of deep water in the various basins. A very marked gradient (positive into the sediment) has been obtained for "soluble" manganese which conforms with our earlier findings for copper. We are in the process of relating soluble contents to nutrient and DOC patterns (i.e., regenerated biota debris), and to the organic/inorganic character of the sedimentary particulates. This work is being continued now in Resurrection Bay which is an oceanographically simplified proxy for Cook Inlet.

A major effort in recent months has been concerned with the uptake of heavy metals by natural marine sediment bacteria populations and transfer to the deposit feeding benthos. As noted in a following section, our research has indicated the vital mediation role played by microorganisms in remobilizing and generally chemically converting heavy metals scavenged by the sediments. At the same time deposit-feeding benthic species, which concentrate heavy metals proportionally much more than, say, fin fish, are at the base of several short but commercially exceedingly important food chains in Alaskan coastal waters. Initial results show that cultured heterogenous marine bacteria strongly concentrate cadmium and that, when used as a food source by detritivore clams, they later show elevated (though not magnified) concentrations. We are presently conducting a set of aquaria experiments to test the effect of hydrocarbons on the growth characteristics of the bacteria and on the uptake and transfer patterns of the heavy metals to higher trophic levels.

II. INTRODUCTION

General Nature and Scope of Study

The primary objective of this program has been to research natural pathways of potentially toxic heavy metals to and through Alaskan Shelf and coastal marine biota (with emphasis on commercially important benthic species) and hence to determine and predict changes likely to result from oil industry activity in this marine zone. Ancillary components of this work include: (1) characterizing the heavy metal inventories of the water, sediment and indigenious biota in those geographical areas for which no background data exists; (2) determining non-biological pathways (rates and routes under both natural and stressed conditions) of the heavy metals as these affect the availability of metals to the organisms; (3) toxicity effects of selected heavy metals to animals which are of major commercial importance under Alaskan environmental conditions.

This program is primarily limited to work on the distribution of those heavy metals specifically mandated by BLM: cadmium, chromium, copper, iron, lead, nickel, zinc, and vanadium.

Specific Objectives

As noted in the previous Annual Report, it was considered that, at the beginning of the current contract period, the baseline survey phase of the program was essentially complete. Various summaries for specific lease areas have been presented both orally and in summary report form at a variety of meetings and an index to this material is included in this report (Appendix V). A set of final summaries, one for each lease area is now being prepared.

Most attention during the current contract period has been given to the specific heavy metal process research studies spelled out in the Work Statement; thus:

(a) Characterization of the flux of heavy metals from the surface sediments into the water column - In general we are concerned here with the question of the "availability" of heavy metals in a form ameiable to uptake by the benthic biota.

This type of research was originally carried out for copper. By choosing rather special oceanographic environments (i.e., basically those in which the primary water column transport processes of advection and diffusion could be unravelled) we were able to determine flux values for the transport of remobilized copper back into the water column and to say something about chemical reactions in the surface sediments. In more recent work we have looked at cadmium, vanadium and manganese, initially in Yakutat Bay and lately in Resurrection Bay when work in the former was not allowed to be continued. We are particularly interested in knowing about the chemical forms of the metals and the nature of the particulate material "scavenging" the metals to the sediments. To this end we have had to collect a large amount of chemical information (nutrients, dissolved organic carbon etc.) which is presented here largely as a mass of apparently unrelated information (Appendix VI). This data will be analyzed, winnowed and correlated by the end of the project.

It was noted above that field areas for this work had to be chosen with care and we have found semi-enclosed fjord basins to be both oceanographically very suitable and also very relevant as regards potential oil pollution. We started field work in Yakutat and Icy Bays but Icy Bay was difficult to handle logistics-wise and was in any case publically damned by the USSGS as a potential harborsite. When OCSEAP interest in the Gulf of Alaska abruptly ceased in favor of Cook Inlet we attempted to transfer our field investigation program to the adjacent Resurrection Bay; a transfer which has been only partially successful to date. Both Yakutat Bay and Resurrection Bay (unlike Cook Inlet proper) contain the requisite sill-basin structures but the former area is hydrographically quite complex.

(b) The role of the microorganisms in mediating chemical transformations at the sediment boundary and in concentrating heavy metals - In particular, we are interested in knowing whether pollutional effects - and particularly from hydrocarbons - at the sediment surface might inhibit or enhance the natural reactions and fluxes.

(c) The role of the detritus deposit-feeding benthos transfer of heavy metals *via* bacteria - We are particularly concerned with the obvious propensity of the detritivore benthos to concentrate heavy metals, including a number of highly toxic elements. In Alaska many benthic community species are of primary commercial importance. At the same time, even though these are detritus food source dominated areas, the nature of transfer of metals from the particulates to the deposit-feeding species is not well known. We have started to look at clams fed on labelled bacteria under aquaria conditions with the results outlined above in the Summary. It is intended to continue these investigations up the food chain by investigating clam-crab (i.e., a commercial species) transfer, although this will now have to be done under other patronage.

III. CURRENT STATE OF KNOWLEDGE

The state of knowledge regarding heavy metal distribution in the marine environment and the relationship to oil pollution was considered in detail in the previous Annual Report. More recent work specifically related to the objectives considered this year are referred in the text as appropriate.

IV. STUDY AREAS

Gulf of Alaska

Sediment and water samples have been collected from the standard hydrographic grids shown as Figures 1 and 2. The intertidal benthic samples for this lease area, from the N.W. Gulf region and from Kodiak Island was collected at the sites given in Figure 3 and tabulated in Tables I-III. The Gulf specific study site has been Yakutat Bay. Standard stations occupied in this fjord are shown in Figure 4.

Lower Cook Inlet

No systematic station grid has been established in this lease area. The initial sediment samples were collected on the original benthic biology grid (stations where Haps core samples were successfully retrieved are shown in Fig. 5). Subsequent sampling trips have mostly attempted to tie in with the changing benthic biology program; sampling localities are shown under the individual sampling trips listed below. The specific study site for this lease area for sediment-water flux studies has been Resurrection Bay (standard stations are given in Fig. 6). Benthic uptake work has mostly been a laboratory aquaria program but *Macoma baltica* samples have been collected from Katchemak Bay and the subtidal *Macoma calcarea* from the benthic grids.

South Bering Sea

The survey grid on which most of the sediment and water column samples were taken is given as Figure 7. Intertidal benthic biota sampling localities are shown in Figure 8 and listed in Table IV. The marine mammal samples and the specialized water samples for copper and lead analysis were collected on non-standard stations as noted below.

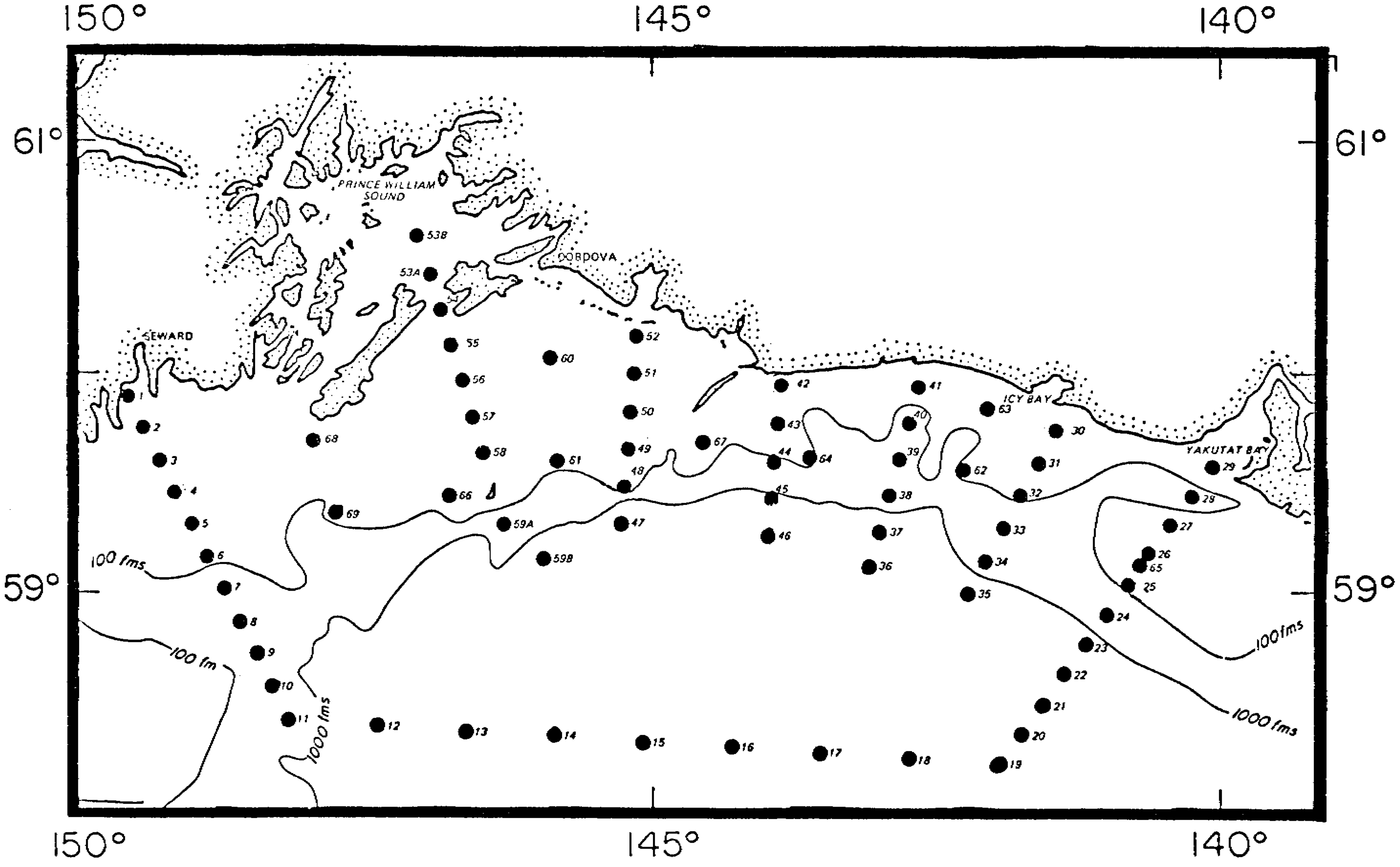

Figure 1. Standard sampling grid N.E. Gulf of Alaska.

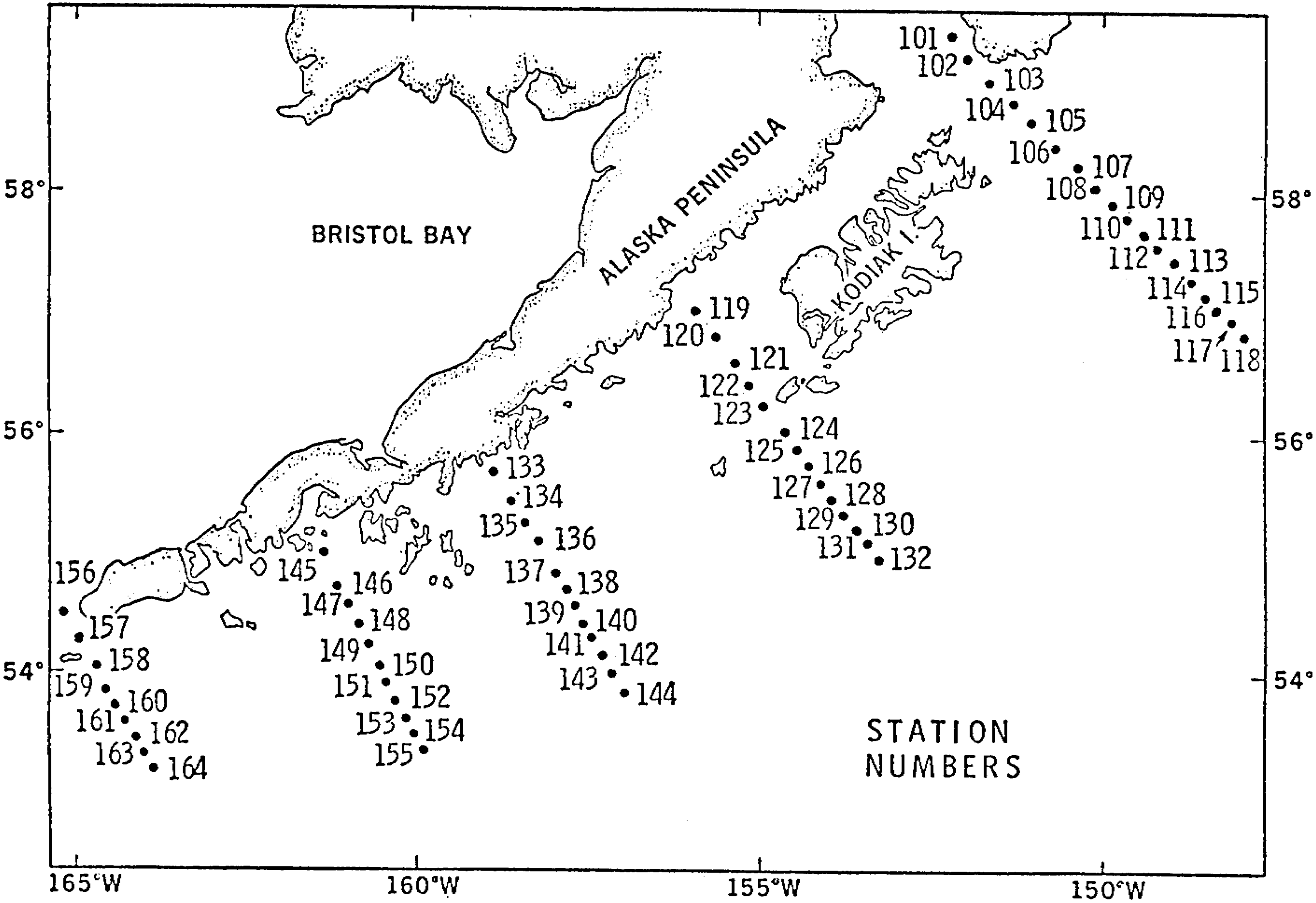

Figure 2. Station grid N.W. Gulf of Alaska.

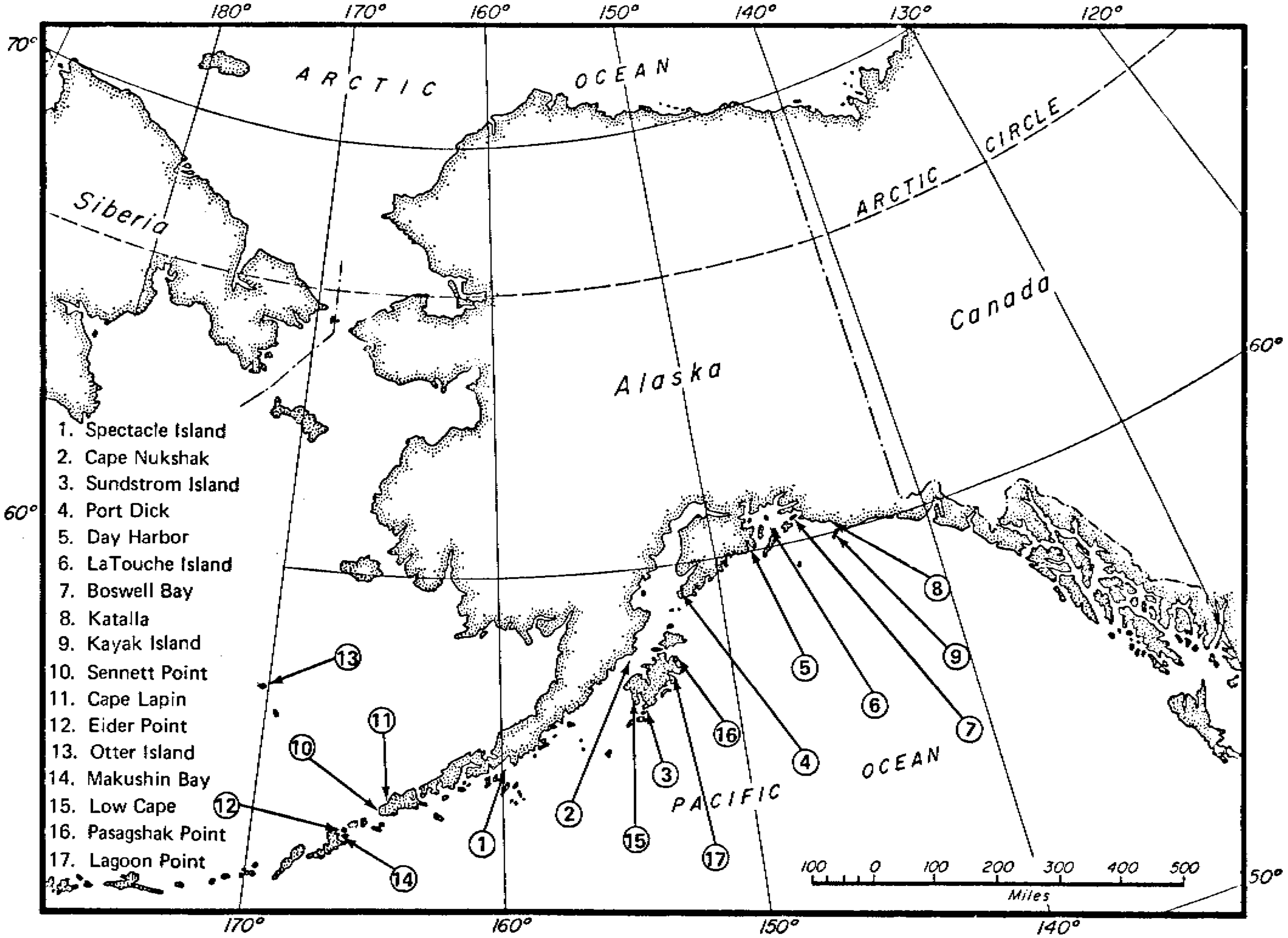

Figure 3. Intertidal biota stations: Gulf and Kodiak.

TABLE I

N.E. GULF OF ALASKA

Localities of Intertidal Benthos Samples

Name	Locality	
Port Dick (Gore Point)	59°13.3	151°10.0
Day Harbor (Anchor Cove)	59°59.7	149°06.0
La Touche Point	59°57.1	148°03.4
Macleod Harbor (Montague Island)	59°53.4	147°47.7
Middleton Island	59°25.2	146°22.5
Zaikof Bay (Montague Island)	60°17.9	147°00.0
Port Etches (Cape Hinchinbrook)	60°21.2	146°36.3
Boswell Bay	60°24.6	146°06.3
Katalla	60°16.5	144°36.5
Cape Yakataga	60°03.8	142°25.9
Yakutat	59°32.3	139°52.5
Kayak Island	59°48.2	144°35.9

TABLE II

N.W. GULF OF ALASKA

Localities of Intertidal Benthos Samples

Name	Locality	
Spectacle Island	55°07.2	159°44.6
Chirikof Island	55°49.6	156°44.1
Cape Nukchak	58°23.4	153°59.4
Low Cape (Trinity Islands)	57°00.0	154°31.5

TABLE III

KODIAK ISLAND

Localities of Intertidal Benthos Samples

Name	Locality	
Sundstrom Island	56°41.5	154°08.6
Three Saints Bay	57°07.8	153°28.7
Sud Island	58°54.3	152°12.4
Lagoon Point (Sitlakidak Island)	57°11.3	153°03.4
Pasagshak Point	57°26.8	152°27.2

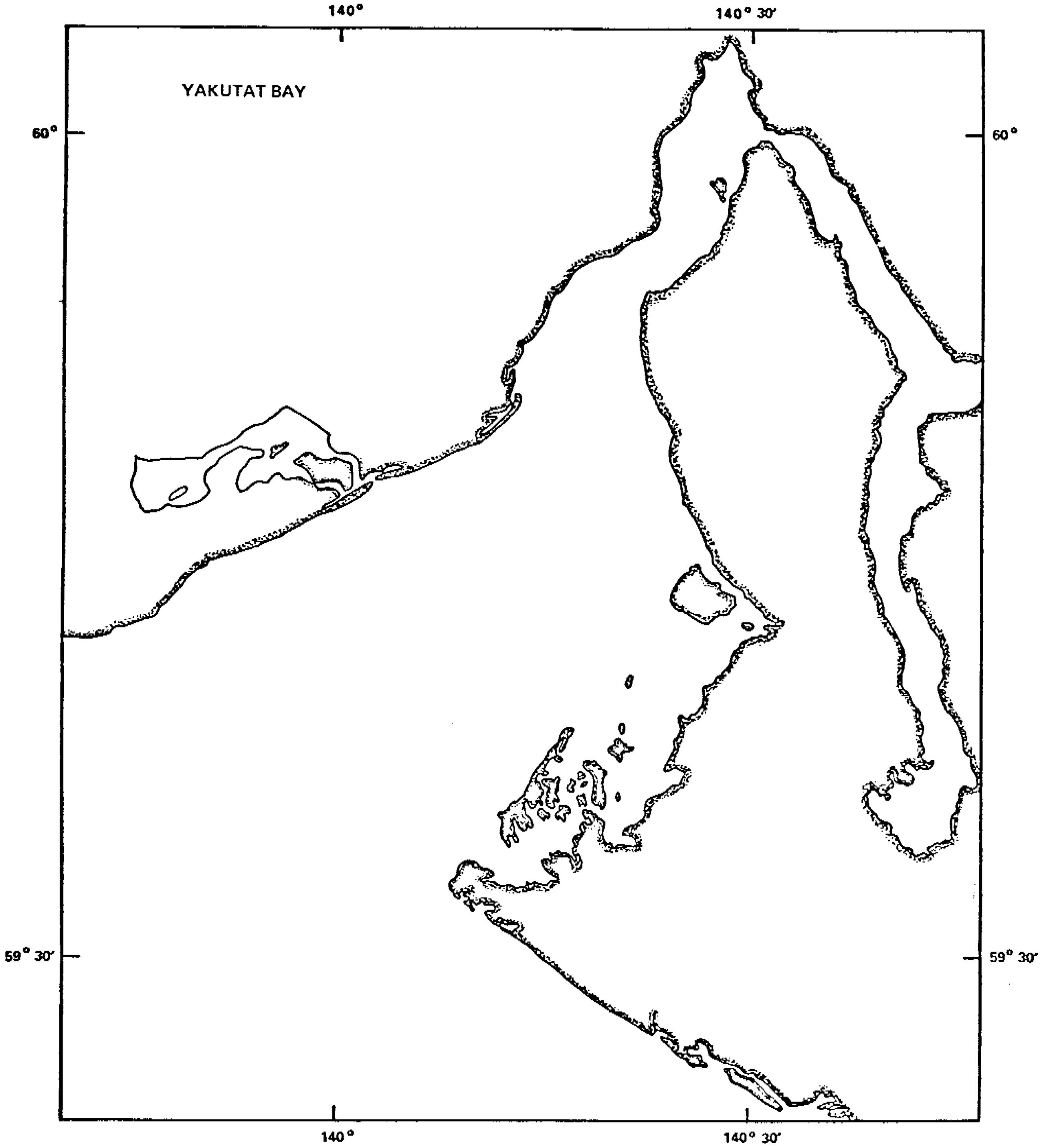

Figure 4. Standard stations in Yakutat Bay.

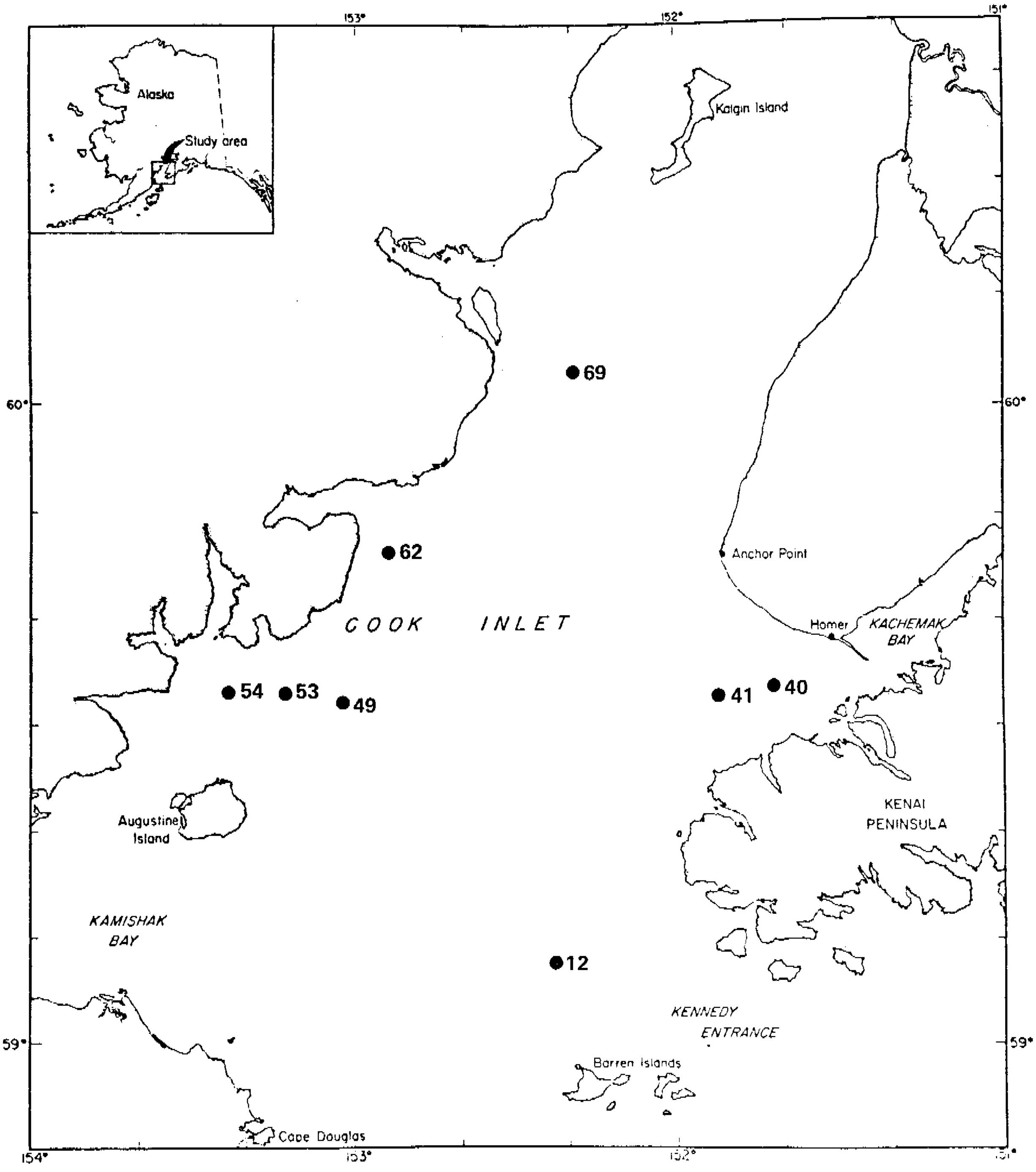

Figure 5. Locations of Haps core samples recovered from Lower Cook Inlet: *Moana Wave*, April 1976.

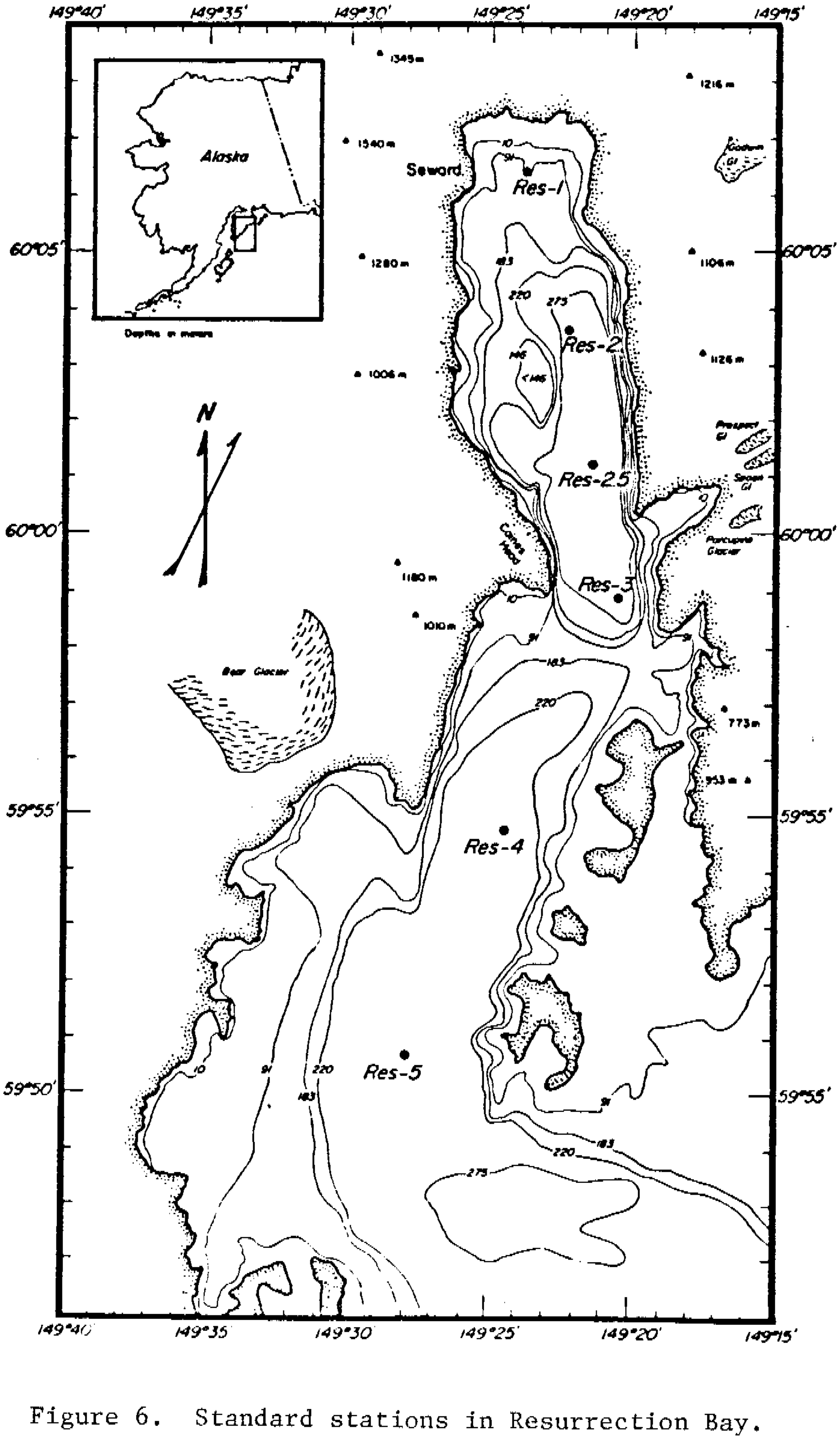

Figure 6. Standard stations in Resurrection Bay.

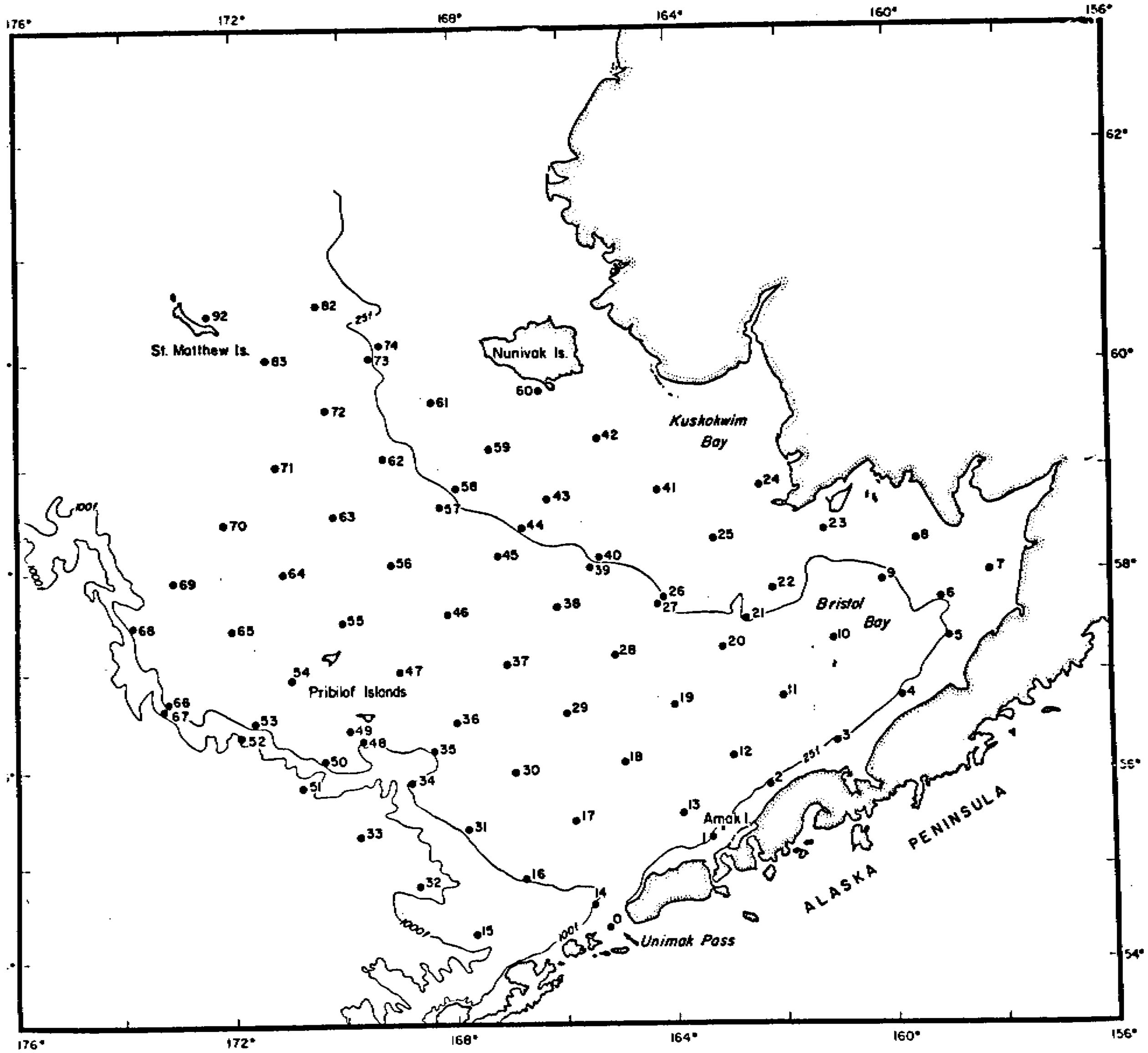

Figure 7. Standard station grid, S. Bering Sea.

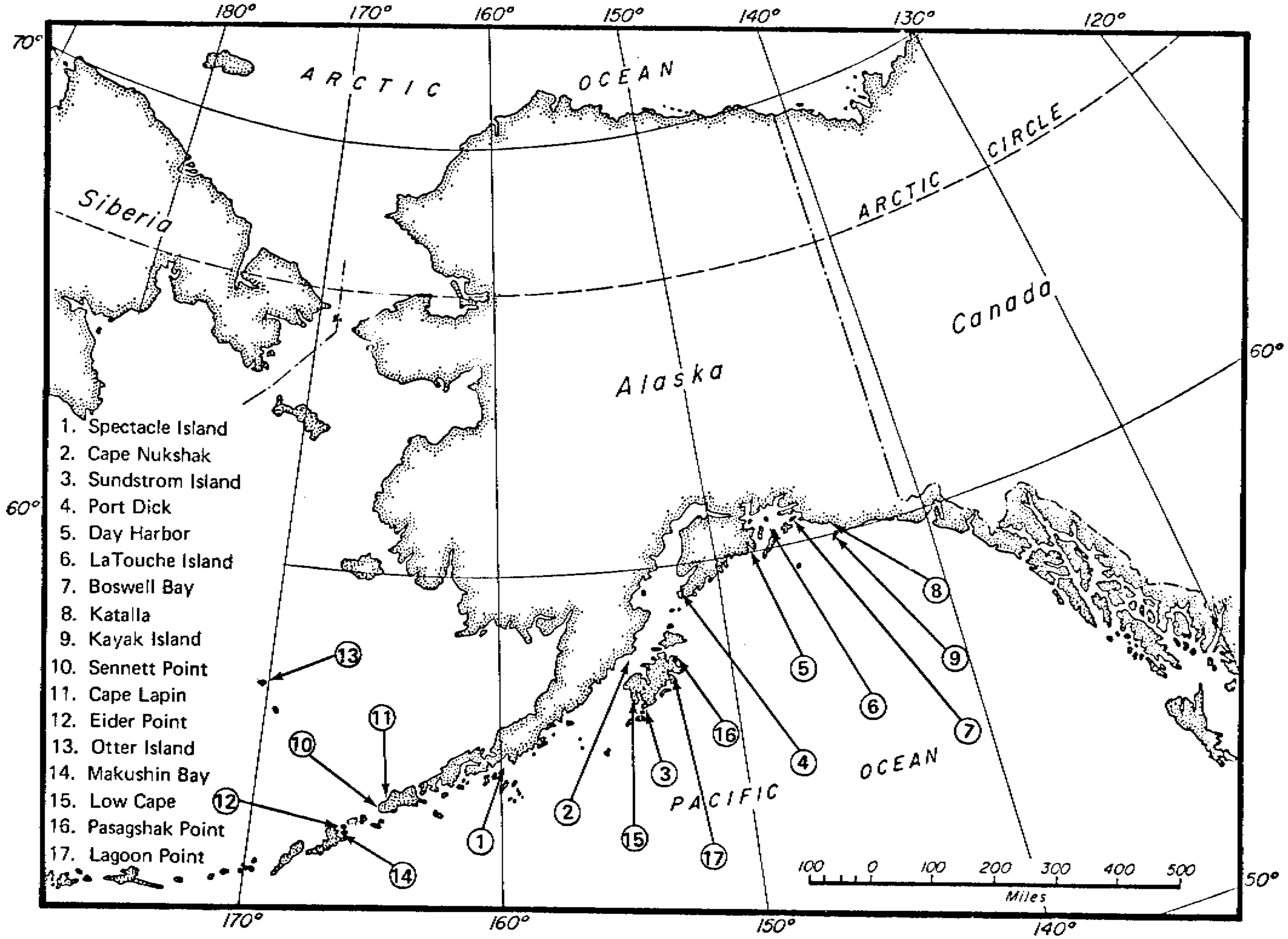

Figure 8. Intertidal biota stations: S. Bering Sea.

TABLE IV

S. BERING SEA

Localities of Intertidal Benthos Samples

Name	Locality	
Akun Island	54°08.5	165°38.7
Amak Island	55°24.1	163°09.3
Crooked Island	58°39.5	160°16.5
Cape Pierce	58°34.4	161°45.5
Point Edward	55°59.5	160°51.6
Cape Mordvinof	54°55.8	164°26.8
Makushin Bay	53°44.0	166°45.8
Zapadai Bay	56°34.1	159°39.8
Otter Island	57°03.0	170°23.8
Cape Lupin (Unimak Is.)	54°56.7	164°08.0
Sennett Point (Unimak Is.)	54°29.1	164°54.4
Eider Point (Unalaska Is.)	53°57.5	166°35.1

Norton Sound and Chukchi Sea

Sediment and water samples were collected on the standard grids shown in Figures 9 and 10 (localities listed in Tables V and VI).

Beaufort Sea

The *Glacier* station grid is shown in Figure 11.

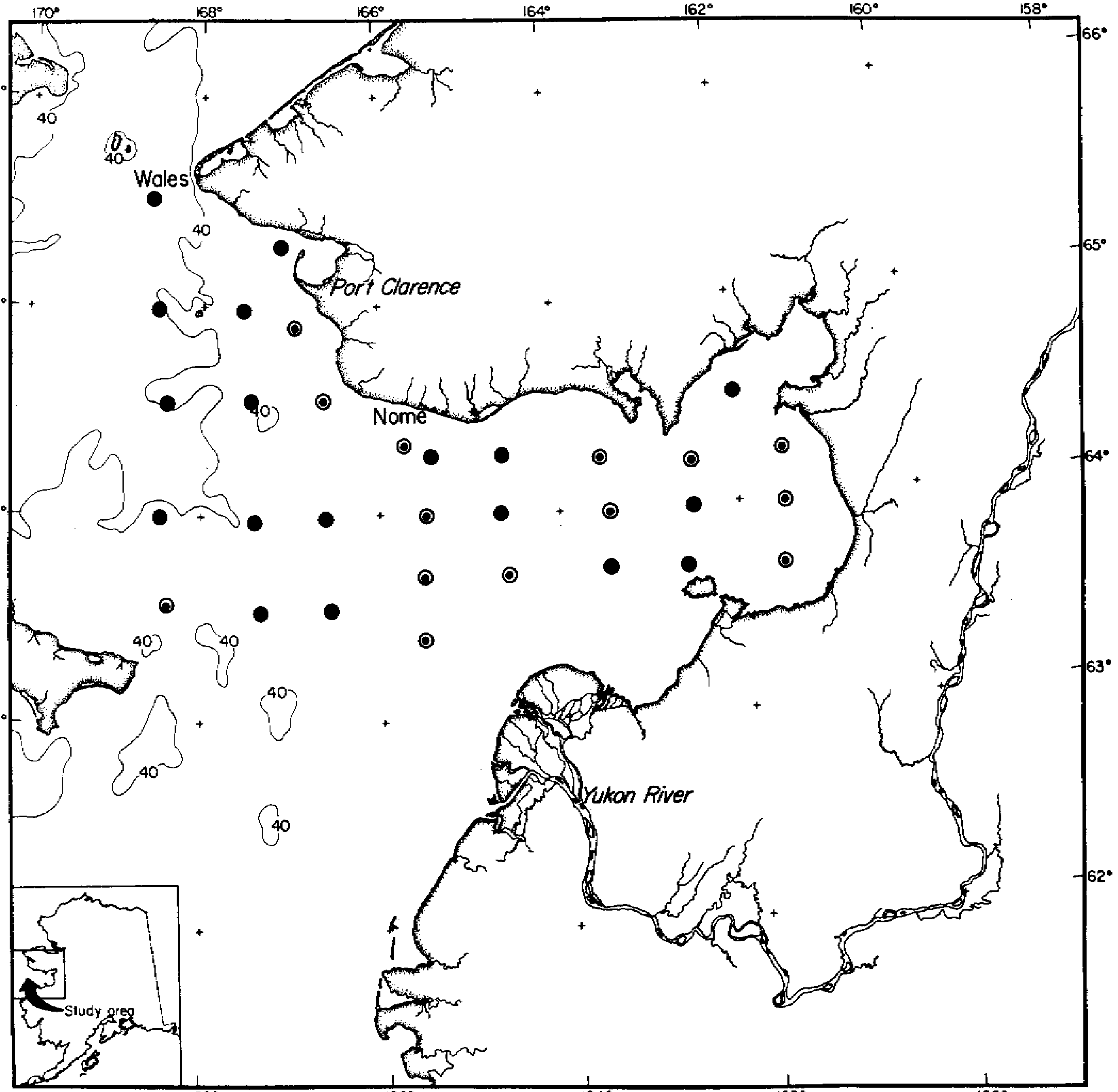

Figure 9. Stations occupied in Norton Sound, *Discoverer*, September 1976.

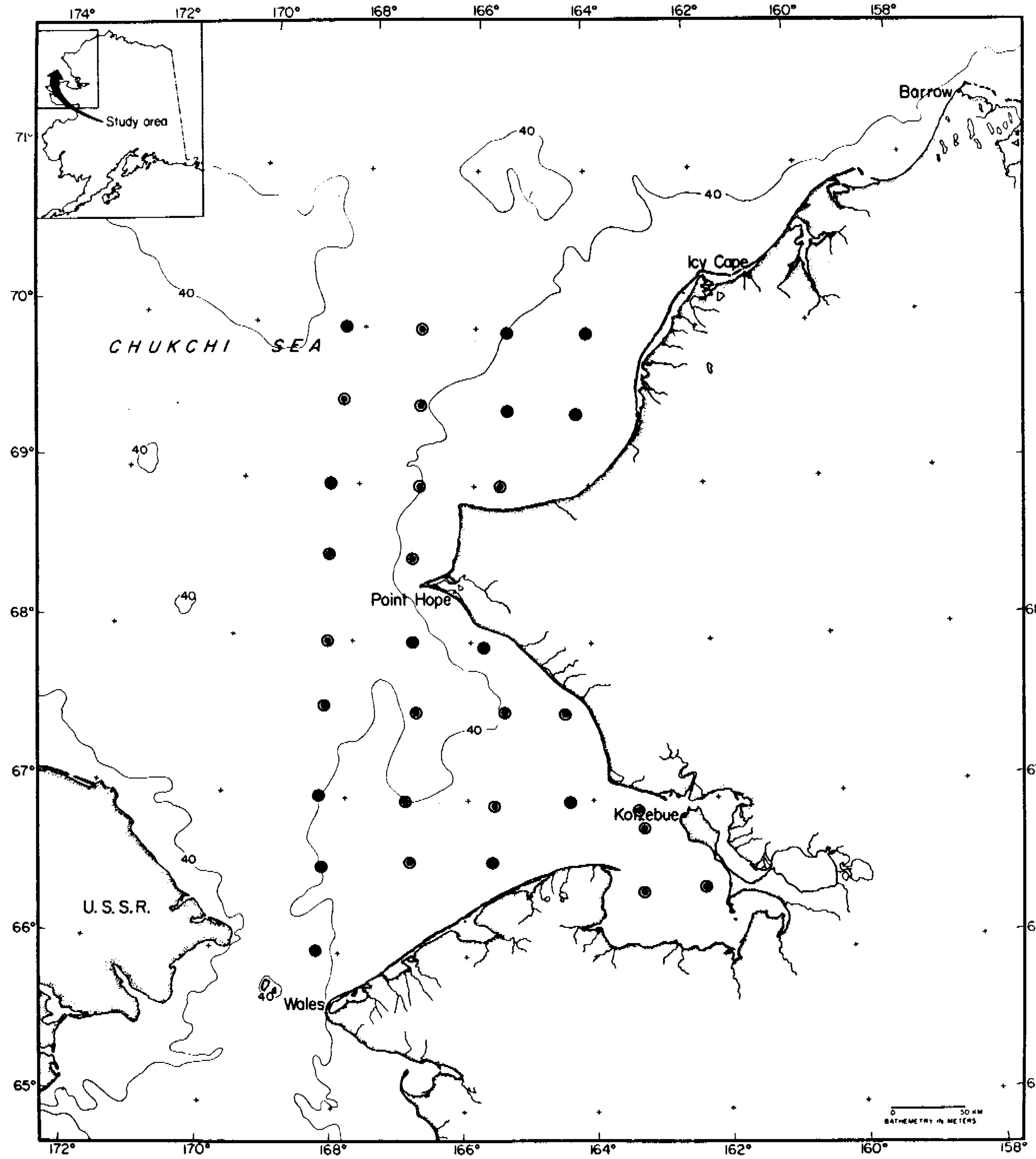

Figure 10. Stations occupied in Chukchi Sea, *Discoverer*, September 1976.

TABLE V

LOWER COOK INLET

R/V *Acona* 4-7 MAY 1977

Intertidal Benthos Collected

Station No.	Locality	Position	Type
1	Kachemak Bay - Mud Bay	59°40 N 151°26 W	*Macoma, Mytilus* *Fucus*, sediment
2	Anchor Point	59°40 N 151°52 W	*Mytilus, Fucus* sediment
3	Outer Bay	59°38 N 151°30 W	*Mytilus, Fucus* sediment
4	Bluff Point - Diamond Creek	59°40 N 151°42 W	*Mytilus, Fucus* sediment

TABLE VI

LOWER COOK INLET

R/V *Acona* June 21-26, 1977

Intertidal Benthos Samples

Station No.	Locality	Position	Type
5	Koyuktulik (Dogfish) Bay	59°14.5 N 151°52.5 W	*Mytilus*, *Fucus*, sediment
6		59°33.2 N 151°36.4 W	Haps core
7	Kasitsna Bay	59°28.8 N 151°34.5 W	*Macoma*, *Mytilus*, *Fucus*, sediment
8		59°03.1 N 153°23.4 W	Haps core
9	Cottonwood Bay	59°38.0 N 153°38.7 W	*Macoma*, *Fucus*, sediment
10	Iniskin Bay	59°43.4 N 153°22.7 W	*Macoma*, *Fucus*, sediment
11	Oil Bay	59°39.1 N 153°18.5 W	*Mytilus*, *Fucus*, sediment
12	Douglas River	59°06.3 N 153°42.2 W	*Mytilus*, *Fucus*, sediment

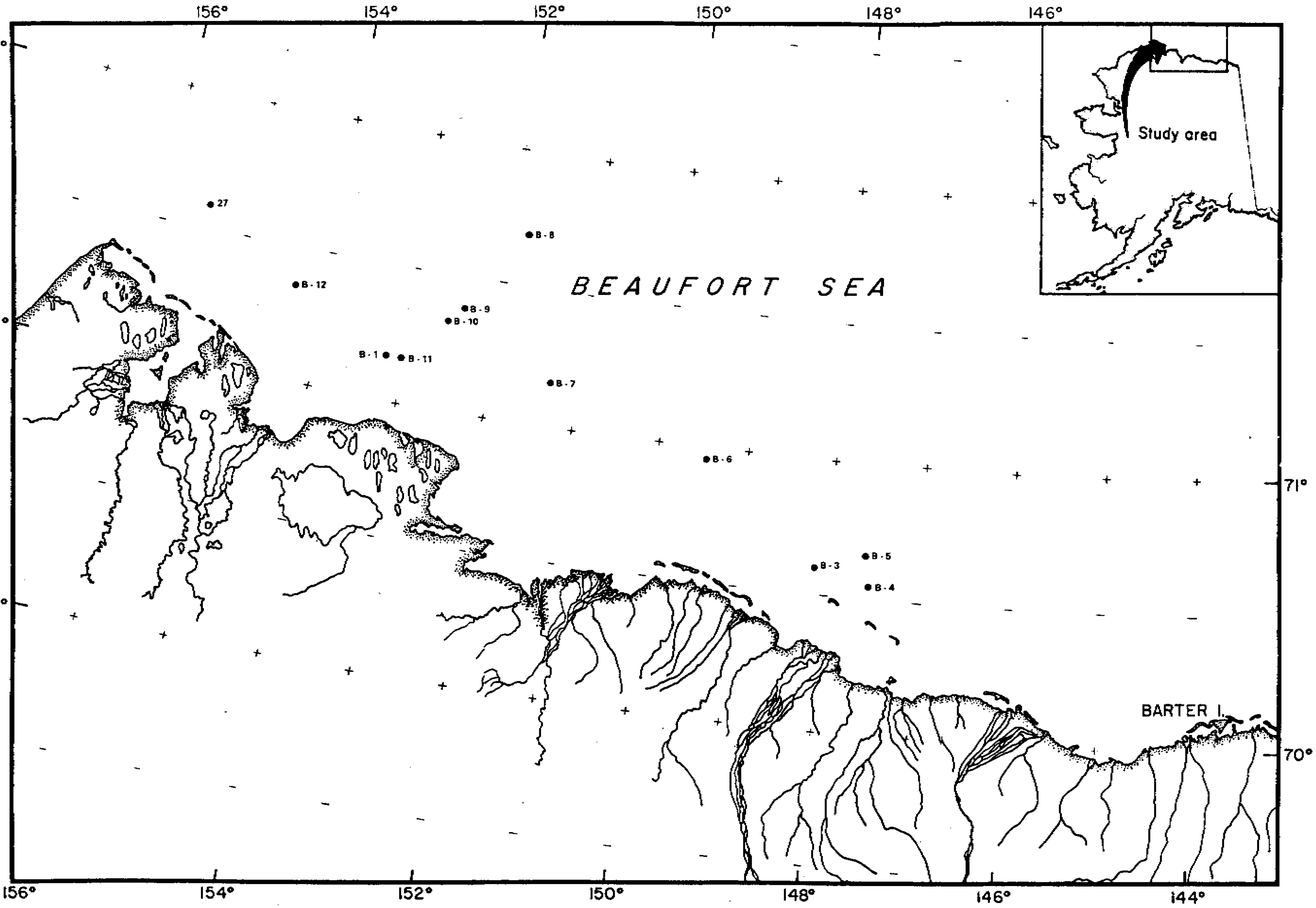

Figure 11. Stations occupied in Beaufort Sea, *Glacier*, August 1976.

V. FIELD AND LABORATORY ACTIVITIES

Field Work 1977-78

1. S. Bering Sea

OSS *Surveyor* 31 March-27 April. Personnel: None from this R.U. Marine mammal samples collected by Dr. Fay. Station locations shown in Figure 12 and listed in Table VII.

2. NEGOA

NEGOA specific study site. R/V *Acona* cruise #240 6-14 April 1977. Personnel: T. Manson, T. Owens, D. Heggie. Hydrographic data, suspended sediment and core samples were taken at four stations in Yakutat Bay (Fig. 13). Major vessel malfunction caused curtailment of the cruise and no stations could be occupied in Icy Bay.

3. Lower Cook Inlet

Specific study site - Kachemak Bay. 2-7 May 1977 (no sampling platform). Personnel: T. Manson. Sediment, *Fucus* and *Mytilus* samples were collected from four intertidal localities (Fig. 14):

a) Inner Bay (Mud Bay)
b) Outer Bay (N.W. of spit)
c) Anchor Point
d) Bluff Point

Macoma samples collected in Inner Bay only (see Table VIII).

4. S. Bering Sea

OSS *Discoverer* 25 May - 5 June 1977. Personnel: None from this R.U. Marine mammal samples were collected for use by Dr. Fay. Station locations are listed in Table IX (Fig. 12).

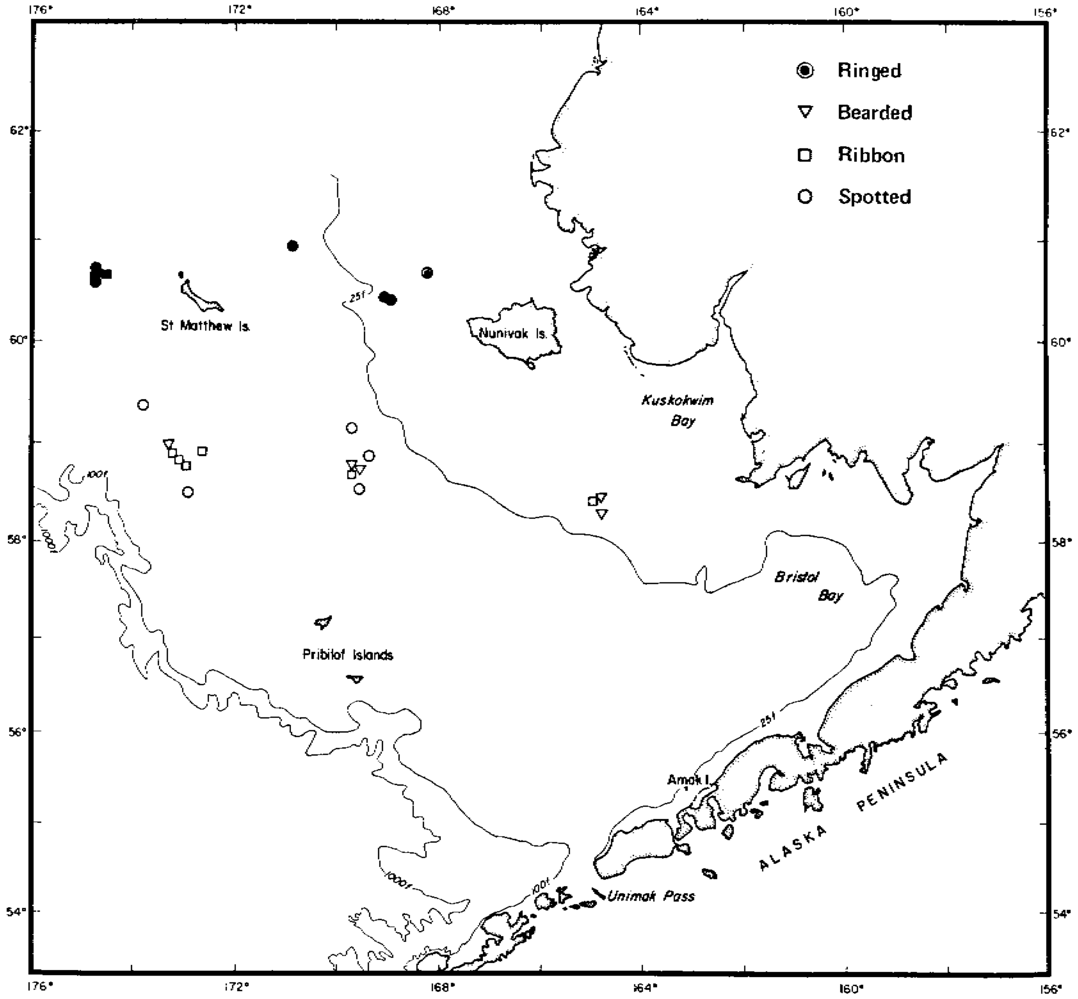

Figure 12. Localities of marine mammal samples collected on *Surveyor* cruise, March-April 1977 and *Discoverer* cruise, May-June 1977.

TABLE VII

BERING SEA

OSS *Surveyor* 31 March - 27 April 1977

Seal samples collected for heavy metal analysis

Sample #	Latitude (N)	Longitude (W)	Species	Sex	Weight (kg)	Age (yrs)
1	58°51.0	173°08.0	Ribbon	F	39.5	1
2	58°51.0	173°08.0	Ribbon	M	102.0	-
3	58°56.0	172°40.0	Ribbon	M	81.8	4
4	58°45.6	172°55.4	Spotted	M	35.0	1
5	59°00.6	173°15.0	Bearded	F	181	6+
6	58°53.0	173°07.0	Ribbon	M	107.3	15
7	58°43.9	169°32.9	Bearded	M	232	12
8	58°48.5	169°41.0	Bearded	F	227	12+
10	59°06.3	169°41.3	Spotted	F	41.8	1
11	58°24.7	164°52.3	Ribbon	F	98.6	3
16	58°21.3	164°49.7	Bearded	F	204.5	2
17			Walrus	F		
28	58°54.2	169°13.6	Spotted	M	89.9	6
29	58°40.1	169°40.3	Ribbon	M	59.9	3
30	58°34.8	169°28.8	Spotted	M	84.0	7
32	59°22.5	173°43.0	Spotted	M	118.0	17

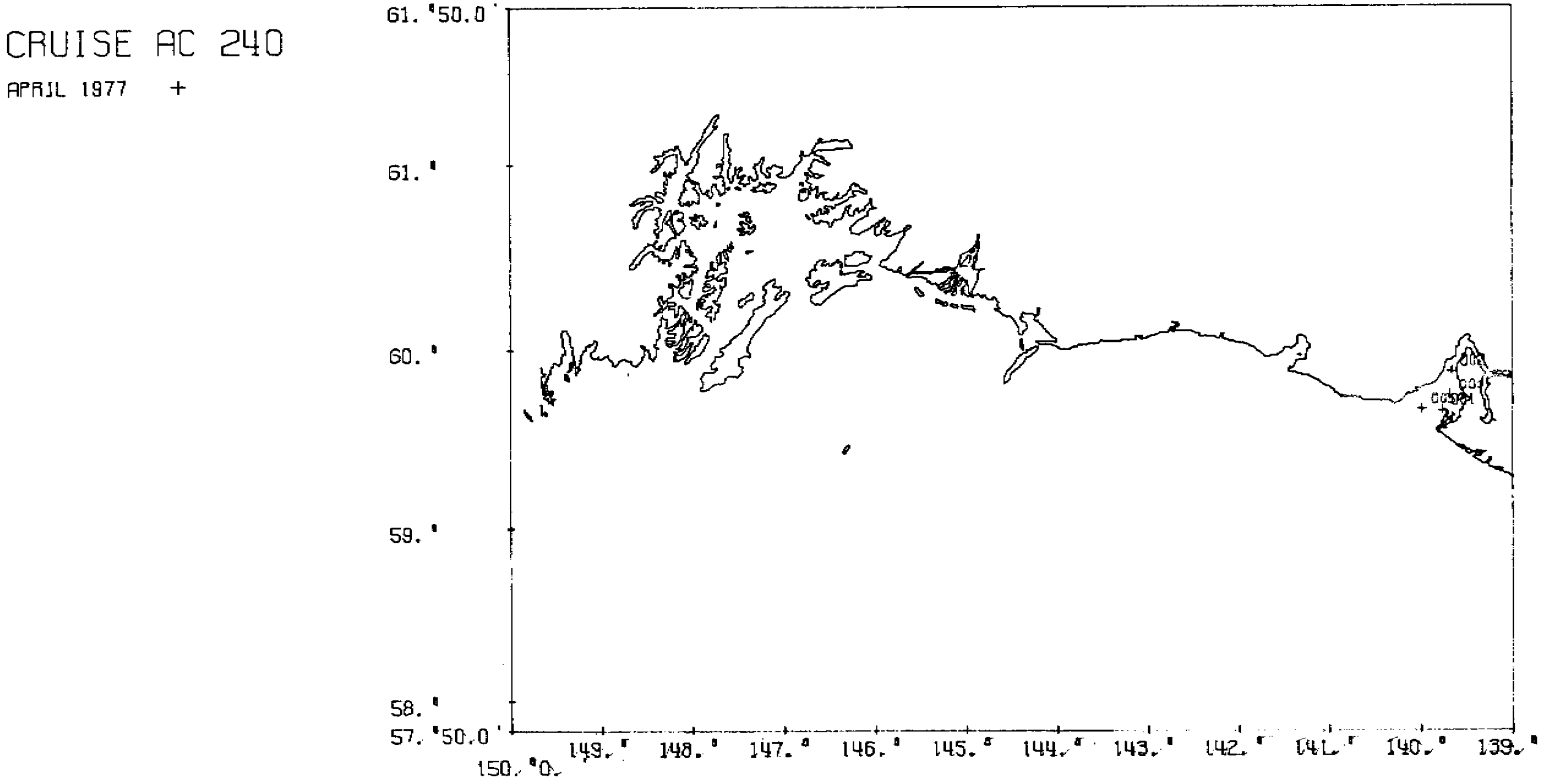

Figure 13. R/V *Acona* Cruise No. 240, April 1977, Stations occupied in Yakutat Bay.

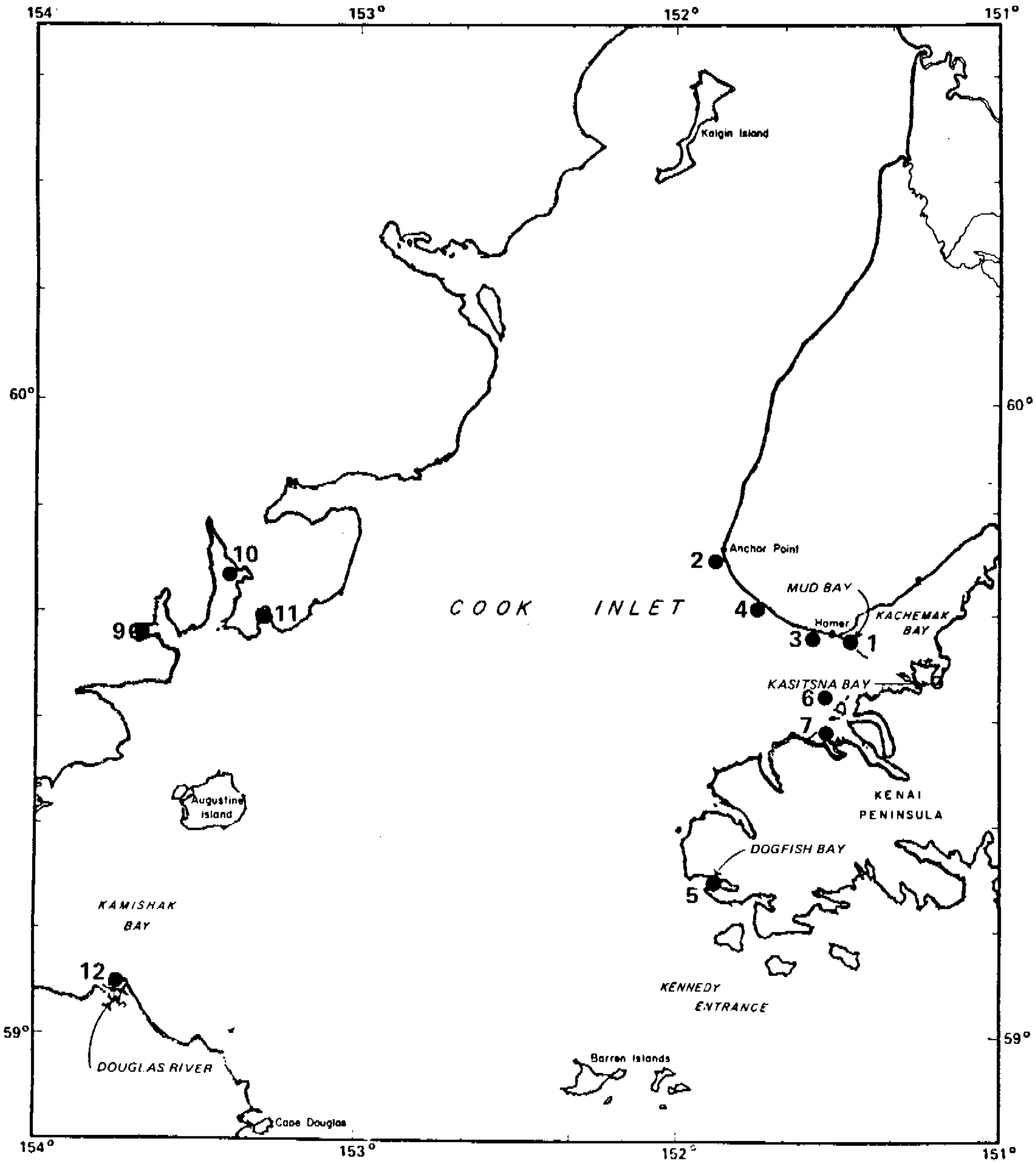

Figure 14. Intertidal sampling localities, Lower Cook Inlet, May and June, 1977.

TABLE VIII

NORTON SOUND (N. BERING SEA)

Discoverer Leg IV - September 8-24, 1976
Station localities and operations

Station No.	Depth	Latitude	Longitude	Sampling Operations
N 1	29 m	63°31.8	168°32.2	van Veen Grab, HAPS, water
N 2	29	63°30.6	167°29.0	van Veen Grab, water
N 3	26.5	63°29.9	166°29.7	van Veen Grab, water
N 4	21	63°19.7	165°29.9	van Veen Grab, HAPS water
N 5	22	63°39.5	165°32.1	van Veen Grab, HAPS water
N 6	13	63°38.4	164°31.0	van Veen Grab, HAPS water
N 7	15	63°38.2	163°30.3	van Veen Grab, water
N 8	15.5	63°42.0	162°28.5	van Veen Grab
N 9	15	63°41.5	161°31.1	van Veen Grab, HAPS, water
N10	37.5	64°01.0	168°26.0	van Veen Grab
N11	40	64°00.4	167°32.1	van Veen Grab
N12	31	63°59.2	166°29.8	van Veen Grab
N12D	26	64°23.5	165°44.8	van Veen Grab, HAPS, water
N13	20	63°59.7	165°29.7	van Veen Grab, HAPS
N14	20	64°01.2	164°28.7	van Veen Grab, water
N15	20	64°00.3	163°30.5	van Veen Grab, HAPS, water
N16	19	64°00.0	162°30.0	van Veen Grab
N17	18.5	64°00.0	161°30.3	van Veen Grab, HAPS, water
N18	23	64°20.2	165°30.0	van Veen Grab
N19	15.5	64°19.4	164°30.4	van Veen Grab
N20	20	64°20.1	163°31.0	van Veen Grab, HAPS, water
N21	19	64°15.25	162°29.7	van Veen Grab, HAPS, water
N22	13	63°30.3	162°00.5	van Veen Grab, water
N23	15	64°17.5	161°30.7	van Veen Grab, HAPS, water
N24	40	64°29.7	168°28.3	van Veen Grab, water
N25	31	64°29.6	167°29.6	van Veen Grab, water
N26	28	64°30.2	166°31.5	van Veen Grab, HAPS, water
N27	46.5	65°00.5	168°26.7	van Veen Grab, water
N28	30	65°00.1	167°31.5	van Veen Grab
N28A	24	64°44.6	167°01.0	van Veen Grab, HAPS
N29	14.5	65°17.8	167°00.4	van Veen Grab
N30		65°30.5	168°31.0	van Veen Grab, water

TABLE IX

BERING SEA

OSS *Discoverer* 25 May - 5 June 1977

Seal samples collected for heavy metal analysis

Sample #	Latitude (N)	Longitude (W)	Species	Sex	Weight (kg)	Age (yrs)
1	60°37.7	174°27.2	Ribbon	M	80.0	10
2	60°36.3	174°37.5	Spotted	F	57.7	10
3	60°36.3	174°37.5	Spotted	M	45.5	0.3
5	60°36.3	174°37.5	Spotted	M	49.1	2
7			Ribbon	M	73.6	7
8	60°26.5	168°55.8	Spotted	F	55.0	4
10	60°24.2	169°49.8	Spotted	M	68.6	5
13	60°35.9	168°10.1	Ringed	M	8.7	1
15	60°56.6	170°48.3	Spotted	F	37.7	<1

5. Lower Cook Inlet

R/V *Acona* 21-26 June, 1977. Personnel: T. Manson. Intertidal sampling trip to collect *Macoma, Mytilus* and *Fucus* (and contiguous sediment) from number of sites in Lower Cook Inlet including the FY 77 designated specific study site (Kachemak Bay), station locations given in Table X.

6. NEGOA

NEGOA specific study site (Yakutat Bay). R/V *Acona* 25-30 July 1977. Personnel: D. C. Burrell, H. V. Weiss, T. Manson, T. Owens, M. Robb. Hydrographic, suspended sediment, nutrient, dissolved and particulate organic carbon, water for heavy metal analysis and interstitial water from cores was taken at a number of stations in Yakutat Bay (Fig. 15). Time limitations prevented any stations being occupied in Icy Bay.

7. S. Bering Sea

U.S.S.R. hydromet vessel *Volna* 23 July-21 August 1977. Personnel: D. T. Heggie. We were requested to participate on this cruise in order to carry out cooperative pollution studies with Soviet scientists. We contracted to do a series of high precision measurements of copper in the euphotic zone. The original objective of this exercise was to do shipboard comparative studies with our Soviet counterparts, but in the event no other heavy metal work of any consequence was carried out. Nevertheless, this was a most useful opportunity to sample from areas of the Bering Sea previously closed to us and we hope that further joint cruises will result. Stations occupied are tabulated in Table XI and shown in Figure 16.

8. Lower Cook Inlet

OSS *Surveyor* 3-17 November 1977. Personnel: T. Manson. Winter collection of sub-tidal benthic species: *Macoma calcarea* and crab. These samples were collected *via* trawl in cooperation with the benthic biology program.

TABLE X

S. CHUKCHI SEA

Discoverer Leg IV - September 8-24, 1976
Station localities and operations

Station No.	Depth	Latitude	Longitude	Sampling Operations
C 1	53	65°59.8	168°20.5	van Veen Grab, water
C 2	49	66°30.1	168°24.1	van Veen Grab, water
C 3	31	66°30.5	167°01.6	van Veen Grab, HAPS, water
C 4	15.5	66°30.0	165°39.2	van Veen Grab
C 5	14	66°18.1	163°13.5	van Veen Grab, HAPS, water
C 6	15	66°23.3	162°14.4	van Veen Grab, HAPS, water
C 7	14	66°44.5	163°17.0	van Veen Grab, HAPS, water
C 7A	13.5	66°52.5	163°09.4	van Veen Grab, HAPS, water
C 8	35	67°00.3	168°26.2	van Veen Grab, water
C 9	42	67°00.2	167°01.9	van Veen Grab, HAPS, water
C10	24	66°58.0	165°46.9	van Veen Grab, HAPS, water
C11	26.5	67°00.0	164°20.0	van Veen Grab
C12	48	67°31.6	168°20.0	van Veen Grab, HAPS, water
C13	46.5	67°30.3	167°02.5	van Veen Grab, HAPS, water
C14	38.5	67°28.9	165°39.5	van Veen Grab, HAPS, water
C15	17	67°26.2	164°18.2	van Veen Grab, HAPS, water
C16	59	68°01.2	168°28.6	van Veen Grab, HAPS, water
C17	52	67°58.8	167°01.5	van Veen Grab, water
C18	28	67°57.3	165°47.8	van Veen Grab, water
C19	52	68°30.0	168°22.0	van Veen Grab, HAPS, water
C20	31.5	68°28.1	167°03.0	van Veen Grab, HAPS, water
C21	51	69°00.3	168°29.3	van Veen Grab
C22	46	68°59.2	166°59.7	van Veen Grab, HAPS
C23	20	69°00.9	165°37.0	van Veen Grab, HAPS
C24	51	69°30.0	168°21.9	van Veen Grab, HAPS
C25	46	69°30.0	167°04.1	van Veen Grab, HAPS
C26	33	69°30.1	165°32.0	van Veen Grab
C27	22	69°29.5	164°11.2	van Veen Grab
C28	45	70°00.7	168°19.4	van Veen Grab
C29	46.5	70°00.0	167°01.2	van Veen Grab, HAPS
C30	40	69°58.5	165°33.4	van Veen Grab
C31	30	69°58.1	164°00.4	van Veen Grab

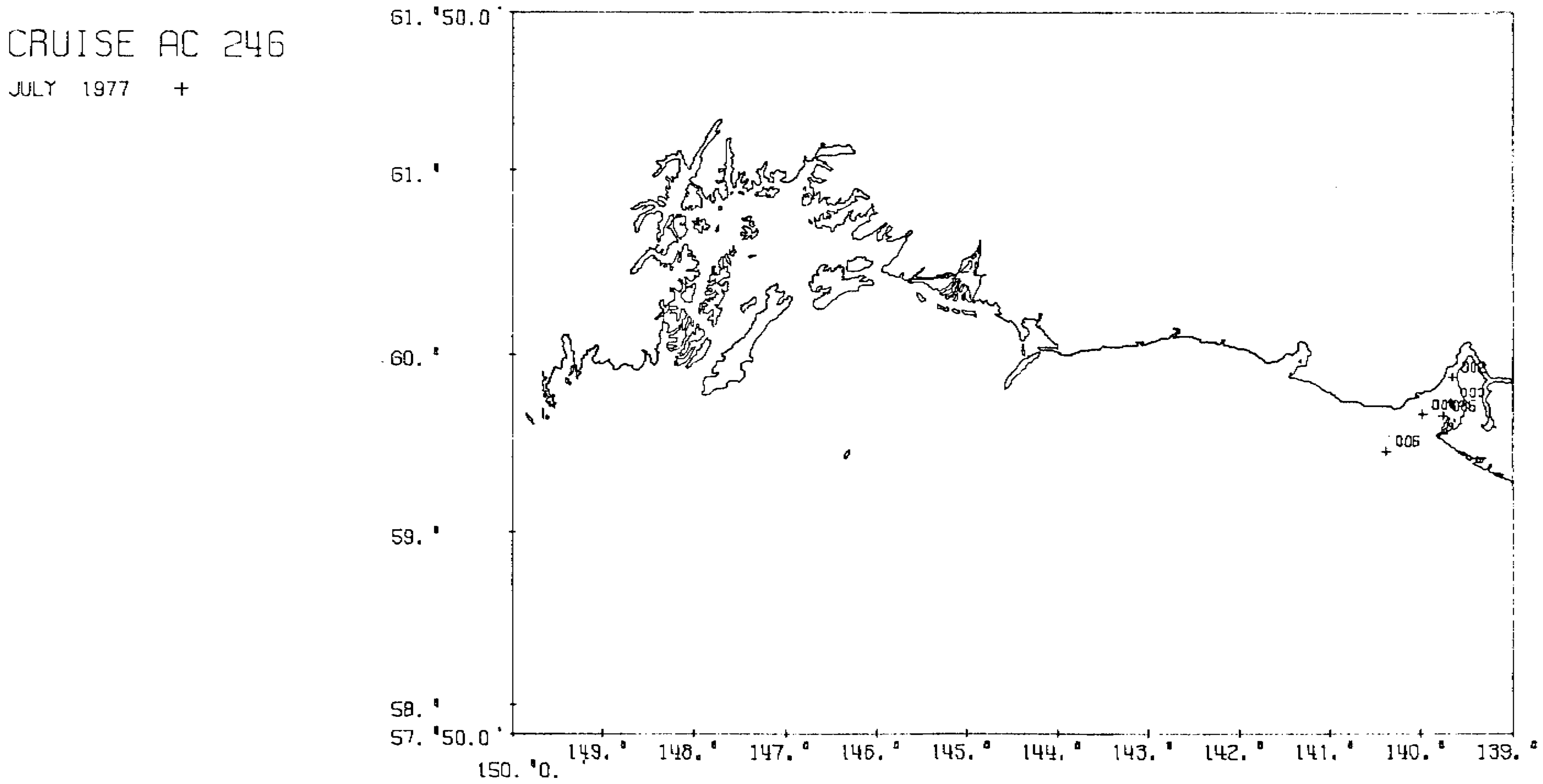

Figure 15. R/V *Acona* Cruise No. 246, July 1977, stations occupied in Yakutat Bay.

TABLE XI

BERING SEA

U.S.S.R. Hydromet Vessel *Volna*, July-August 1977

Locations of heavy metal samples

Station no.	Sample type	Depth (m)	Latitude (n)	Longitude (w)
01	VP	125	57°30	173°20
03	VP	2700	57°59	175°00
05	VP	1140	58°30	176°40
07	VP	225	59°35	178°10
09	VP	115	59°55	174°57
11	VP	70	61°20	173°12
13	VP	70	63°00	173°40
15	VP	50	62°30	171°40
16	SF		62°15	170°50
17	VP	44	62°00	170°00
19	VP	29	61°30	168°10
21	VP	62	60°49	171°32
23	VP	100	59°58	173°20
26	VP	110	57°45	174°10
28	VP	2700	58°15	175°50
30	VP	140	59°01	177°18
32	VP	137	59°12	175°48
34	VP	85	60°37	174°05
36	VP	58	62°02	172°17
38	VP	57	62°45	172°40
40	VP	41	62°15	170°50
42	VP	38	61°45	169°05
44	VP	48	61°32	170°36
45	SF		60°50	171°32
46	VP	58	60°07	172°28
48	VP	139	58°41	174°10

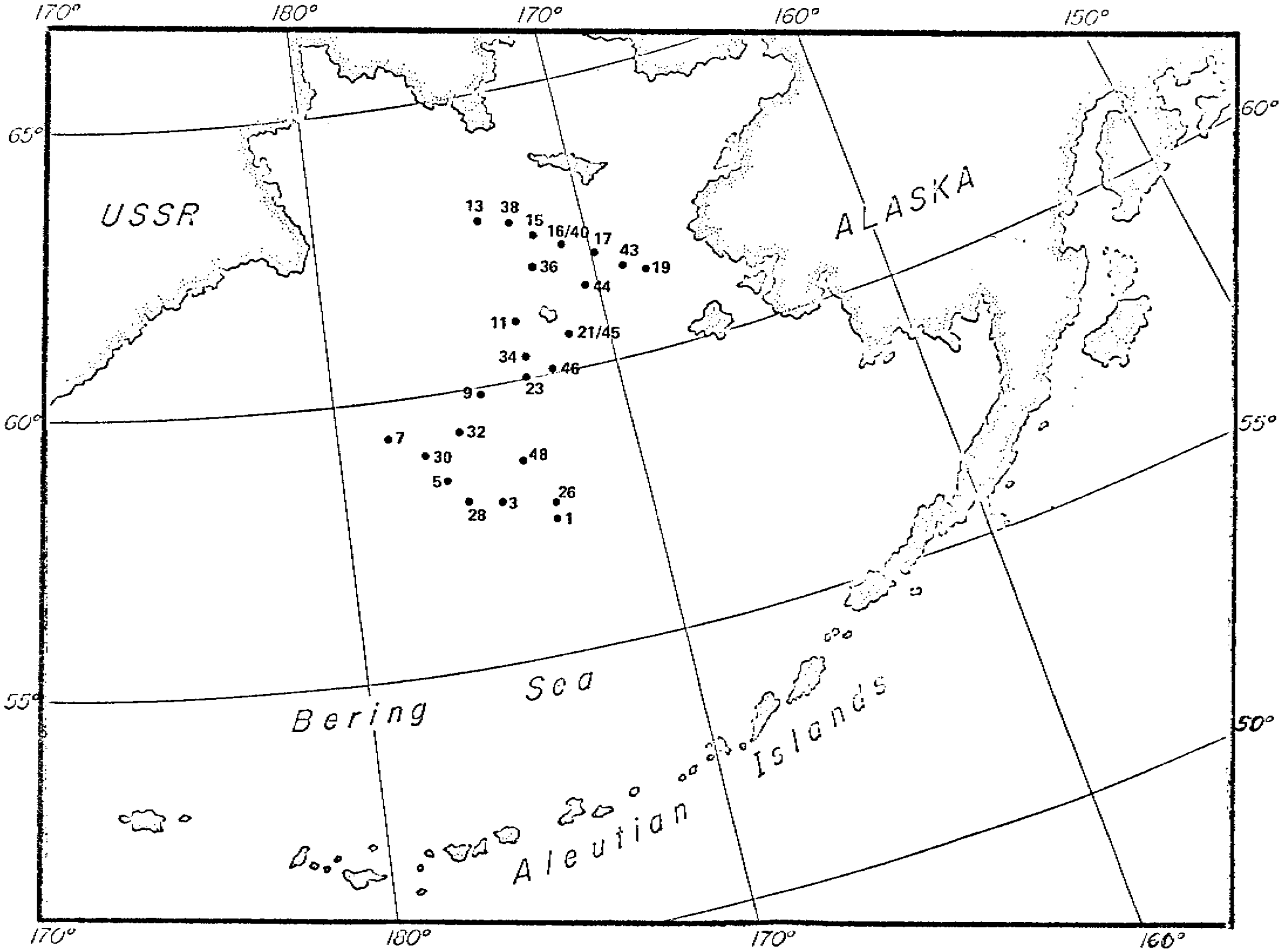

Figure 16. U.S.S.R. hydromet vessel *Volna*, stations occupied in Bering Sea for heavy metal sampling, July-August 1977.

Sediment samples were collected also when possible using the Haps contamination-free corer. Samples collected are listed in Table XII. Additional live samples of the subtidal *Macoma* were collected for laboratory experiments. Stations occupied are listed in Table XIII and the localities shown in Figure 17.

9. Resurrection Bay (Lower Cook Inlet project)

R/V *Acona* #254 28 November-2 December 1977. Personnel: D. C. Burrell, T. Owens, M. Robb, D. Weihs. Winter survey of hydrography, nutrient distributions and other chemical parameters in this estuary as shown in Tables XIV and XV. The primary objective of this cruise was to continue to obtain seasonal data for heavy metal distributions at the benthic boundary and within the water column. This inlet is a proxy for Lower Cook Inlet. Intertidal *Macoma* samples were also collected for aquaria experiments.

10. Lower Cook Inlet

At the time of writing of this report, preparations are being made to make a further sub-tidal benthic sampling trip and also to collect live *Macoma baltica* samples for aquaria experiments.

Field Collection Methods

Biota Samples

Fin fish and trawl samples collected for us by other investigators were placed whole in polyethylene bags and stored frozen. Sub-tidal and intertidal benthos samples collected by our own personnel were hand sorted, placed in clean seawater for 24 hours to allow depuration and stored frozen. The marine mammal (seal) specimens were dissected shipboard and separate tissue samples were stored frozen. In the laboratory, these latter samples were sub-sampled to avoid the outer exposed layers.

TABLE XII

LOWER COOK INLET

Surveyor 3-17 November 1977

Sub-tidal species collected

Station	Surficial Sediment Sample	Sole	Crab[a]	Macoma	Neptunia
B		x			x
5			2		
27	x		1	x	
35			2		x
37	x	x	2	x[b]	
40	x	x	8		x
41			8		
53			4		x
62	x	x	6		x

a - Number of individual samples

b - Live subtidal *Macoma calcarea* to be used for aquaria experiments

TABLE XIII

LOWER COOK INLET

Surveyor 3-17 November 1977

Operations & Sample Locations

Station	Sample	Lat N	Lat W	Distance (nm)
B	Trawl	59°39.2'	151°45.7'	
		59°39.5'	151°46.9'	1.0
5	Trawl	59°01.6'	153°01.4'	
		59°03.4'	152°59.3'	2.2
27	Trawl	59°16.0'	153°33.2'	
		59°16.7'	153°36.6'	1.8
	Haps	59°15.0'	153°29.0'	
35	Trawl	59°27.2'	153°17.9'	
		59°27.3'	153°19.3'	1.5
37	Trawl	59°40.8'	151°13.6'	
		59°40.2'	151°14.8'	1.0
	Haps	59°41.2'	151°17.8'	
40	Trawl	59°35.7'	151°47.7'	
		59°36.4'	151°49.0'	1.1
	Haps	59°33.6"	151°44.6'	
41	Trawl	59°33.3'	151°53.9'	
		59°33.2'	151°56.0'	1.1
53	Trawl	59°32.2'	153°08.0	
		59°31.8'	153°10.6'	1.6
62	Trawl	59°40.8'	152°56.4'	
		59°46.0'	152°56.5'	0.8
	Haps	59°46.0'	152°56.2'	

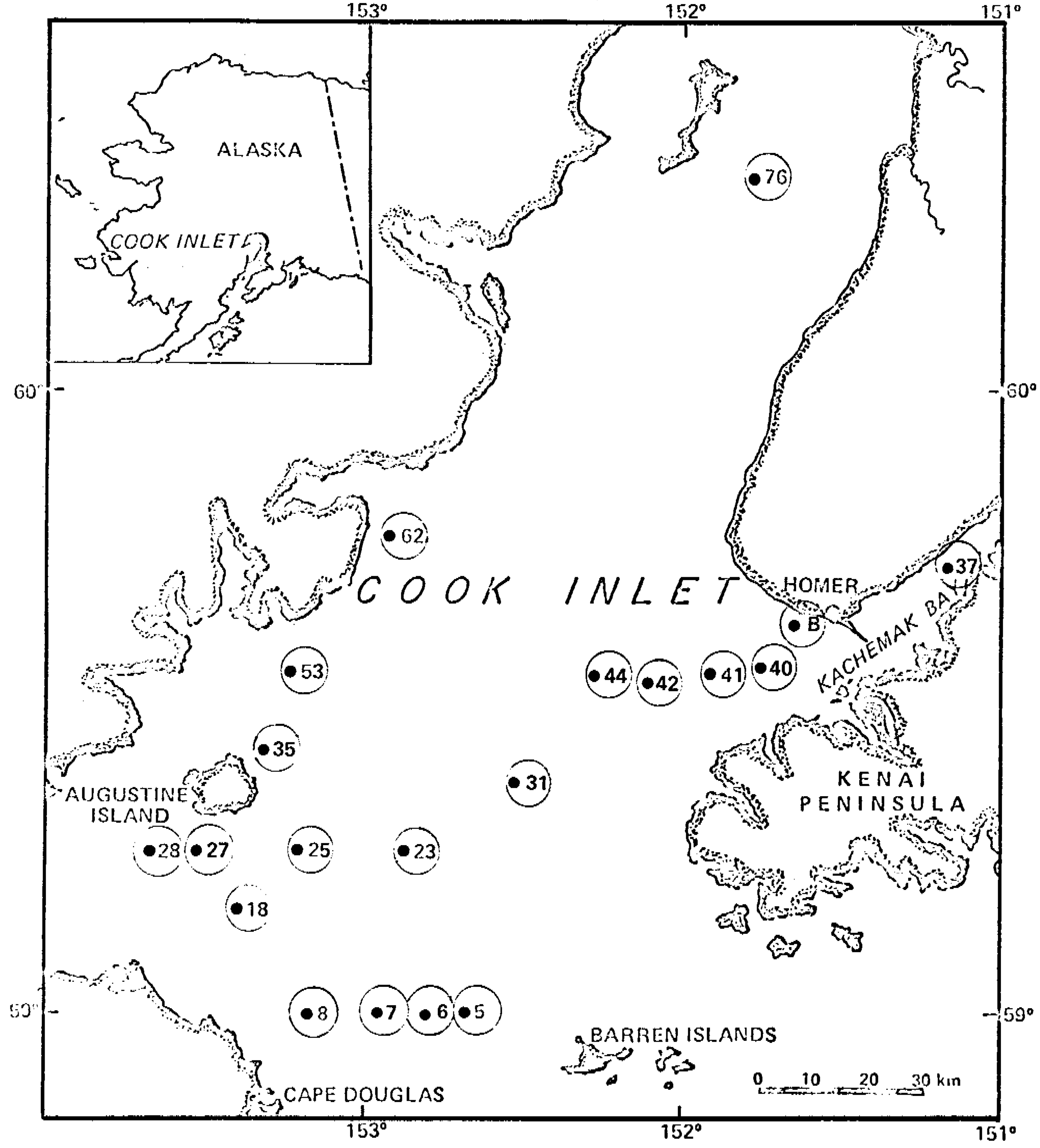

Figure 17. Lower Cook Inlet, *Surveyor*, 3-17 November 1977.

TABLE XIV

RESURRECTION BAY

R/V *Acona* No. 254 December 1977

Station Locations

Resurrection Bay

Res 1	60°06.5'	149°23.8'
Res 2	60°03.5'	149°23.4'
Res 2.5	60°01.2'	149°21.5'
Res 2.5 A	60°01.2'	149°23.0'
Res 2.5 B	60°01.2'	149°20.6'
Res 3		
Res 3.5	59°57.9'	149°20.7'
Res 4	59°54.7'	149°24.5'

Aialik Inlet

A1	59°53.7'	149°41.4
A3	59°45.7'	149°41.3'

TABLE XV

RESURRECTION BAY

R/V *Acona* Cruise 254 - December 1977

Operations

Physical and Chemical Observations

11.28	0856	001	Res 1	38 m	STD
11.29	0041	009	Res 2	168 m	STD, Hydro, Nuts
	0316	010	Res 3.5 A	278 m	STD, Hydro, Nuts
	0600	011	Res 2.5 B	275 m	STD, Hydro, Nuts
	1352	014	Res 3.5	193 m	STD, Hydro, Nuts
	1518	015	Res 4	255 m	STD, Hydro, Nuts
11.30	2125	0.7	Res 2.5	289 m	STD, Hydro, Nuts SS, Doc, Poc. TM
12.1	1511	020	A 1		STD, Hydro, Nuts
12.2	0730	024	A 2		STD

Many of the biota samples collected by biological investigators unfortunately had to be rejected for heavy metal analysis because of suspected or demonstrated contamination.

Sediment Samples

Most sediment samples recovered specifically for extractable heavy metal contents have been taken using the Haps stainless-steel corer as described in the previous Annual Reports. Samples for interstitial water heavy metal flux studies were obtained in plastic core liners in a Benthos corer (using a stainless-steel core cutter but no metal barrel). The cores were extruded in the usual way but within a glove bag under a nitrogen atmosphere and directly into a series of Reeburgh-type non-metallic squeezers.

Water Samples

We have now standardized on a system for collecting water samples at sea for soluble heavy metal analysis. Since we have experimented with a number of procedures (and have had others forced on us because of the limitations of various sampling platforms) it would seem useful at this point to summarize our experience and make recommendations for future collection.

Early OCS work was carried out (and is still being performed to some extent) on NOAA vessels. None of these are specifically equipped to recover good contamination-free samples and therefore all collection procedures employed have and will be a compromise to some extent. For example, it is now an anathema in the chemical oceanographic community to collect water samples for this purpose from wire-hung bottles. All the samples collected to date from the *Surveyor*, *Discoverer* and *Oceanographer* have been so obtained and these data must be suspect to some extent because of this. Similarly, trace metal chemists, where they must use discrete samplers for deep waters, have virtually standardized on the go-flo type which contains no contaminating inner parts and which is isolated from the sea surface. The latter is inevitably contaminated because of discharges from the vessel. This type of bottle is still not ideal and further modifications are to be expected but it is a major advance on the samplers which were standard NOAA vessel equipment in the early days of the OCSEAP project. We have also samplers which are dedicated solely to this purpose and are specially cleaned and carefully stored. Use of ships Rosette sampling bottles is less than ideal because these are general purpose samplers.

On *Acona* sampling trips the following trace metal sampling techniques are employed:

1. Use of 10 ℓ Niskin go-flo bottles which are used only for this purpose. Each bottle is acid cleaned and carefully stored and all samples taken are identified with the individual bottle.

2. These samplers are hung on Kevlar non-metallic line wound on a drum coated with non-metallic material and the bottles are tripped with coated messengers. The line is run out over a wooden block.

3. Water is directly pressure filtered (using nitrogen at 10 lb/sq in) from the bottle through an in-line filter and into a storage container. The nitrogen used to pressurize the bottle is filtered and the water filter holder and collection is done within a glove bag.

4. Filters used are washed, stored in acid and changed in a hood.

5. Sample collection bottles are all from a single batch which was carefully cleaned according to a standardized sequence and these bottles have been subsequently re-cleaned and re-cycled.

A different sampling procedure was attempted on the recent *Volna* cruise where only shallow water samples were required. In this case, water was pumped to and through the in-line filter directly using acid washed 3/4" I. D. polyethylane tubing and a high capacity Masterflex tube pump. Concurrently water samples were taken *via* a submersible pump installed on a CSTD system. A comparison of these data - which clearly demonstrates contamination from the bottles - will be given in the next report.

The problems of collecting uncontaminated water samples for heavy metal analysis are, of course, well known. We have never been happy with the procedures and equipment available on the NOAA vessels most often assigned to this project. As noted in the Discussion sections the means of the soluble metals correspond very closely to the generally accepted values for open waters but in every batch some obviously anomolous values have been rejected and some data sets have been discarded entirely from the earlier cruises. Because soluble heavy metal analysis is an exceedingly expensive operation, we have also tended not to analyze more recent sample batches which have not been collected according to the methods outlined above (e.g., those from the Chukchi and Beaufort Seas).

The same clean water sampling procedure has also been used in the estuarine field areas for obtaining samples for nutrient, dissolved and particulate organic carbon and suspended sediment analysis.

Laboratory Analysis Program

1. Soluble Cu, Pb and Cd by DPASV

The techniques used here are basically as described in previous Annual Reports. The limiting step is collection, as described above.

2. Soluble Cr and Se by GLC - Dr. T. A. Gosink

Procedures given in previous Annual Reports.

3. NAA of water - Dr. D. E. Robertson

We are in the middle of the seawater neutron activation analyses. Because of the tremendous amounts of ^{24}Na (15.4 hrs) which are produced during neutron irradiation of seawater, INNA of seawater is applicable only for those elements in seawater which have relatively long half-life activation products. None of the short-lived neutron activation products of interest could possibly be measured instrumentally, since the ^{24}Na, ^{38}Cl, ^{42}K and ^{82}Br are orders of magnitude more abundant and completely mask the gamma-ray contributions of the activation products of interest. We have developed radiochemical separation schemes for analyses of short-lived activation products of interest and have already, or are presently employing them for the determination of V, As and Ag. For the INAA of sea salts, the neutron irradiated samples are stored for about one month to allow these relatively short-lived interfering radionuclides to decay to tolerable concentrations.

The month-old activated sea salts are then transferred into a constant counting geometry (small polyethylene vials or stainless steel planchets) and counted directly on a Ge(Li) diode detector or a dual coincidence gamma-ray spectrometer. The following elements are then measured: Zn, Co, Sb, U, Cs, Rb, Sr, Fe and Sc.

4. Soluble Mn and Cu by NAA - Dr. H. V. Weiss

This method is based upon the simultaneous isolation of copper and manganese from seawater by cocrystallization with 8-hydroxyquinoline (oxine). The crystals are irradiated with neutrons, and following simple radiochemical purification steps radio-induced ^{64}Cu and ^{56}Mn are quantified by gamma-ray spectrometry.

Chemicals. A solution was prepared to contain 10% (w/v) oxine in ethyl alcohol. Manganese and copper carrier solutions contained 10 mg ml^{-1} of cation in distilled water. Comparators were 1 and 4 μg ml^{-1} of manganese and copper, respectively. Hydrogen sulfide gas was of CP quality, while other chemicals were of AR grade.

Isolation of Copper and Manganese from Seawater. Seawater was acidified with concentrated hydrochloric or nitric acid to a final concentration of 1% (v/v). Aliquots (250 ml) were transferred to containers and received 10^{-2} μCi of a high specific activity ^{64}Cu (10^2 μCi g^{-1}Cu) or 0.1 ml of a carrier-free ^{54}Mn. The solution was warmed for 1 hr on a hot-plate to approximately 80°C to equilibrate the radioelement with its counterpart in the sample. After cooling, an oxine solution (2.5 ml) was stirred into the sample and ammonium was encouraged by agitation with a rod. After the solution stood for 1 to 2 hrs, the crystals were collected on sintered glass of medium porosity. The isolated crystals, together with those adhering to the container walls, were dissolved in dilute nitric acid (1.6 N). The gamma-ray activity of the solution was measured in a well-type NaI(Tl) detector and compared with a tracer standard.

Treatment of Seawater Samples. Seawater was collected on two occasions 20 ft below the surface off the end of the pier at the Scripps Institution of Oceanography, La Jolla, California. One collection took place on 2 July 1976, while the other was not dated. At the time of collection the samples were acidified - the undated with nitric acid and the dated with hydrochloric acid (10 ml 1^{-1} of seawater) - and then filtered through a millipore membrane (0.45 μm). Aliquots (250 g) were transferred to plastic beakers; Mn (0.2 μg) and

Cu (2.0 μg) were added to some aliquots. ^{54}Mn tracer was then added, and the elements were cocrystallized. The solution was next passed through a small filter membrane (1 cm diam) that was supported in a 7-ml polyethylene, snap-top, irradiation vial whose bottom was perforated with approximately 10 holes (0.05 cm diam). The ^{54}Mn gamma-ray activity of the separated crystals was measured and compared with a standard to correct for the fraction of oxine that adhered to the walls of the sample container.

Blanks. The copper and manganese content was determined, at least in duplicate, for oxine (250 mg), ethyl alcohol (2.5 ml), and ammonium hydroxide (2.5 ml). These reagents were used in these amounts in the preirradiation processing and were not common to the other procedure used in the comparative study. For future reference, these elements were also quantified in 2.5 ml aliquots of high-purity nitric acid (Ultrex, J. T. Baker).

Comparators. Each comparator solution (1 ml) was irradiated separately.

Irradiation. Samples, comparators, and blanks were irradiated for 2 hrs at full-power in the TRIGA Reactor, University of California, Irvine, California. The flux was 1 x 10^{12} neutrons cm^{-2}sec^{-1}, and the specimens were rotated about the reactor core at 1 rev/min^{-1}.

Radiochemical Purification and Measurement. After irradiation the sample or blank was quantitatively transferred with 50 ml of 3 N HCl to a vessel that contained 1 and 2 ml of copper and manganese carriers, respectively. All blanks received a standard quantity of ^{54}Mn and, except for the oxine blank, they also received 250 mg of oxine. H_2S gas was bubbled for 30 sec through the solution, and the resultant

CuS precipitate was collected by filtration. The filtrate was made ammoniacal, and the precipitated oxinate was collected and then dissolved in 50-ml concentrated HNO_3. The solution was heated over a flame for several minutes to degrade the oxine and, while hot solid $KBrO_3$ was added to precipitate MnO_2. After cooling in an ice-bath, the precipitate was separated by filtration.

The corresponding carrier was added to the comparator, and the Mn comparator was spiked with a standard quantity of ^{54}Mn. Copper was precipitated as described above; the Mn comparator was brought to 50 ml with concentrated HNO_3, heated, and then treated with $KBrO_3$.

All precipitates to be measured were collected on membrane filters, covered with a complementary paper disc, and bagged in polyethylene.

The induced radioactivities were measured flat against the surface of a 38-cm Ge(Li) detector coupled to a 4096 pulse-height analyzer. The gamma-ray pulses were accumulated for 10 to 20 min under live-time counting conditions. The pulse-height data were fed into a computer which provided the net counting rate for the 511 and 847 KeV photopeaks of ^{64}Cu and ^{56}Mn. The count rate was normalized for the ^{54}Mn yield determined prior to irradiation and for the lapse of time from the end of the irradiation.

Carrier Yield Determinations. The ^{54}Mn photopeak (834.8 KeV) of MnO_2 precipitates was measured at least 3 days after irradiation with a flat NaI(Tl) detector that was coupled to a 400-channel analyzer. The net count rate was corrected for the ^{54}Mn yield that was determined after the cocrystallization step. To permit comparison of these data with the ^{54}Mn standard solution, which was gross counted with a well detector, a factor was derived to normalize the different counting modes. A sample, determined to be radiochemically pure by gamma-ray spectrometry, was dissolved in concentrated HCl and counted in the same manner as the standard. With the factor derived from these two sample counts, the ^{54}Mn standard was adjusted to permit comparison of pulse-height analyzed samples with the solution standard, a process which provided the Mn carrier yield.

The filter membrane containing the precipitated copper was folded and inserted into a 1.3-ml, snap-top, polyethylene vial to which 0.6 ml of distilled water was added. Standards (0.6 ml of carrier solution) placed in similar vials also received a blank filter membrane to reproduce volume and geometric conditions. Samples and standards were irradiated for precisely 60 sec in a pneumatic tube facility with the reactor at full power. The 511-KeV photopeak of ^{64}Cu was measured in the manner described for the sample. After correction for decay from the end of the irradiation, comparison of the reirradiated samples with standards allowed calculation of the copper carrier yield.

The normalized ^{56}Mn and ^{64}Cu of the original irradiation were corrected for these yields. Upon comparison of fully normalized samples and comparator photopeaks, the weight of element in the sample was computed.

Results. In at least four assays during the cocrystallization step, the recovery of Mn and Cu was 99.8 ± 1.3 and 100.4 ± 1.4%.

Data show that following the initial acidification 0.003 ± 0.001 and 0.022 ± 0.004 μg of Mn and Cu were added to the sample by way of oxine, ethyl alcohol, and ammonium hydroxide. If nitric acid of the quality analyzed had been used in the acidification process, an additional 0.003

± 0.001 and 0.005 ± 0.001 of the respective elements would have been introduced.

Discussion. In the crystallization step, copper and manganese were carried quantitatively with the solid phase. However, in subsequent processing the 5 to 10% of the oxine that adhered to the container walls was not transferred to the irradiation vial. A quantitative transfer was effected expeditiously by dissolution with acid. However, this treatment was precluded, since dissolved oxinate underwent degradation during the neutron bombardment which complicated the subsequent precipitation of the oxinate in the radiochemical purification of manganese.

The loss of metal-carrying oxine was corrected by measurement of the ^{54}Mn yield after transfer to the irradiation vial. Since Mn and Cu were completely cocrystallized, this yield also applied to Cu. Further, by not adding additional reagents before the irradiation, the blank was also minimized.

At the end of a 2-hr irradiation period, 1.2×10^3 and 3.5×10^4 photopeak counts min^{-1} were accumulated per microgram of Cu and Mn. Thus submicrogram amounts of these elements quantifiable with acceptable counting statistical error. Since the usual concentrations of Mn and Cu in seawater center around tenths of a part per billion (ppb) for Mn and ppb for Cu, even the modest irradiation schedule adopted provides for adequate sensitivity.

5. Soluble Vandium by NAA - Dr. H. V. Weiss

Chemicals and tracer. Iron carrier solution was prepared by dissolving 99.999% pure iron powder in *aqua regia* and diluting with distilled water to a final concentration of 10 mg ml. Vanadium-48 solution in the carrier-free form was prepared as vanadium(1V) in 0.1 M hydrochloric acid.

Vanadium standard (2 μg ml) was made from a commercial 100-ppm standard prepared from ammonium metavanadate. Other reagents used were of analytical reagent grade.

Instruments. The ^{48}V tracer was gamma-counted with an NaI(Tl) well-type detector coupled to a scaler. The neutron-induced ^{52}V was measured with a 38-cm^3 Ge(Li) detector associated with a 4096-channel pulse-height analyzer. The pulse-height data were transferred onto magnetic tape and thence into a computer, which provided the net counting rate for the 1434-keV photopeak of neutron-activated vanadium.

Isolation of vanadium from seawater. Iron carrier (1 mg/100 g of sample) was added to a weighed amount ($\leqslant$ 100 g) of acidified seawater. A known ^{48}V activity, usually about 10^4 cpm, was also added. Some samples were also treated with 0.1 ml of the vanadium standard at this stage. The solution was kept at 70-80° for 1 hr to facilitate exchange between the various oxidation states of vanadium in solution. After cooling, the pH was adjusted to about 7 with 8 M ammonia and the precipitate was coagulated by warming, and collected on a sintered-glass disc of medium porosity, washed with water to remove residual salts and dissolved in a small volume of 8 M nitric acid. The solution was transferred to a 7-ml polyethylene irradiation vial and brought to a final weight of 5.00 ± 0.05 g with 8 M nitric acid (4.13 ml). The recovery of ^{48}V in this solution was determined by comparison of its gamma-ray activity with that of a tracer standard (to provide information on the amount of sample solution transferred to the vial).

Blanks and standards. Three blanks were prepared namely 100 μℓ of the iron carrier solution in 8 M nitric acid, 8 M nitric acid, and 8 M ammonia. The standards were also made up in 8 M nitric acid and contained

0.2 μg of vanadium. Blanks, standards and samples all had the same volume, obtained by weighing the solution, the specific gravity of which was known.

Irradiation and measurement. Samples, blanks and standards were irradiated sequentially, each for 180 sec, in the pneumatic tube assembly of the TRIGA nuclear reactor at the University of California, Irvine, California. The thermal-neutron flux at the terminal end of this assembly is $3 \times 10^{12} n.cm^{-2} sec^{-1}$. After irradiation the sample was transferred to a 14-ml polyethylene vial, and the original vial was rinsed once with 1.5 ml of distilled water, the rinse being added to the irradiated solution. The sample was positioned in the center of the Ge(Li) detector and separated from it by a plastic beta-particle absorber, 2 cm thick. The gamma-ray pulses were accumulated for 180 sec, commencing 90 sec after the end of the irradiation. The instrumental dead-time at the beginning and end of the counting interval was recorded. The 1434-keV photopeak of ^{52}V was corrected for the mean dead-time value and the isotopic yield in the initial isolation step. The corresponding quantity of vanadium was calculated by simple proportion from standards corrected for dead-time.

6. Dissolved Oxygen

Oxygens are determined using the Chesapeake Bay Institute Technique (Carpenter, 1965). The samples are drawn from the niskin bottles and pickled with 1 ml of 3 M manganous chloride and 1 ml of sodium hydroxide-potassium iodide solution (670 g and 600 g per liter respectively). The sample can then be stored for as long as a few days before analysis. The analyses consists of acidifying the sample with 1 ml of 10 N sulfuric acid and titrating the sample with 0.2 M sodium thiosulfate to a clear endpoint in the presence of starch using a micropipet-buret.

7. Nutrients

Nutrient analyses were made using Technicon Autoanalyzer procedures based on the manual methods of Murphy and Riley (1967) for reactive phospherous and Armstrong, Sterns, and Strickland (1967) for dissolved silicon, nitrite. Ammonia was measured by the phenol-hypochlorite method of Koroluff (1970), as adapted by Shawyk and MacIssac (1972).

Ammonia: Ammonia is determined by the Berthelot reaction in which hypochlorous acid and phenol react with ammonia in aqueous alkaline solution to form indophenol blue, an intensely blue chromophore with an absorption maximum at 637 nm.

Orthosilic Acid: Orthosilic acid is determined by its reaction with molybolate in aqueous acidic solution to form silicomolybdic acid. In this procedure stannous chloride is used to reduce silicomolybdite acid to the heteropoly acid which has an absorption maximum at 820 nm.

Nitrate, Nitrite, Nitrite: Nitrite is determined by the Greiss reaction in which sulfanilamide and N-(l-naphthyl) ethylenidiamine dihydrochloride (NNED) reacts with nitrite in aqueous acidic solution to form an intensely pink diazo dye with an absorption maximum at 570 nm. Nitrate, after it is reduced to nitrite by passage through a column containing copperized cadmium filings, is determined in an identical manner. Thus, the sum of nitrate plus nitrite is determined in the nitrate procedure.

Orthophosphate: Phosphate is determined as phosphomolybdic acid which in its reduced form in the presence of antimony has an absorption maximum at $\sim$ 880 nm.

The nutrient concentrations are then calculated from comparison with standards made in an artificial salt solution (∿ the same salinity as the samples) after correcting for any refractive compounds that may be in the sample. This correction is made by running a sample with the color producing agents replaced by suitable solutions.

8. Salinity

Salinity was measured on board ship with a Guildline 8400 Autosal.

9. Dissolved and Particulate Organic Carbon

This procedure is a modification of the method of Strickland and Parsons (1968) as used by Loder (1971) and as outlined by the Oceanography International Corporation for use with their total carbon system. Two prepared glass fiber filters (Gelman AE, 42 mm, 4.5 μ, prebaked at 500°C for 4 hr) are placed on a standard Millipore vacuum filter apparatus and approximately 1ℓ of seawater is filtered. If samples were held for longer than one hour (as was normal) $MgCl_2$ was added (final concentration equaled ∿ $10^{-5}M\ Hg^{++}$) to retard biological activity. The filters are then placed in separate 10 ml ampules (prebaked at 500°C for 4 hr) containing 0.2 gm $K_2S_2O_8$, 0.25 ml of 6% H_3PO_4 and 5 ml of deionized-triple distilled water is added to this. Two 5-ml aliquots of the filtrate are placed in 10 ml ampules containing 0.2 gm $K_2S_2O_8$ and 0.25 ml of 6% H_3PO_4. All four ampules are then flushed with purified oxygen to remove CO_2 and then sealed for future analysis. On every cruise reagent blank ampules were made up (these consist of an ampule with 0.2 gm $K_2S_2O_8$ and 0.25 ml of 6% H_3PO_4 and various volumes of water). Standards are then prepared using the same reagents and dextrose where the carbon concentrations range from 0.0-3.2 mg C/ℓ for DOC and 0.0 - 2560 μg C/ampules for POC. The water used in this process is deionized-triple distilled and was found to contain 0.77 ng C/ℓ. The ampules are baken in a pressure bomb at 175°C for 24 hrs to oxidize the organic material to CO_2. After cooling to room temperature, the samples are analyzed using a Beckman IR (model 1215) and recorded on a Sargent recorder equipped with a disc integrater. The standards were then plotted as integration units *vs.* carbon concentration with the integration of 0.0 mgC taken as zero. The reagent blank is the value of a linear regression line through the points of integration units *vs.* volume for the reagent blank ampules. The DOC value is the carbon concentration corresponding to the value of the sample integration units minus the reagent blank on the DOC standards graph. The POC value in the carbon concentration corresponding to the integration units of the sample filter minus the integration units of the blank filter of the POC standards graph divided by the volume of the filtered water.

10. AAS Analysis of Biota Tissue - (Dr. D. C. Burrell)

Procedures used for the preparation of biota tissue for atomic absorption analysis prior to the 1977-78 contract period have been described in previous reports. The following outlines procedures currently in use: The sample is freeze dried, ground to a fine powder and approximately one grain of the tissue is weighed onto a tared watch glass (quartz where a freon/oxygen mix is subsequently used in the furnace). Each sample is prepared in duplicate or triplicate depending upon the amount of available material. Samples prepared thus are then oxidized in a low temperature plasma ashing furnace. It was found that a R.F. power setting of 50 watts and pressure of 1.5 torr works well in maintaining low ashing temperatures in the chambers, but it then takes up to 48 hrs to effectively ash some tissue (especially orchard leaf standards). After oxidation the contents of each watch glass are transferred to an all-teflon digestion bomb. Three ml of Ultrex grade nitric acid are added and digestion effected for 2 hrs in a 90°C water bath. After cooling, the contents are transferred to 30 ml centrifuge tubes and diluted to 25 ml. These solutions are then analyzed *via* carbon furnace or flame (depending on concentrations) atomic absorption. The standard curves run with each batch are prepared by adding standards to a matrix prepared in bulk for each type of tissue sample. NBS standard samples are carried through with each batch of samples to monitor accuracy.

11. INAA of Biota - (Dr. D. E. Robertson)

In practice, the instrumental neutron activation analysis (INAA) of biological tissue samples consists of encapsulating a 10-1000 mg sample of dried tissue (fresh to dry weight ratios should be obtained) in a cleaned plastic irradiation vial, and neutron irradiating the sample and appropriate standards to an integral thermal neutron exposure of about 10^{17} n/cm^2. After the irradiation, the samples and standards are transferred into standard counting geometries and counted on a Ge(Li) detector at optimum times following the irradiation to measure both short- and long-lived neutron activation products. Two to four days out of the reactor the major neutron activation products are ^{24}Na and ^{82}Br, but normally high enough concentrations of ^{42}K and ^{76}As are present for accurate measurements. Some of the data for As, Br, Na and K are included in this report.

After the samples have been out of the reactor for about two weeks, most of the ^{24}Na and much of the ^{82}Br have decayed to tolerable levels, and a new suite of long-lived neutron activation products can be instrumentally measured including Rb, Cs, Fe, Zn, Ag, Co, Cr, Hg, Se, Sb, and Sc.

12. Sediment Size Analysis

Sediment size analysis has been by standard sieve and pipette analysis. Samples from the Gulf of Alaska, Norton Sound and the Chukchi Sea have been fractionated into clay, sand and gravel only with divisions at 4 and -1 ϕ

respectively. The S. Bering Sea samples collected on the June 1975 *Discoverer* cruise have been fractionated into 1/4 ϕ sizes from -0.75 to 10.

13. Particulate Organic Carbon

Has been described above.

14. Particulate Load

PL determinations were made using a modification of the method of Strickland and Parsons (1968). This method included a blank determination for every sample. Two preweighed nucleopore filters (47 mm, 4.5 μ) are placed on a standard Millepore vacuum filtering apparatus and approximately one liter of seawater is filtered (the top filter represents the sample and the bottom filter is the blank). Then 10 ml of distilled water is filtered in order to wash salt from the filters, and the filters are then stored until they can be reweighed. The volume of the filtered seawater is then measured. The particulate load is the increase in the weight difference of the two filters divided by the volume of seawater filtered. Note that the filters must be dried to a constant weight before weighing (60°C for 12 hrs). This procedure was done in duplicate for all samples.

15. Thermal Analysis of Clay Samples - (Dr. A. S. Naidu)

A set of ten random clay samples collected from the S. Bering Sea have been selected for X-ray diffraction analysis and subsequent stepwise heat treatment. For this study, the < 2 μm size fraction of magnesium saturated clays mounted on porous porcelain slides were taken. As noted in the 1976-77 Annual Report, the X-ray diffractiograms on these samples both before and after glycol solvation were already available and these latter have also been used to identify the constituent mineral types. The thermal treatment consisted of subjecting the magnesium saturated clay slides to step-wise heating at 300°C for one hour followed by 550°C for a second hour period using a calibrated muffle furnace. Diffractograms were obtained at the end of each heating period.

16. Al Contents of Particulate Sediments - (Dr. H. V. Weiss)

Details of analysis procedure not available.

17. Hg Species in Sediments - (Dr. H. V. Weiss)

a. Elemental and readily reducible mercury in sediment samples was added to weighed quantity of sediment in an aeration vessel. The mixture was treated as for the determination of Hg in seawater (see methods in Annual Reports) except that the reducing agent was not added. Subsequently the analysis was repeated on the same material after the addition of stannous chloride. The responses were quantified by the method of standard additions.

b. For reducible and organic species of mercury extractable into seawater, sediment was shaken for 1 hour together with 150 ml of unacidified bottom seawater of known mercury content. After separation by centrifugation, half of the seawater was immediately analyzed for reducible mercury. The remainder of the water was acidified with 0.5 ml of nitric acid, irradiated with U.V. light, and analyzed for mercury as before.

18. Extractable Heavy Metals from Sediments

Prior to the 1976-77 contract period, the basic Chester and Hughes extraction procedure was used in order that methodology could be standardized among the various University of Alaska sub-contractors. The outline of this method is as follows: The sediment sample is placed in a plastic whirl pack and freeze-dried for 24 hours. After removal from the freeze drier the sample is crushed to a powder with finger pressure only while still in plastic. One gram is weighed out, removing gravel pieces with forcepts, into a polypropylene bottle. 50 ml of the acid-reducing reagent (25% acetic acid - 1 M hydroxylamine hydrochloride) is added to the bottle which is then mechanically shaken for 4 hours. After settling and filtration through a millipore membrane (HA) into a 50 ml calibrated erlermeyer flask, 2 ml of Ultrex grade nitric acid are added and the solution is evaporated on a hot plate to evolution of acid fumes or until the solution has been reduced to about 2 ml. This latter is then cooled, diluted to 50 ml with distilled water and analyzed *via* atomic absorption analysis.

For the 1976-77 contract period we were requested by BLM to utilize an acid extraction method which had been adopted by BLM contractors in other parts of the country. This method was briefly as follows: The sediment sample was freeze-dried and crushed as described above. 1-2 gm of the dried powder was then placed in a teflon beaker and leached with 50 ml of 25% v/v acetic acid for 2 hr. This solution was filtered, evaporated, diluted and analyzed as described above.

A new extraction procedure will be used for samples collected during the 1977-78 contract period.

19. Laboratory Aquaria Experiments

a. A mixed population of marine heterotrophic bacteria was obtained from marine sediment in Resurrection Bay, diluted and plated on solid medium (Difco Marine Agar 2216) for storage. The plates were incubated at room temperature for two weeks.

Two flasks of marine broth* were made, for a control population for a test population. The test medium was enriched with .1 ppm $CdCl_2$ from a 1000 ppm $CdCl_2$ aqueous solution, then both solutions were adjusted toa pH of 7.5 with NaOH and autoclaved. The flasks were inoculated with cells grown on solid medium. The cells were incubated for 7 days at room temperature.

Aliquots of 15 mls were taken every 24 hr from each flask for cadmium analysis. These samples were first centrifuged for 30 minutes at 20 mg, supernatant (broth) removed and the cell pellet remaining resuspended in natural seawater. The cell slurry was centrifuged again at the above speed and time, seawater supernatant poured off and the cell pellet frozen. Frozen pellets were freeze-dried, weighed, and dissolved in 1 ml of Ultrex nitric acid concentrate. Samples were analyzed by graphite furnace Atomic Absorption Spectroscopy, Perkin Elmer 360 (Fig. 18).

b. *Macoma baltica* were collected from the tidal flats at the head of Resurrection Bay with help from the Seward Marine Station. The clams were placed in a static, natural seawater system on mud from their original habitat. This population was maintained for the control. On day seven of the bacterial culture, a viable cell pellet was obtained from the Cd enriched broth and used to inoculate a petri dish of autoclaved mud. Ten clams were placed on the plate from the control tank and put into a static natural seawater system. The clams were maintained

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* Marine Nutrient broth - and undefined media used for optimizing growth of bacteria. Containing soytone, 1 g; Trypticase, 1 g; Yeast extract, 1 g; Mud extract, 100 mls and natural sea H_2O, 900 mls. Mud extract was made in the lab by autoclaving a mixture of marine sediment 1 kg + 1 ℓ of sea H_2O. Aludoy solution was filtered, preserved under toluene and refrigerated.

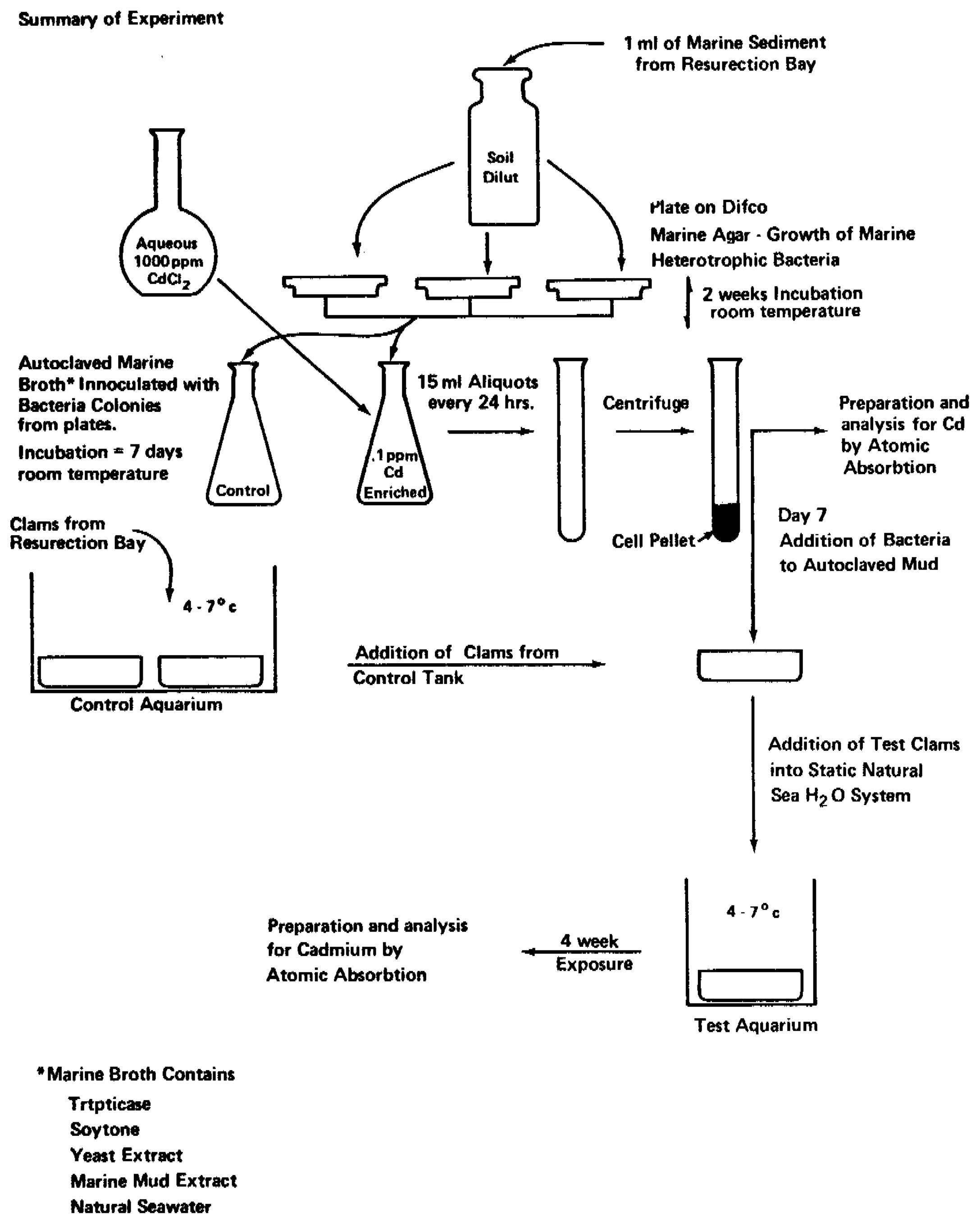

Figure 18. Food chain transfers; aquaria experiments.

in this tank for four weeks. Samples were made at 2 weeks and 4 weeks. Clams were placed in a small container with fresh sea H_2O for 2-4 hours and allowed to void their digestive system and to clean their outer surfaces of debris. They were removed from the clean tank frozen and freeze-dried. The freeze-dried tissue was removed from the shell, weighed, and dissolved in 1 ml of concentrated Ultrex Nitric acid. Cadmium analysis was done by atomic absorption on the Perkin Elmer 360, graphite furnace.

VI. and VII. RESULTS AND DISCUSSION

Gulf of Alaska and Kodiak Island

We have sampled the Gulf of Alaska over two field seasons. Basically the standard hydrographic grids shown in Figures 1 and 2 have been used, but the vessels used could generally only occupy a fraction of the grids per sampling trip. Samples for the northwest Gulf region are very sparse and there was no opportunity to cover the shelf region immediately adjacent to Kodiak Island. Stations occupied on the early *Acona* cruises are given in Figures 19-21; cruise plots for the later NOAA vessels have been given in previous Annual Reports.

A detailed discussion of the concentrations of soluble heavy metals in the Gulf waters has been given in the 1977 Annual Report. Concentration are uniform throughout the area, and uniformly low (Table XVI). Dr. T. A. Gosink (see Appendix I) has noted that water column samples also show lower than average values for both selenium and chromium; particularly the former except for surface waters contain copious quantities of biological material. In addition to contents in water filtered at 0.4 μm, a number of analyses of coexisting particulate contents have been obtained by the Battelle N.W. Laboratories. As would be expected, particulate heavy metal fractions are enhanced in near shore *versus* deep water and in near-bottom waters as compared with surface; this reflects the increased total particulate sediment loads in these zones. In the case of vanadium, where we have data for both soluble and particulate contents, the particulate fraction constitutes, on average, a negligible 3% of the total vanadium in the water column. Soluble mercury speciation has been discussed by Weiss *et al.* (Abstract included in Appendix III).

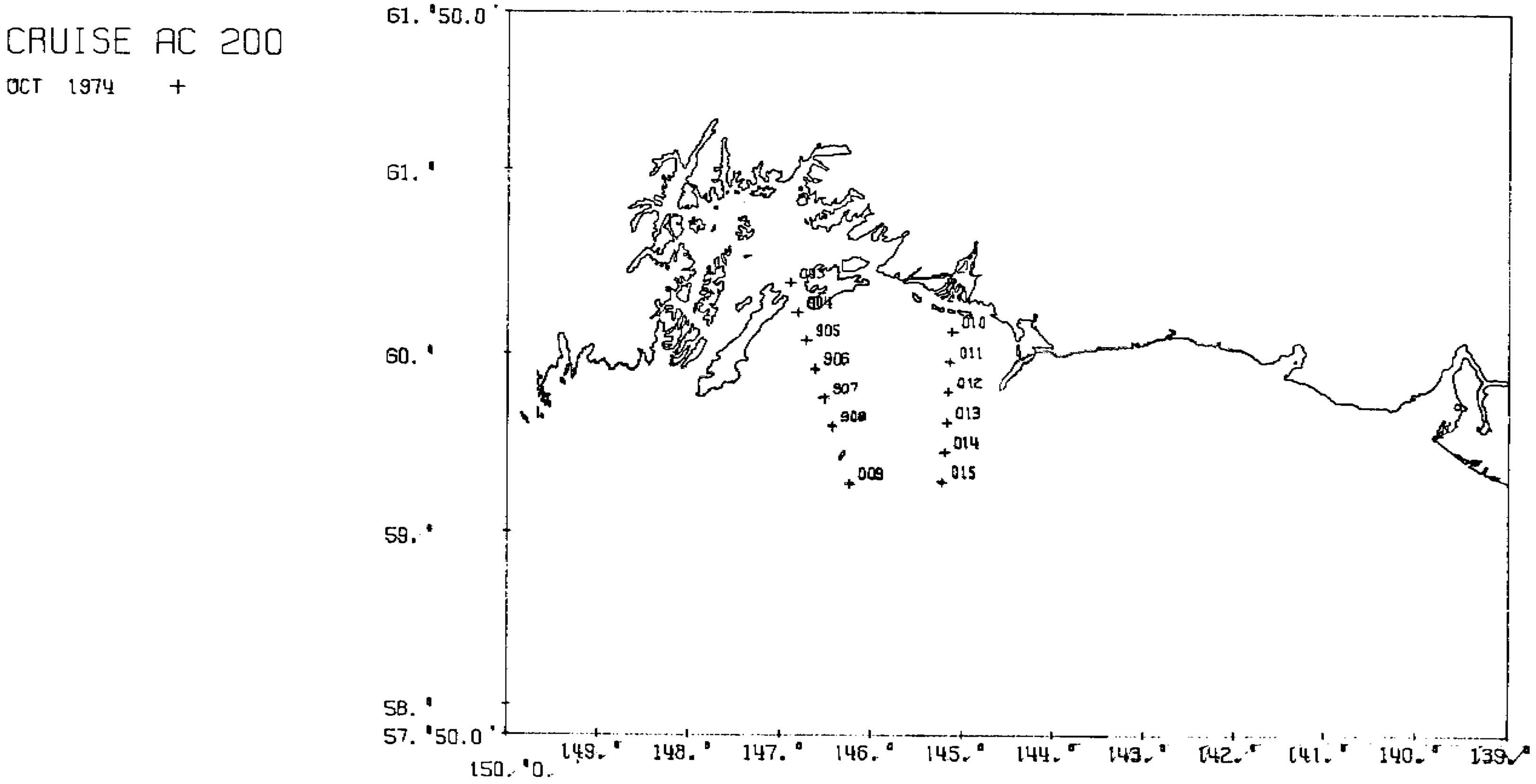

Figure 19. Station localities, R/V *Acona* #200, October 1974.

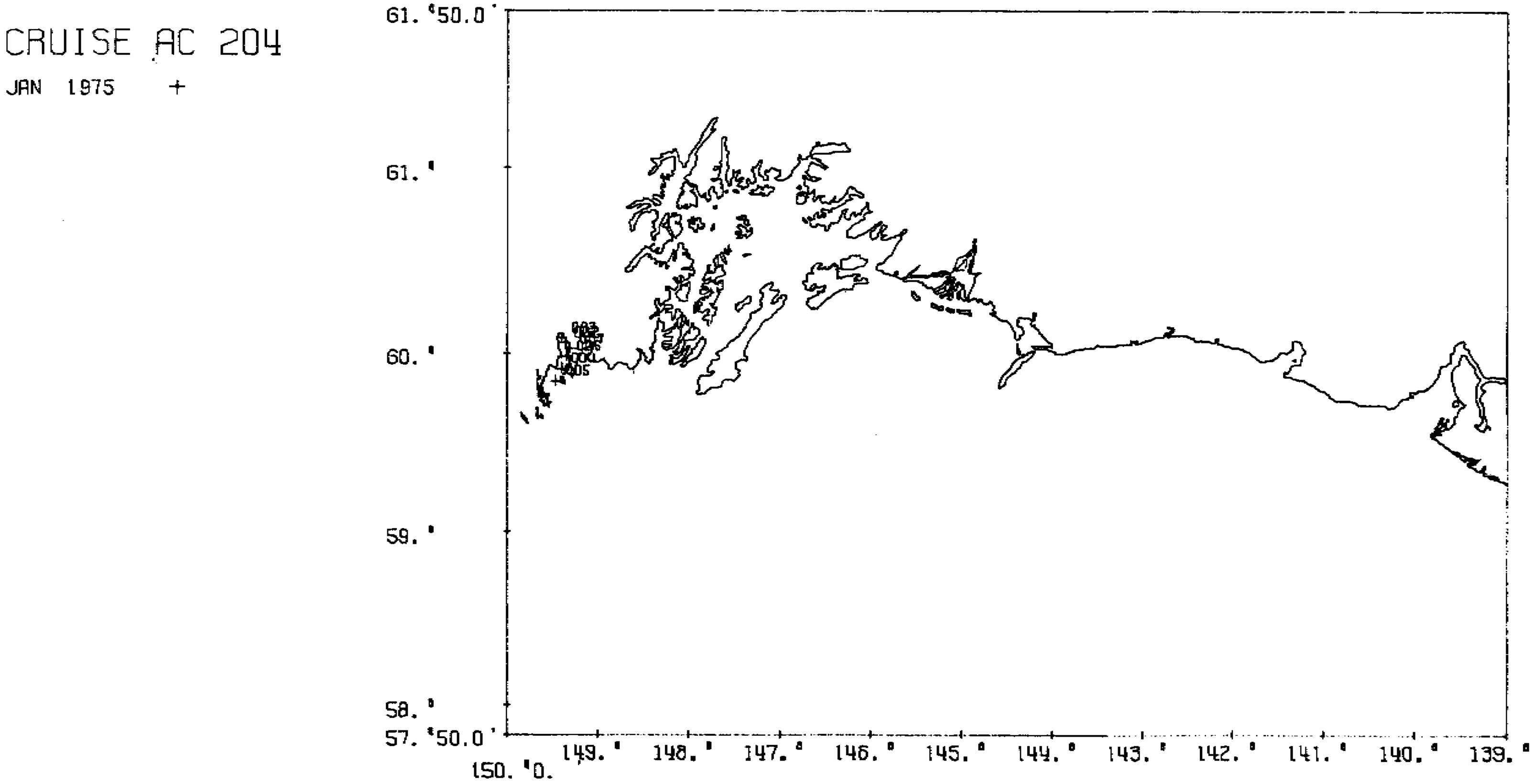

Figure 20. Station localities, R/V *Acona* #204, January 1975.

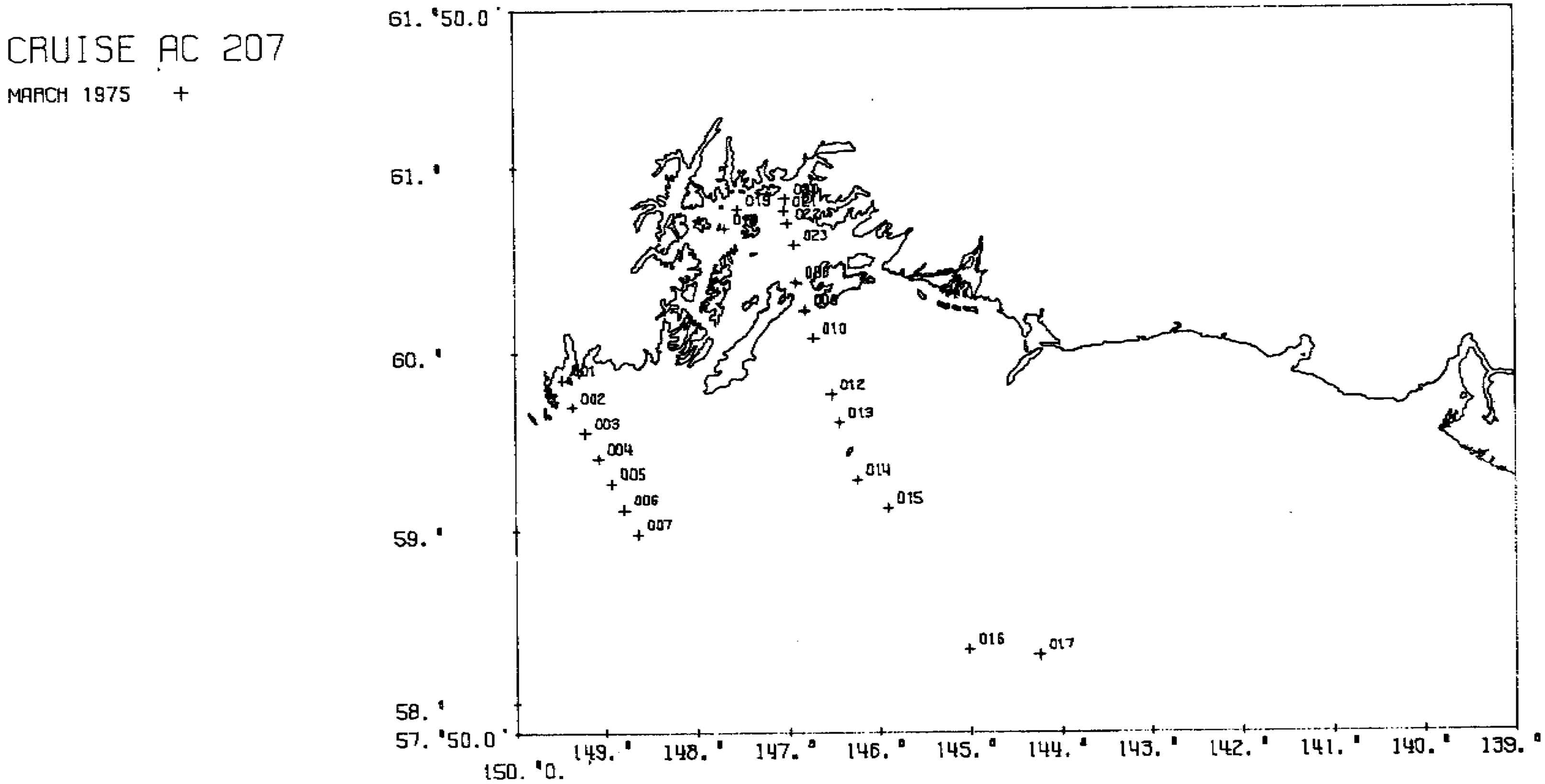

Figure 21. Station localities, R/V *Acona*, #207, March 1975.

TABLE XVI

SOLUBLE TRACE ELEMENT CONCENTRATIONS

Mean of Gulf of Alaska Bottom Waters
(μg/ℓ soluble fraction <0.4 μ)

Element	Gulf of Alaska mean	Technique	Oceanic mean[a]
Ag	0.009[b]	E	0.04
Cd	0.03	A	0.1
Cu	0.2	A	0.5
Hg	0.007	C	0.03
Ni	0.65	D	1.7
Pb	0.04	A	0.03
V	1.5	B	2.5
Zn	0.3	A	5.0

A - differential pulse, thin-film anodic stripping voltammetry (D. C. Burrell)
B - thermal neutron activation (D. E. Robertson)
C - ambient temperature atomic absorption (H. V. Weiss)
D - solvent extraction flame atomic absorption (D. C. Burrell)
E - solvent extraction graphite filament atomic absorption (D. C. Burrell)

[a] - Brewer (1975)
[b] - surface estuarine-fjord water

Pelagic and sub-tidal benthic biota analysis has been very poorly covered in the Gulf. We have published a few values for, for example, crab and *Neptunea* which indicate the overall importance of the benthic communities. Our most comprehensive data set is for the interidal samples collected by Zimmerman's group (Fig. 3; Tables I-III), notably *Fucus* and *Mytilus*, both species which have been extensively used as environmental indicater of heavy metal impingement elsewhere. A summary of these data is given as Tables XVII-XX. Some beach stations were occupied several times over but seasonal data are neither available nor, unfortunately, do we have the necessary ancillary environmental data to permit a more thorough analysis of these data. Certainly no anomolously high values are apparent (except possibly for Cu in *Fucus*) and contents of these particular heavy metals are as low as any reported from elsewhere. Some literature data are given in Table XXI for comparison. These latter include samples from both unpolluted (e.g., New Zealand) and presumably impacted areas (e.g., Bristol Channel of U.K.). How far any legitimate comparison can be made, is, however, an open question. Analytical techniques have varied greatly between laboratories and we would, for example, suspect the literature Cd values cited here. Zinc might appear, *a priori*, to be a useful index metal, but one notoriously subject to contamination during handling and analysts.

Heavy metal contents of the crab samples are similarly low and uniform. *Neptunea* however is very high in cadmium and high in copper and zinc. This observation is paralleled in the Bering Sea and is commented on further below.

The final summary of data for the heavy metal contents of the sediments for all the cruises over the NEGOA grid is given in Table XXII. We have explained our reasons for determining the extractable, i.e., non-

TABLE XVII

N. E. GULF OF ALASKA

MYTILUS

μg/g dry weight

	Cd	Cu	Ni	Zn	Hg
Port Dick (Gore Point)	11.0	8.5	2.0	80	--
Anchor Cove (Day Harbor)	6.0	10.5	<10.0	126	
	6.0	11.5	< 5.0		0.20
	10.5	5.5	1.0	68	
Squirrel Bay	4.5	16.0	<10.0	146	0.15
La Touche Point (Latouche Island)	3.0	7.0	< 5.0		
	5.5	8.5	3.5	52	
Macleod Harbor (Montague Island)	4.5	10.0	<10.0	110	0.25
	4.0	9.0	< 5.0		
Zaikof Bay (Montague Island)	4.5	9.0	<10.0	120	0.35
	4.5	11.0	< 5.0		
Port Etches (Cape Hinchinbrook)	4.0	10.0	< 5.0		
Boswell Bay (Hinchinbrook Island)	3.0	9.5	<10.0	64	0.35
	3.0	6.5	1.0	40	
Katalla (Copper River)	6.0	11.0	4.5	90	
Kayak Island (Cape St. Elias)					
Middleton Island					
Cape Yakataga	5.0	16.5	<10.0	170	0.45
Yakutat					

TABLE XVIII

N. E. GULF OF ALASKA

FUCUS

µg/g dry weight

	Cd	Cu	Ni	Zn	Hg
Port Dick (Gore Point)	3.5	8.0	9.5	16	-
Anchor Cove	1.5	9.5	<10.0	17	0.30
(Day Harbor)	3.5	27.0	15.5	22	-
	3.0	7.0	14.5	13	-
Squirrel Bay	1.5	3.5	<10.0	12	0.25
La Touche Point (Latouche Island)	3.0	6.0	5.5	-	-
Macleod Harbor (Montague Island)	4.0	17.0	8.0	22	-
Zaikof Bay	1.5	2.5	<10.0	5	0.45
(Montague Island)	4.0	17.0	9.0	16	-
Port Etches (Cape Hinchinbrook)	2.5	10.5	7.5	15	-
Boswell Bay (Hinchinbrook Island)	1.5	13.0	<10.0	9	0.70
Katalla (Copper River)	2.0	17.0	10.0	16	-
Kayak Island (Cape St. Elias)	4.0	6.0	15.0	17	-
Middleton Island	1.5	7.0	<10.0	12	0.05
Cape Yakataga	2.0	37.5	<10.0	25	0.10

TABLE XIX

MYTILUS

Heavy metal contents (μg/g dry weight)
Mean of duplicates

N. W. Gulf

Locality	Cd	Cu	Ni	Zn
Cape Nukchak	6.3	9.0	3.2	82
Cape Nukchak*	4.5	12.4	<5	
Low Cape (Trinity Is.)	5.8	10.1	3.6	77

Summer 1976 collection except * summer 1975.

Kodiak Island

Locality	Cd	Cu	Ni	Zn
Sandstom Island	10.3	8.0	3.4	107
Sandstom Island*	5.2	8.4	<5	-
Three Saints Bay*	6.1	10.2	<5	-
Lagoon Point	5.8	9.6	1.3	102
Pasagshak Point	2.5	9.3	1.6	115

Summer 1976 collection except * summer 1975.

TABLE XX

FUCUS

Heavy metal contents (μg/g dry weight)
Mean of duplicates

N. W. Gulf of Alaska

Locality	Cd	Cu	Ni	Zn
Cape Nukchak*	4.3	7.0	9.3	15
Cape Nukchak	4.1	6.8	6.8	17
Spectacle Island	3.8	1.4	6.0	10
Kodiak Island				
Sandstom Island*	2.3	2.0	5.3	8
Sandstom Island	3.0	3.8	6.1	19
Three Saints Bay*	3.1	3.5	5.5	18
Lagoon Point	3.9	1.5	6.7	17
Pasagshak Point	3.5	1.8	4.3	23

Summer 1976 collection except * summer 1975.

TABLE XXI

CONCENTRATION OF HEAVY METALS IN *MYTILUS* AND *FUCUS* FROM OTHER AREAS

(Means; mg/kg dry weight)

		Cd	Cu	Ni	Zn
Mytilus -	California	5	7	-	284
	N.Z.	10	9	10	91
	Spain	3	10	-	250
Fucus -	UK	13	10	-	190
	Spain	3	20	-	220

TABLE XXII

N.E. GULF OF ALASKA SEDIMENTS

Station Number	Cruise	Sediment Size (%) Clay	Silt	Sand & Gravel	Extractable Metals (mg/kg) Cd	Cu	Ni	Zn	Fe	Mn
01	y	62	38	--	tr	14	12	37	6380	125
02	z				tr	6	5	31		
03	y	68	32	--	tr	9	9	27	6350	115
04	y	69	31	--	tr	9	10	30	6740	105
05	y	60	20	20	tr	8	5	14	1880	53
	z				tr	7	6	21		
06	y	33	23	44	tr	7	4	17	2210	65
07	y	42	22	36	tr	6	4	23	2270	50
53A	x				tr	31	12	26		
53	x				tr	12	8	13		
	z				tr	11	8	22		
54	z				tr	13	8	22		
55	x				tr	15	9	15		
	y				tr	17	5	22	3770	99
56	x				tr	8	8	9		
57	x				tr	14	7	13		
	y	27	33	40	tr	13	3	12	2000	91
58	x				tr	13	5	17		
	y	50	47	3	tr	18	5	16	3400	81
52	x				tr	31	12	25		
	y				tr	24	4	23	4020	116
	z				tr	17	13	39		
51	x				tr	20	9	16		
	z				tr	19	11	33		
50	y	62	38	--	tr	14	9	27	7250	130
49	x				tr	26	6	18		
	z				tr	12	11	37		
48	x				tr	14	7	16		
	y	31	34	35	tr	10	6	19	3470	85
42	x				tr	19	6	16		
	y	30	60	10	tr	15	10	24	6780	115
43	x				tr	24	6	17		
	y	60	36	4	tr	12	11	22	6660	90
44	x				tr	17	6	16		
	z				tr	11	4	13		
41	x				tr	23	7	17		
	y	50	50	--	tr	19	7	30	4420	100
40	x				tr	23	6	17		
	y	55	45	--	tr	20	7	21	3640	101
39	y	39	61	--	tr	14	7	29	4000	80
37	x				tr	9	7	16		

TABLE XXII

CONTINUED

Station Number	Cruise	Sediment Size (%) Clay	Silt	Sand & Gravel	Extractable Metals (mg/kg) Cd	Cu	Ni	Zn	Fe	Mn
30	x				tr	8	4	10		
31	x				tr	30	3	6		
	y	36	62	2	tr	15	9	23	6375	110
32	x				tr	19	3	12		
	y	48	52	--	tr	14	8	22	5105	90
33	z				tr	7	2	12		
34	x				tr	21	4	15		
28	y	40	53	7	tr	13	7	19	2590	105
27	y				tr	8	5	21	2260	115
25	y	20	34	46	tr	4	3	13	1200	50

x - *Oceanographer* February 1975
y - *Silas Bent* 31 August-17 September 1975
z - *Discoverer* 23 November-2 December 1975

lithogenous or "available" fraction at length elsewhere. It is not possible to summarize the relationships between total heavy metal contents and these extraction values for this area because separate sample sets (and mostly different elements) have been determined. The overall relationships are, however, well known from other areas; for example, that a metal such as Cd is largely loosely bound whereas a majority of the copper is likely to be structural. It is fairly clear that the extractable contents correlate with sediment grain size - again as would be expected - but we were unable to obtain sufficient sediment size analyses to quantify the relationship in this area. The mean grain size is finer than sediments of the Bering Sea so that extractable contents are correspondingly higher. Clay minerology for the <1 and 2 µm fractions for the N.E. and N.W. Gulf regions (localities of Figs. 1 and 2) are given in Tables XXIII and XXIV respectively. These clay minerologies have been discussed by Naidu *et al* (1977; Abstract included in this report) who note the preponderance of illite and chlorite with subordinate amounts of a degraded (reduced K) illite fraction.

The data of Table XXII are grouped in transects seawards from the N.E. coast. There is a suspicion of enhancement of copper in the nearshore as compared with the deeper water stations. Such an observation would be consistent with enhanced vertical transport by inorganic sediment and organic detritus in the near-shore zone.

The results of the analyses for mercury species together with the total mercury content of these sediments appear in Table XXV. The total mercury contents of sediments from the Gulf of Alaska sediments ranged between 11-67 µg/g dry weight. The amount of elemented and readily reducible mercury in the sediments was less than 2% of the total for all samples, and, with the exception of one sample (#110), only small quantities of these species were

TABLE XXIII

N. E. GULF OF ALASKA

A. S. Naidu, Analyst.

Clay mineralogy of < 1 and 2 µm fractions (weighted peak area percents).

Sample No.	Treatment	Expandable component <2 µm	Expandable component <1 µm	Illite <2 µm	Illite <1 µm	Kaolinite <2 µm	Kaolinite <1 µm	Chlorite <2 µm	Chlorite <1 µm	Kaolinite +Chlorite <1 µm
1	a	1	t	45	42	0	-	54	-	58
	b	0	-	45	45	0	-	55	-	55
	c	2	-	47	41	0	-	51	-	59
3	a	4	6	45	47	0	t	51	47	-
	b	0	0	47	51	0	t	53	49	-
	c	5	7	45	40	0	t	50	53	-
4	a	3	7	45	44	0	t	52	49	-
	b	t	0	57	50	0	t	43	50	
	c	6	6	44	43	0	t	50	51	-
5	a	5	-	41	-	0	-	54	-	-
	b	0	-	53	-	0	-	47	-	-
	c	7	-	42	-	0	-	51	-	-
6	a	4	2	47	48	0	-	49	-	50
	b	t	-	46	56	0	-	54	-	44
	c	7	8	39	44	0	-	54	-	48
7	a	10	7	32	38	0	t	58	55	-
	b	-	0	-	43	0	t	-	57	-
	c	8	3	37	37	0	t	55	60	-
25	a	4	6	58	54	0	t	38	41	-
	b	0	0	66	61	0	t	34	39	-
	c	4	7	57	54	0	t	39	39	-
28	a	2	2	51	48	0	t	47	51	-
	b	t	0	56	54	0	t	44	46	-
	c	t	2	52	47	0	t	48	51	-
31	a	2	2	43	48	0	-	55	-	50
	b	0	-	44	51	0	-	56	-	49
	c	3	-	39	39	0	-	58	-	61
32	a	3	5	35	37	0	0	62	58	-
	b	t	0	46	44	0	0	54	56	-
	c	3	3	39	34	0	0	58	63	-

TABLE XXIII. CONTINUED

Sample No.	Treatment	Expandable component <2 μm	Expandable component <1 μm	Illite <2 μm	Illite <1 μm	Kaolinite <2 μm	Kaolinite <1 μm	Chlorite <2 μm	Chlorite <1 μm	Kaolinite +Chlorite <1 μm
39	a	6	5	44	38	0	0	50	58	-
	b	t	0	50	43	0	0	50	57	-
	c	4	4	40	36	0	0	56	60	-
40	a	6	t	38	45	0	-	56	-	-
	b	0	-	36	43	0	-	64	-	57
	c	5	t	35	41	0	-	60	-	59
41	a	4	6	46	31	0	0	50	63	-
	b	t	6	47	41	0	0	53	59	-
	c	5	3	45	37	0	0	50	60	-
42	a	5	5	35	32	0	0	60	63	-
	b	0	0	47	38	0	0	53	62	-
	c	3	1	40	37	0	0	57	63	-
43	a	5	7	36	37	0	0	59	56	-
	b	t	0	46	47	0	0	54	53	-
	c	4	5	42	34	0	0	54	60	-
48	a	4	5	40	36	0	-	56	-	59
	b	0	-	51	50	0	-	49	-	50
	c	7	3	37	40	0	-	57	-	57
50	a	5	5	34	37	0	0	61	59	-
	b	0	0	45	40	0	0	55	60	-
	c	5	3	41	39	0	0	54	58	-
52	a	2	6	48	51	0	0	50	44	-
	b	1	0	53	56	0	0	46	44	-
	c	2	4	56	48	0	0	42	48	-
57	a	6	-	44	53	0	-	50	-	47
	b	0	-	48	52	0	-	52	-	48
	c	5	?	42	42	0	-	53	-	58
58	a	5	7	42	36	0	0	53	56	-
	b	0	1	52	47	0	0	48	52	-
	c	3	3	37	31	0	0	60	65	-

Treatments:

a - Glycol saturation
b - K+ glycolated
c - Mg++ glycolated

TABLE XXIV

N. W. GULF OF ALASKA

A. S. Naidu, Analyst.
Clay mineralogy of <1 and 2 μm fractions (weighted peak area percents).

Sample No.	Treatment	Expandable component <2 μm	Expandable component <1 μm	Illite <2 μm	Illite <1 μm	Kaolinite <2 μm	Kaolinite <1 μm	Chlorite <2 μm	Chlorite <1 μm	Chlorite+ Kaolinite <1 μm
104	a	6	5	54	53	0	0	40	41	-
	b	0	0	53	54	0	0	47	46	-
	c	7	9	37	43	0	0	54	51	-
119	a	7	8	60	54	0	-	33	-	38
	b	0	-	64	64	0	-	36	-	36
	c	11	3	53	58	0	-	36	-	39
120	a	9	10	55	52	0	0	36	38	-
	b	0	0	57	62	0	0	43	38	-
	c	7	9	54	49	0	0	39	42	-
121	a	10	8	53	49	0	0	37	43	-
	b	0	0	53	48	0	0	47	42	-
	c	9	7	47	45	0	0	44	48	-
124	a	13	12	47	39	0	0	40	49	-
	b	0	0	47	54	0	0	53	46	-
	c	9	10	39	39	0	0	52	51	-
134	a	7	10	45	44	0	0	48	46	-
	b	0	0	48	55	0	0	52	45	-
	c	10	8	45	47	0	0	45	44	-
135	a	13	14	52	45	0	0	35	41	-
	b	0	2	58	49	0	0	42	49	-
	c	19	11	37	43	0	0	44	46	-

Treatments:

a - Glycol saturation
b - K+ glycolated
c - Mg++ glycolated

TABLE XXV

N E. GULF OF ALASKA

Discoverer - Leg III, 23 November-2 December 1975.
H. V. Weiss, Analyst
Mercury species in sediment.

		Hg (%)			Extractable into Seawater (%)		
Station	Total Mercury (ng/g)	Sample wt (g)	Elemental	Readily Reducible[a]	Sample wt (g)	Reducible	Organic[b]
2	67.1	4.5	<0.06[c]	0.30	28.1	<0.01	0.45
5	33.4	2.2	<0.28	0.90	28.3	<0.02	1.20
7	48.5	2.4	<0.18	0.18	22.2	1.03	<0.02
8	34.3	4.5	<0.12	0.28	25.9	0.85	<0.02
25	31.3	1.6	<0.40	0.64	25.7	<0.02	<0.02
26	29.8	3.9	<0.18	1.01	37.3	0.34	0.34
29	23.2	3.6	<0.24	0.86	25.9	<0.03	0.03
30	10.8	3.1	<0.60	<0.60	41.9	1.85	17.6
33	39.4	2.7	<0.18	0.51	25.9	<0.02	<0.02
39	65.0	2.4	<0.12	0.62	28.0	<0.01	0.77
44	32.6	2.4	0.31	0.31	24.8	<0.02	3.07
48	46.0	2.2	0.22	0.65	21.3	<0.02	0.65
49	51.4	3.3	<0.12	0.39	26.4	0.19	0.01
50	60.3	3.8	<0.08	0.33	27.0	0.17	0.83
51	50.0	3.7	<0.10	0.20	26.2	<0.02	0.20
52	53.3	4.8	<0.08	0.38	28.5	0.38	<0.01
53	46.8	3.2	<0.14	0.21	28.0	<0.02	0.21
54	42.3	6.0	<0.08	0.47	27.2	0.24	<0.02
56	31.6	3.5	<0.18	0.32	20.8	0.32	0.63
57	59.5	2.5	<0.14	0.34	28.4	<0.01	<0.01
58	35.5	2.7	<0.20	1.41	25.1	<0.02	0.85
59A	59.2	5.0	<0.06	0.34	26.2	0.17	0.34
60	57.4	2.7	<0.12	0.35	24.3	<0.01	<0.01
61	45.2	3.8	<0.18	0.71	23.0	0.03	0.03
62	28.0	3.8	<0.18	0.40	26.4	0.02	0.20
68	54.5	2.1	<0.18	0.92	26.5	0.01	0.55
69	51.6	4.1	<0.10	0.39	41.0	0.10	4.10
110	19.2	1.8	<0.58	0.58	15.5	4.74	6.77

[a] Corrected for elemental mercury

[b] Corrected for reducible mercury

[c] Calculated on the basis of 0.2 ng detection limit.

extractable into seawater. In contradistinction to the other sediments which were mud-like in character, #110 consisted of sand; apparently this composition allowed for release of essentially half of the mercury and that which was released was substantially readily reducible. Some sediments give evidence that an organic moiety is also extracted into seawater. These distributions are considered in more detail by Weiss *et al.* (*op cit*).

Overall it appears unnecessary to obtain more sediment data for the Gulf. As in the case of soluble contents we have demonstrated that Alaskan shelf regions are clean and correspond to other such environment elsewhere.

Lower Cook Inlet

We have previously described the hydrography of Cook Inlet (Rosenberg *et al.*, 1967) and the distribution of suspended sediments and bottom sediment facies (Sharma and Burrell, 1970). Cook Inlet is an almost textbook example of a well mixed estuary with mixing dominated by an intense tidal regime. The tidal range is second only to the Bay of Fundy and very strong currents are generated, especially in the Forelands narrows. The central portion of Cook Inlet therefore tends to be swept clear of fine grained sediment and the benthic biota distributions are very patchy. We have previously demonstrated (Rosenberg *et al.*, *op cit*) that a liquid pollutant added to the mainstream portion of the inlet (ammonia in this specific example) is dispersed and diluted almost instantaneously.

The suspended sediment input into the head of Cook Inlet is exceedingly high. This material is overwhelmingly very fine grained glacial till. The current structure ensures that this sediment is carried long distances down and out of the inlet. As would be expected, the outflowing turbid water is concentrated on the western side and there is some deposition of sediment in this region (e.g., Kamshak). Inflowing marine water is confined largely to the eastern side.

Heavy metals within the water column are strongly partitioned onto the suspended sediment. In S. Central Alaska this latter material is overwhelmingly inorganic (glacially ground rock flour) and there is no evidence for large scale desorption of metals where rivers meet seawater such as appears to be frequently the case in temperate zones. Preliminary evidence from the organic chemistry program indicates that Cook Inlet sediment does not sorb petroleum hydrocarbons to any extent (presumably because of the highly polar nature of this material) and therefore significant desorption of metals in the event of a major oil spill would not be expected. In any case, even given the worse possible case, the increased concentration of metals per unit of water would be negligible.

Because of the hydrographic regime in Cook Inlet, the average surficial sediment in the lease area is relatively coarse and concentrations of extractable ("available") heavy metals released (per unit of dry weight; Burrell, 1977) are generally lower than in the other coastal areas studied. Attempts were made to recover sediment core samples suitable for heavy metal analysis at every benthic grid station on the March-April 1976 *Moana Wave* cruise but because of the generally coarse nature of the substrate, suitable samples were obtained at only the nine localities shown in Figure 22. Extractable heavy metal contents are given in Tables XXVI and XXVII.

Very little heavy metal chemistry work was authorized in this area prior to October 1977. To effect a rapid biota baseline survey we had, however, previously attempted to obtain a representative collection of intertidal *Fucus*, *Mytilus* and *Macoma baltica* samples, initially *via* a shore-based collection in the vicinity of Homer (Table XXVIII) and from both sides of the inlet in June 1977 (Table XXIX). These intertidal localities are shown in Figure 23. *Fucus* and *Mytilus* are commonly used "pollution index species". Heavy metal concentrations for these are given in Tables XXX and XXXI. The data are comparable with those obtained for the Gulf of Alaska and the S. Bering Sea as given elsewhere in this report; no anomolous trends are evident.

Since there was, not unexpectedly, no immediate evidence of heavy metal pollution in Cook Inlet it seemed to us clear that the essential heavy metal chemistry needs in Cook Inlet concerned the uptake of metals by indigenous benthic organisms and subsequent transfer along food webs, coupled with research on changes in natural patterns likely to be induced by local pollution. It must be understood that benthic organisms are in intimate contact

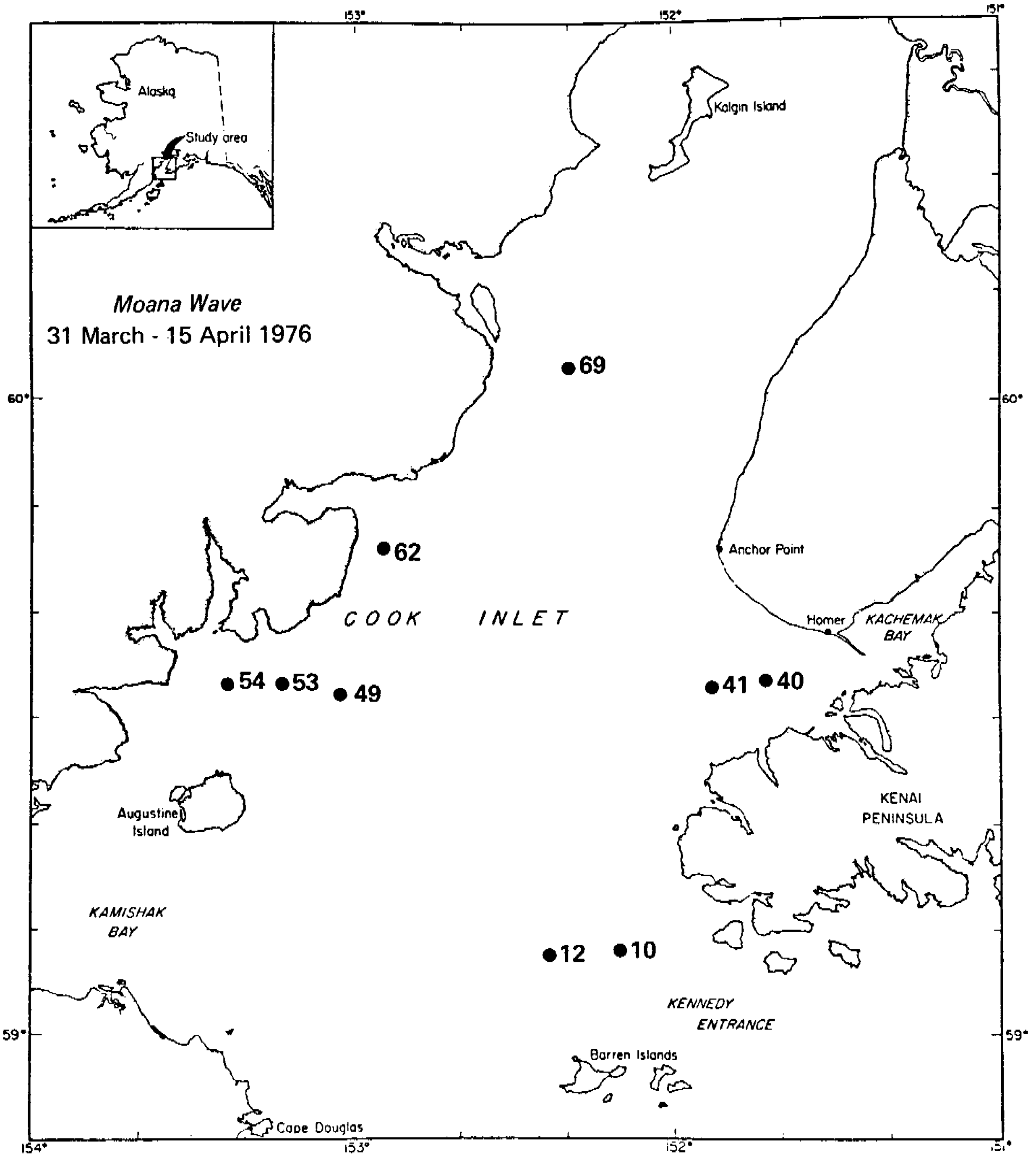

Figure 22. Lower Cook Inlet. *Moana Wave*, March-April 1976, Haps core samples recovered.

TABLE XXVI

LOWER COOK INLET

Moana Wave 31 March-15 April 1976
Heavy metal contents of sediment extracts (mg/kg)

Station	Cd	Cu	Ni	Zn	Fe	Mn
62	<0.25	16.8	3.7	13.7	2810	176
56	<0.25	16.9	7.9	34.3	3830	113
53	<0.25	17.2	5.9	17.8	3685	112
49	<0.25	15.1	4.1	14.7	3310	100
10	<0.25	3.6	1.8	10.5	500	70
12	<0.25	3.0	<1.2	5.2	690	136
41	<0.25	3.0	1.3	11.6	1125	40
69	<0.25	11.9	2.9	10.0	1240	62
40	<0.25	6.7	2.9	19.6	3230	420

TABLE XXVII

LOWER COOK INLET

Moana Wave March 31 - April 15, 1976
T. A. Gosink, Analyst

Chromium contents of sediment extracts (mg/kg).

Station No.	Depth (m)	Cr (mg/kg)
4	26	2.0
10	25	2.5
11	29	3.2
12	38	2.3
18	133	2.4
19	100	1.9
25	55	1.9
26	64	2.7
30	71	1.7

TABLE XXVIII

LOWER COOK INLET

Shore based collection 4-7 May 1977
Intertidal Benthos Collected

Station No.	Locality	Position	Type
1	Kachemak Bay - Mud Bay	59°40 N 151°26 W	*Macoma, Mytilus* *Fucus*, sediment
2	Anchor Point	59°40 N 151°52 W	*Mytilus, Fucus* sediment
3	Outer Bay	59°38 N 151°30 W	*Mytilus, Fucus* sediment
4	Bluff Point - Diamond Creek	59°40 N 151°42 W	*Mytilus, Fucus* sediment

TABLE XXIX

LOWER COOK INLET

R/V *Acona* June 21-26, 1977

Intertidal Benthos Samples

Station No.	Locality	Position	Type
5	Koyuktulik (Dogfish) Bay	59°14.5 N 151°52.5 W	*Mytilus*, *Fucus*, sediment
6		59°33.2 N 151°36.4 W	Haps core
7	Kasitsna Bay	59°28.8 N 151°34.5 W	*Macoma*, *Mytilus*, *Fucus*, sediment
8		59°03.1 N 153°23.4 W	Haps core
9	Cottonwood Bay	59°38.0 N 153°38.7 W	*Macoma*, *Fucus*, sediment
10	Iniskin Bay	59°43.4 N 153°22.7 W	*Macoma*, *Fucus*, sediment
11	Oil Bay	59°39.1 N 153°18.5 W	*Mytilus*, *Fucus*, sediment
12	Douglas River	59°06.3 N 153°42.2 W	*Mytilus*, *Fucus*, sediment

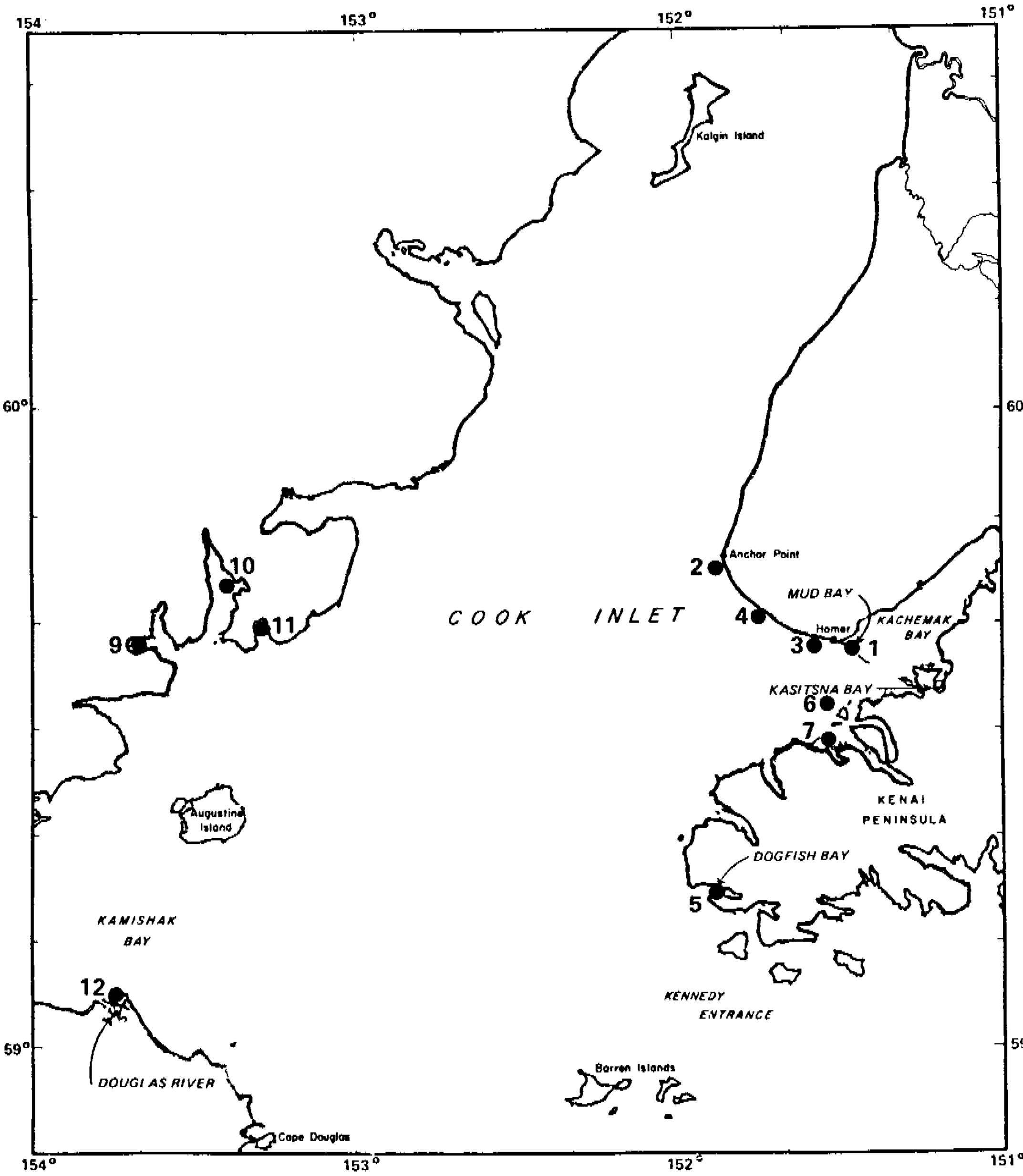

Figure 23. Lower Cook Inlet, intertidal benthos collection sites, May and June 1977.

TABLE XXX

LOWER COOK INLET

Shore based collection - 4-7 May 1977

R/V *Acona* cruise 21-26 June 1977

Heavy metal contents of *Mytilus* samples (μg/g dry weight)

Sample No.	Cd	Ni	Cu	Zn
01	2.5 ± 0	3.0 ± 0.8	11.0 ± 0	68 ± 30
02	3.3 ± 0	4.3 ± 0.5	5.5 ± 0.6	98 ± 0
03	2.5 ± 0	4.5 ± 0	6.5 ± 1.5	138 ± 20
04	4.5 ± 0.3	3.6 ± 0.9	8.0 ± 0	123 ± 20
05	3.3 ± 0	1.8 ± 0.7	5.5 ± 0.6	88 ± 12
07	1.7 ± 0.7	2.3 ± 0.4	4.0 ± 1.2	113 ± 15
11	1.0 ± 0	1.8 ± 0.6	8.0 ± 0	63 ± 7
12	2.5 ± 0	2.1 ± 0.7	5.7 ± 0.8	68 ± 15

TABLE XXXI

LOWER COOK INLET

Shore based collection - 4-7 May 1977

R/V *Acona* cruise 21-26 June 1977

Heavy metal contents of *Fucus* samples (μg/g dry weight)

Sample No.	Cd	Ni	Cu	Zn
01	5.2 ± 1.5	4.5 ± 1.5	9.2 ± 0.8	22 ± 3
03	10.1 ± 0.7	11.2 ± 1.0	10.0 ± 0.8	21 ± 1
04	12.2 ± 0.6	12 ± 3	5.8 ± 0.8	16 ± 4
05	9.3 ± 1.5	4.0 ± 1.0	5.5 ± 3	11 ± 1
09	8.4 ± 0.6	8.2 ± 1.0	10.8 ± 0.8	10 ± 0
10	7.0 ± 3	11 ± 2	8 ± 2	5 ± 0

with the major heavy metal reservoir - the deposited sediments - and that these organisms tend to concentrate metals and are commonly sensitive to changes in substrate levels. Of overwhelming importance in Lower Cook Inlet is the fact that many benthic organisms (crab, clams, shrimp) are the base of a major industry. Further, Feder and his benthic biology group have shown that the highly important crab populations are largely feeding on detritivore clams; the food web is short and detritus-dominated. Since the sediments constitute the major marine trace metal reservoir, and it has been demonstrated that those latter may be remobilized by a variety of reactions which are believed to be largely microbially mediated, the importance of researching sediment - higher benthic organism transfers seems very clear. This program was developed in two directions, of which the laboratory portion is described elsewhere. The complementary field program was initiated with the collection and analysis of a set of *Macoma* samples and the localities referenced above. These data are given in Table XXXII.

We participated in a second benthic sampling cruise in November 1977 (Fig. 24 and Table XXXIII). The objective here was to obtain both food web and substrate samples. The distribution of benthic fauna in Cook Inlet is, however, very patchy and the collection (Table XXXIV and XXXV) was less comprehensive than was initially hoped. Heavy metal contents of the subtidal *Macoma calcarea*, tanner and dungeness crabs and sole specimens are given in Tables XXXVI and XXXVII. (The accuracy and precision tests applicable to this set of numbers is given as Table XXXVIII). Contents of all these heavy metals in the crab species is relatively low. The values given are for whole organisms (minus carapace). Table XXXIX gives some very preliminary values for metal contents in specific organs and tissues of crab from this region. Cadmium and copper is heavily concentrated in the gut

TABLE XXXII

LOWER COOK INLET

Shore based collection - 4-7 May 1977

R/V *Acona* cruise 21-26 June 1977

Heavy metal contents of *Macoma* (μg/g dry weight)

Sample No.	Cd	Ni	Cu	Zn
01	0.18 ± 0	13.0 ± 0.5	31.5	220 ± 30
07	0.03	13.7 ± 0.6	26 ± 2.5	190 ± 5
09	0.04 ± .01	12.9 ± 0.4	44 ± 2.5	340 ± 30
10	<0.03	10.0 ± 0.3	17 ± 4	220 ± 20

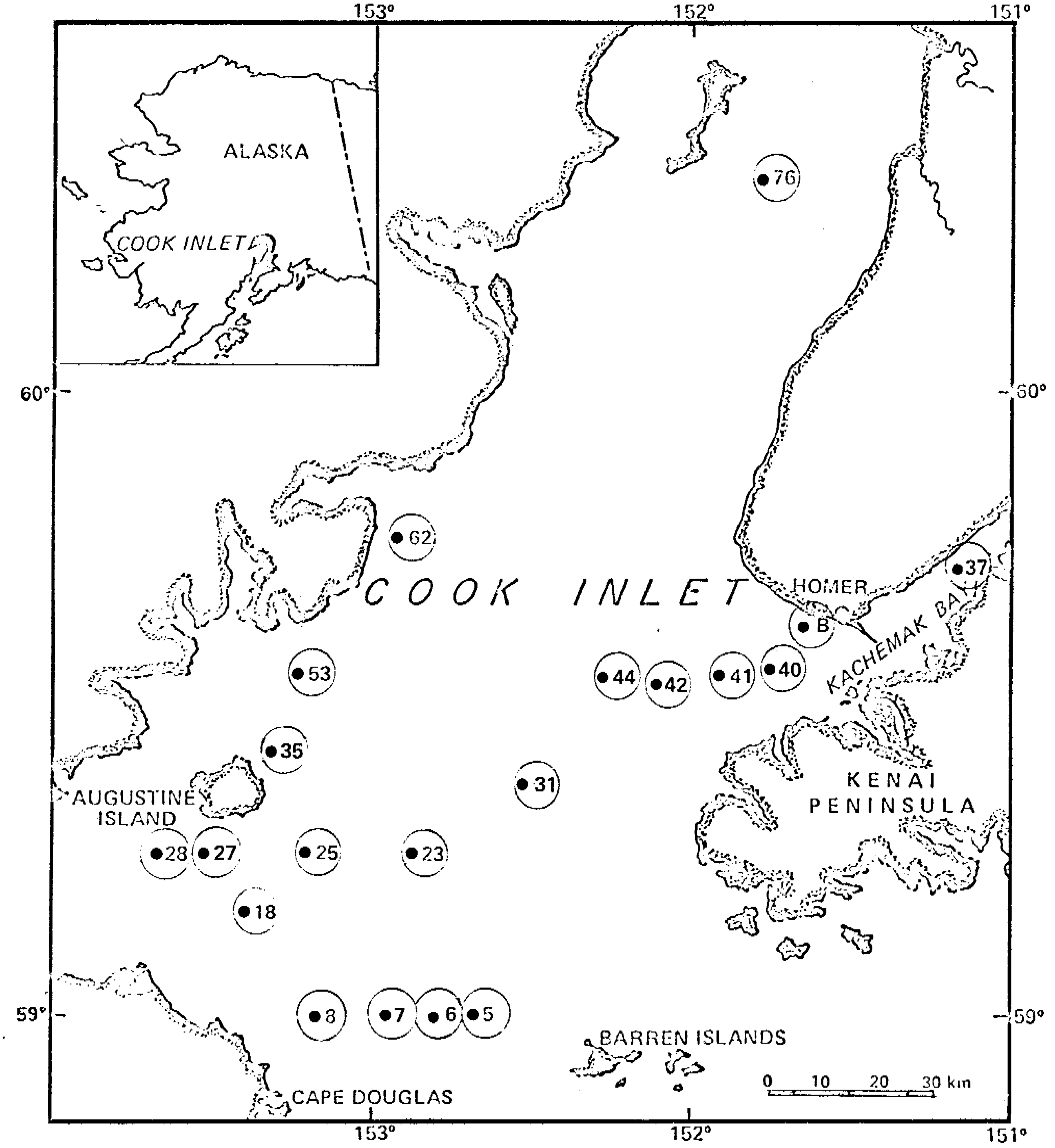

Figure 24. Lower Cook Inlet, sub-tidal benthos collection localities, *Surveyor*, November 1977.

TABLE XXXIII

LOWER COOK INLET

Surveyor 3-17 November 1977

Operations & Sample Locations

Station	Sample	Lat N	Lat W	Distance (nm)
B	Trawl	59°39.2'	151°45.7'	
		59°39.5'	151°46.9'	1.0
5	Trawl	59°01.6'	153°01.4'	
		59°03.4'	152°59.3'	2.2
27	Trawl	59°16.0'	153°33.2'	
		59°16.7'	153°36.6'	1.8
	Haps	59°15.0'	153°29.0'	
35	Trawl	59°27.2'	153°17.9'	
		59°27.3'	153°19.3'	1.5
37	Trawl	59°40.8'	151°13.6'	
		59°40.2'	151°14.8'	1.0
	Haps	59°41.2'	151°17.8'	
40	Trawl	59°35.7'	151°47.7'	
		59°36.4'	151°49.0'	1.1
	Haps	59°33.6"	151°44.6'	
41	Trawl	59°33.3'	151°53.9'	
		59°33.2'	151°56.0'	1.1
53	Trawl	59°32.2'	153°08.0	
		59°31.8'	153°10.6'	1.6
62	Trawl	59°40.8'	152°56.4'	
		59°46.0'	152°56.5'	0.8
	Haps	59°46.0'	152°56.2'	

TABLE XXXIV

LOWER COOK INLET

Surveyor 3-17 November 1977

Sub-tidal species collected

Station	Surficial Sediment Sample	Sole	Crab[a]	Macoma	Neptunia
B		x			x
5			2		
27	x		1	x	
35			2		x
37	x	x	2	x[b]	
40	x	x	8		x
41			8		
53			4		x
62	x	x	6		x

a - Number of individual samples

b - Live subtidal *Macoma calcarea* to be used for aquaria experiments

TABLE XXXV

LOWER COOK INLET

O.S.S. *Surveyor* 3-17 November 1977

Species Data

Sample	Species	Sea	Weight (gm)	Length (mm)
27	*Macoma calcarea*	-	-	-
27a	Tanner Crab	-	-	-
37	*Macoma calcarea*	-	-	-
37a	Curl fin sole	-	-	-
37b	Tanner Crab	M	910	132
37c	Tanner Crab	M	910	126
40a	Tanner Crab	M	1360	152
40b	Dungeness Crab	F	260	105
40f	Tanner Crab	-	-	-
40h	Dungeness Crab	F	250	108
40k	Flat head sole	-	-	-

TABLE XXXVI

LOWER COOK INLET

O.S.S. *Surveyor* 3-17 November 1977

Heavy metal contents of *Macoma calcarea* (μg/g dry weight)

Individual determinations

Station No.	Individual Sample	Cd	Ni	Cu	Zn	Pb
27	--	1.2	5.7	230	115	16
37	d	3.1	1.6	130	65	5
	e	0.6	1.7	140	70	8
	f	--	2.0	230	50	15
	g	1.0	1.6	130	70	2

Heavy metal contents of sole samples (μg/g dry weight)

Triplicate determinations

Station No.	Sample	Cd	Ni	Cu	Zn	Pb
37a	Curl fin	<0.13	<0.25	--	27 ± 11	0.95 ± 0.1
40k	Flat head	<0.13	<0.25	--	25.0 ± 0.7	1.04 ± 0.12

TABLE XXXVII

LOWER COOK INLET

O.S.S. *Surveyor* 3-17 November 1977

Heavy metal contents of Tanner Crab (μg/g dry weight)

Triplicate Determinations

Station No.	Sample	Cd	Ni	Cu	Zn	Pb
27	a	0.10 ± 0.03	<0.25	23.3 ± 1.5	148 ± 5	1.71 ± 0.04
	b	0.05 ± 0	<0.25	31.8 ± 3.5	137 ± 7	1.11 ± 0.18
	c	0.08 ± 0.03	<0.25	69.6 ± 2.9	115 ± 5	0.92 ± 0.07
40	a	0.08 ± 0.03	<0.25	17 ± 8	140 ± 40	0.92 ± 0.14
	f	<0.05	<0.25	14 ± 5	129 ± 17	1.05 ± 0.05

Heavy metal contents of Dungeness Crab (μg/g dry weight)

Triplicate Determinations

Station No.	Sample	Cd	Ni	Cu	Zn	Pb
40	b	<0.05	<0.25	32	185 ± 9	0.64 ± 0.09
	h	<0.05	<0.25	16 ± 5	202 ± 1	0.62 ± 0.10

TABLE XXXVIII

LOWER COOK INLET

O.S.S. *Surveyor* 3-17 November 1977

Biota analysis: Accuracy and precision data

Triplicate determinations

NBS Standard No. 1571: Orchard leaves

Metal	This Study	NBS Certified
Cd	0.12 ± 0.04	0.11 ± 0.02
Ni	1.1 ± 0.1	1.3 ± 0.2
Cu	15 ± 5	12 ± 1
Zn	25 ± 3	25 ± 3
Pb	40 ± 5	45 ± 3

NBS Standard No. 1577: Bovine liver

Metal	This Study	NBS Certified
Cd	0.55 ± 0.02	0.27 ± 0.04
Cu	196 ± 7	193 ± 10
Zn	132 ± 10	130 ± 10
Pb	0.33 ± 0.03	0.36 ± 0.08

TABLE XXXIX

LOWER COOK INLET

O.S.S. *Surveyor* 3-17 November 1977

Heavy metal contents of crab organs and tissues
μg/g dry weight

	Cd	Ni	Cu	Zn
Eggs	<0.13	0.5	26	125
Eggs	<0.13	0.5	28	250
Gut	33.0	0.8	59	144
Muscle	<0.13	0.6	25	200

organs. Zinc is present in elevated concentration in the eggs and shows evidence of being more evenly distributed through muscle tissue rather than being concentrated in the usual "storage" organs. This feature has been noted previously with regard to Bering Sea seals.

In marked contrast to these carnivorous benthic animals, the deposit feeding clams show considerably higher overall concentrations of all the heavy metals, Cd, Cu, Ni and Pb, except for zinc. In the case of the latter metal the subtidal *Macoma* data of Table XXXVI are in notable contrast to those of the intertidal *Macoma baltica* of Table XXXII (and the Ni values show a reverse trend).

It is evident that the detritivore infauna is capable of concentrating not insignificant amounts of metals which are passed on, but apparently not magnified, to the next trophic level. The circumstances under which uptake of metals from the sediments could be enhanced is the subject of the laboratory investigations described in a following section.

Bering and Chukchi Seas

Water and sediment samples were largely collected on single, separate sampling trips to the S. Bering Sea (*Discoverer*, June 1975) and to Norton Sound and the southern portion of the Chukchi (*Discoverer*, September 1976). In addition, we have received a miscellaneous collection of trawl samples from the *Miller Freeman*, most of which were deemed unsuitable for true metal analysis, a few intertidal benthos samples (Fig. 8) and a reasonably representative suite of seal tissue samples as noted below.

Soluble Cd, Cu, Pb and Zn values were tabulated and discussed in previous reports (see index). The comments on these metals given above for the Gulf region and considered to apply to the S. Bering Sea also but data for the latter region are for unfiltered samples only. Water samples collected in Norton Sound and the S. Chukchi Sea were, of necessity, obtained using the ships wire-hung rosette sampler and have been archived without soluble metal analysis as noted earlier in this report.

In view of the difficulty in obtaining good samples for trace metal analysis we expended some time and effort in designing a suitable collection system for deployment in the summer of 1977 on the U.S.S.R. hydromet vessel *Volna*. The cruise track for this joint U.S. - U.S.S.R. operation (Fig. 16) covered an area of the central Bering Sea which we had been unable to visit previously. The sampling routine is described earlier in this report. Subsequently, laboratory analysis was performed on these samples for dissolved copper and lead contents with the results given in Table XL.

The stations occupied for this survey straddle the continental break (Table XI) but, coincidently, mostly cover that portion of the Alaskan shelf west of Nunivak Island from which the seal specimens discussed below had been collected the previous spring. It was hoped that by this time we would

TABLE XL

BERING SEA

U.S.S.R. Hydromet vessel *Volna* July-August 1977
Soluble heavy metal contents (μg/ℓ; filtered at 0.4 μm)

Station No.	Depth (m)	Cu	Pb
1	0	0.21	(0.41)[a]
	10	0.14	
	25	0.28	(0.48)
	50	0.33	(0.21)
	75	0.22	
3	0	0.08	0.09
	10	0.16	0.16
	25	0.12	0.17
	50	0.14	0.10
	75	0.19	0.09
5	0	0.16	0.10
	10	0.15	0.16
	25	0.14	0.13
	50	0.19	0.22
	75	0.24	0.25
7	0	0.10	0.08
	10	0.16	0.14
	25	0.22	0.15
	50	0.37	0.19
	75	0.38	0.14
9	0	0.25	0.31
	10	0.38	0.20
	25	0.32	0.10
	50	0.22	0.05
	75	0.34	0.18
11	0	0.25	0.31
	10	0.27	0.21
	25	0.27	0.14
	50	0.26	0.03
	65	0.77	0.66
13	0	0.38	0.15
	10	0.19	0.03
	25	0.15	0.06
	50	0.20	0.17
	65	0.25	0.21

TABLE XL (Continued)

Station No.	Depth (m)	Cu	Pb
15	0	0.21	0.20
	10	0.17	0.21
	25	0.22	0.49
	45	0.34	0.26
17	0	0.67	0.42
	10	0.39	0.24
	25	0.22	0.16
	40	0.49	0.33
19	0	0.41	0.14
	10	0.65	0.33
	25	0.75	0.34
21	0	0.36	0.21
	10	0.38	0.16
	25	0.22	0.13
	50	0.30	0.21
	58	0.64	0.14
23	0	0.16	0.10
	10	0.25	0.21
	25	0.32	0.24
	50	0.28	0.20
	75	0.44	0.17
26	0	0.28	0.21
	10	0.35	0.44
	25	0.56	0.54
	50	0.23	0.09
	75	0.24	0.38
28	0	0.27	0.21
	10	0.35	0.27
	25	0.21	0.09
	50	0.41	0.31
	75	0.33	0.24
30	0	0.24	0.24
	10	0.37	0.18
	25	0.42	0.13
	50	0.25	0.18
	75	0.29	0.20

TABLE XL (Continued)

Station No.	Depth (m)	Cu	Pb
32	0	0.49	0.23
	10	0.74	0.68
	25	0.40	0.30
	50	0.43	0.40
	75	0.31	0.12
34	0	0.50	0.20
	10	0.35	0.10
	25	0.22	0.07
	50	0.25	0.10
	75	0.65	0.22
36	0	0.89	0.36
	10	0.55	0.38
	25	0.64	0.36
	50	0.62	0.42
38	0		
	10		
	25	0.84	0.18
	50	0.55	0.55
40	0	0.62	0.26
	10	0.74	0.32
	25	1.02	0.53
	40	0.65	0.39
42	0	0.60	0.10
	10	0.63	0.20
	25	0.87	0.26
	35	0.92	0.60
44	0	0.62	0.10
	10	0.41	0.07
	25	0.45	0.11
	45	0.47	0.11
46	0	0.54	0.26
	10	0.60	0.57
	25	0.59	0.11
	50	1.53	0.37
48	0	0.59	0.32
	10	0.20	0.21
	25	0.65	0.28
	50	0.31	0.38
	75	0.33	0.27

[a] - Contamination suspected

have received the ancillary hydrographic and nutrient data taken on this cruise which would have immeasurably aided our interpretation. The following features are particularly noteworthy however: (a) the mean ranges for both lead and copper (Fig. 25) closely conform with those given earlier for the Gulf of Alaska. This would be expected, of course, since mean soluble concentrations can only vary between narrow limits in open ocean water. However, it is only recently that these fractions of μg/ℓ ranges have been suggested for these metals: our data at once adds support to these levels for unpolluted open ocean water and at the same time adds confidence to the accuracy of our data; (b) There is a clear indication of an increase in both of these heavy metals adjacent to the sediment surface. These samples were filtered at 0.4 μm, and, in general, the suspended sediment load is very small. However, we suggest that sediment resuspension is prevalent on the shelf bottom, and especially adjacent to the shelf break. Although unfortunately, there is no nephelometry data, upwelling at the break and advective resuspension of nutrient particles would fit in with our general theory regarding the high productivity of this region. We suggest that the elevated trace metal contents reflect the presence of particulate material finer than the filter cut-off size; (c) Table XLI shows surface water profiles for copper and lead at two stations down to 60 and 85 cm. The values are mostly eratic although still within the same range so that contamination seems unlikely. However, the surface film samples, particularly for lead, shows marked higher concentrations. It is suggested that this feature indicates atmospheric supply of lead and deposition *via* fallout or washout.

Although we have good soluble data for these two metals only, it is suggested that no anomolous patterns in the soluble heavy metals are to be expected and that the ranges determined for the Gulf of Alaska will be

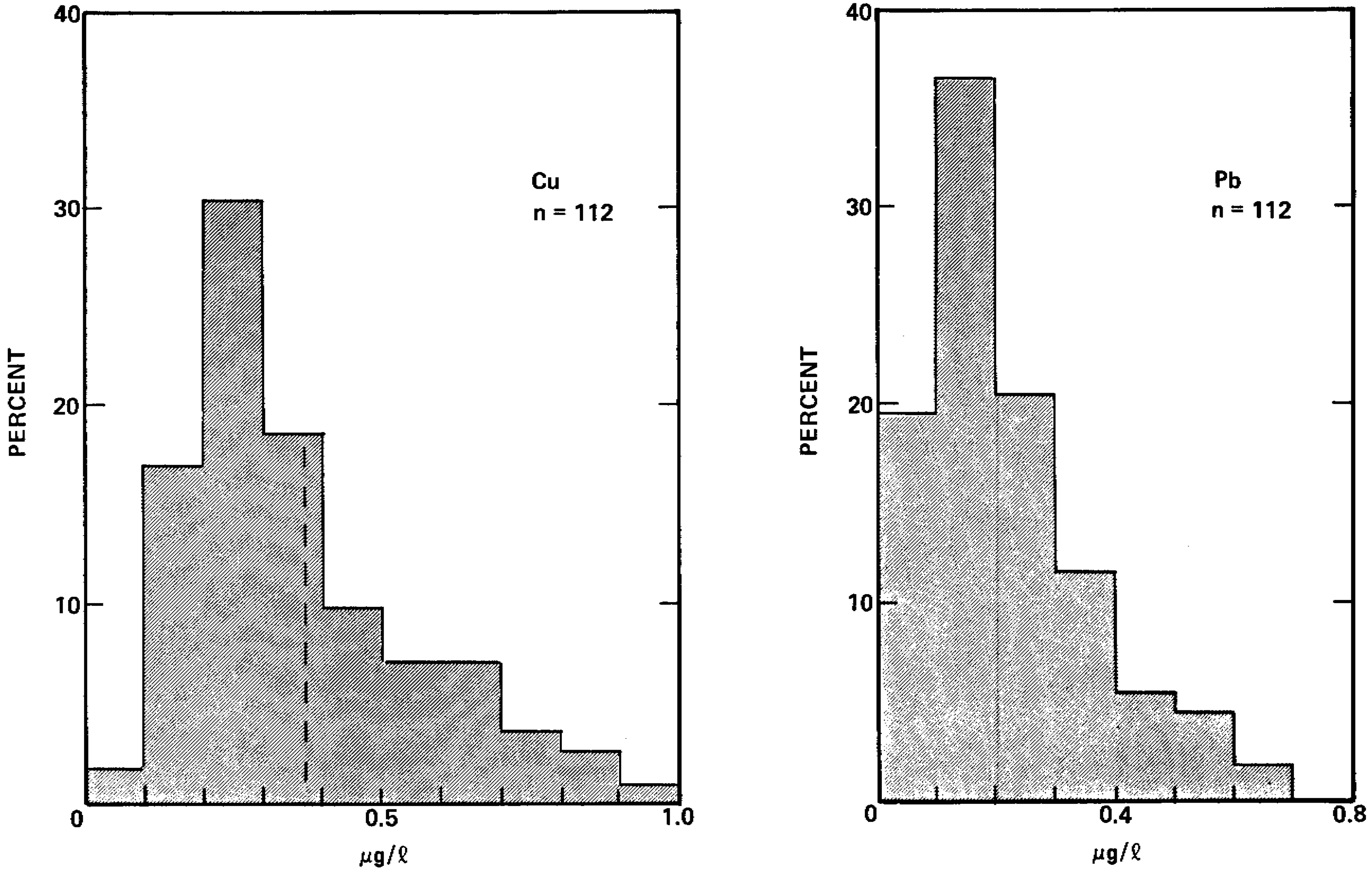

Figure 25. Range of Cu and Pb soluble data, Bering Sea, *Volna*, July-August 1977.

TABLE XLI

BERING SEA

U.S.S.R. Hydromet vessel *Volna* July-August 1977
Soluble (0.4 μm) heavy metal contents at sea surface (μg/ℓ)

Station No.	Depth (cm)	Cu	Pb
16	0[a]	0.73[b]	2.48[b]
	10	0.30	0.13
	20	0.17	0.08
	30	0.35	0.15
	45	0.33	0.19
	60	0.60	0.14
45	0[a]	0.25[b]	0.46[b]
	10	0.26	0.15
	20	0.24	0.17
	30	0.28	0.08
	45	0.16	0.06
	60	0.30	0.12
	85	0.19	0.19

[a] - collected on 1 mm pore size polyethlene screen.

[b] - data for unfiltered samples

applicable here also. Again the contribution to the water column budget for suspended particulates is negligible.

Size fractionation data for the S. Bering Sea area are given in Table XLII (stations of Fig. 7) and percent fractions of clay and mud respectively are contained in Figures 26 and 27. It is appearent that the sediments are considerably coarser, on average, than those of the Gulf of Alaska discussed previously. (This fact is also of interest in the quest for the reasons for the enhanced productivity in the Bering Sea since the latter is a detritus dominated economy and this is usually correlated with an abundance of fine grained sediment; however, we are talking in gross generalities here.) This "courseness" is immediately reflected in the extractable heavy metal contents which for the most part were below the detection limits of the method at that time. Extractable nickel, zinc (and some iron and manganese) data are listed in Table XLIII. (It should be noted that this latter set of data is not directly comparable with either the Gulf samples, or those from Norton Sound considered below, since, at the request of BLM, the extraction procedure was changed in 1977 to align our procedure with those used by BLM contractors elsewhere in the country.) Naidu and Mowatt (1977; Abstract included with this report) have discussed the clay minerology of the <2 μm fraction. Representative analyses are shown in Table XLIV; degraded illite and chlorite predominates.

The trend noted for the S. Bering Sea is more apparent for the suite of sediment samples collected in Norton Sound, and to a lesser extent in the Chukchi Sea. Norton Sound in particular appears to be swept clear of fines; size fractionation data are listed in Tables XLV and XLVI. Figure 28 illustrates the distribution of clay sized material. Naidu *et al.* (1977; Abstract included with this report) have recorded that illite, degraded

TABLE XLII

S. BERING SEA

O.S.S. *Discoverer* - June 1975
Sediment Size Fractionation Data (%)

Station #	Clay	Silt	Sand	Gravel
01	7.82	19.57	72.61	0
03	0.02	0.30	82.81	16.86
05	0.04	0.10	22.44	76.92
06	1.78	0.61	97.61	0
07	0	0.11	81.42	18.48
08	0	0.15	99.85	0
09	0	0.02	93.01	6.96
10	10.42	8.68	80.90	0
11	9.67	5.66	84.67	0
13	8.23	30.73	61.04	0
14	5.30	6.46	46.97	41.26
16	9.65	28.01	62.34	0
17	13.64	49.92	36.44	0
19	7.45	33.28	59.27	0
20	7.80	6.41	88.79	0
21	6.82	3.75	89.43	0
22	6.50	2.80	90.70	0
23	1.69	0.23	98.08	0
24	0.06	0.11	46.83	53.00
25	0.30	0.26	99.44	0
26	7.21	7.02	85.77	0
27	6.98	8.25	84.77	0
28	9.74	36.85	47.21	6.21
29	6.96	30.99	62.05	0
31	7.83	15.27	76.90	0
34	7.97	17.45	74.58	0
37	8.66	25.70	65.63	0
38	8.65	44.28	47.07	0
39	7.90	15.37	76.73	0
40	8.30	7.65	84.04	0
41	2.46	0.63	96.91	0
42	1.22	1.26	97.51	0
43	7.26	7.47	85.00	0
44	6.23	8.67	85.10	0
45	6.31	34.29	59.40	0
46	8.15	31.22	60.63	0
47	7.15	21.35	71.51	0
48	7.81	6.80	60.52	24.87
49	15.20	53.66	31.14	0
50	7.76	10.38	81.86	0

TABLE XLII (Continued)

Station #	Clay	Silt	Sand	Gravel
54	9.76	30.48	57.12	2.64
55	7.14	11.16	81.70	0
56	6.72	30.87	67.41	0
57	6.72	12.47	80.81	0
58	0.58	0.73	98.69	0
59	7.64	9.18	83.18	0
60	2.28	3.52	74.99	19.22
61	20.26	2.66	77.08	0
62	6.84	18.45	74.72	0
63	10.01	39.50	50.49	0
64	12.46	31.05	56.49	0
65	8.28	32.13	59.59	0
66	7.10	24.18	68.72	0
68	7.05	29.59	63.37	0
69	8.09	33.85	58.06	0
70	16.82	43.22	39.23	0.73
71	8.04	22.95	69.01	0
72	8.89	45.06	46.05	0
73	9.54	19.84	70.62	0
82	6.63	5.20	88.17	0
83	9.97	39.43	50.82	0
92	23.80	46.16	24.84	5.20

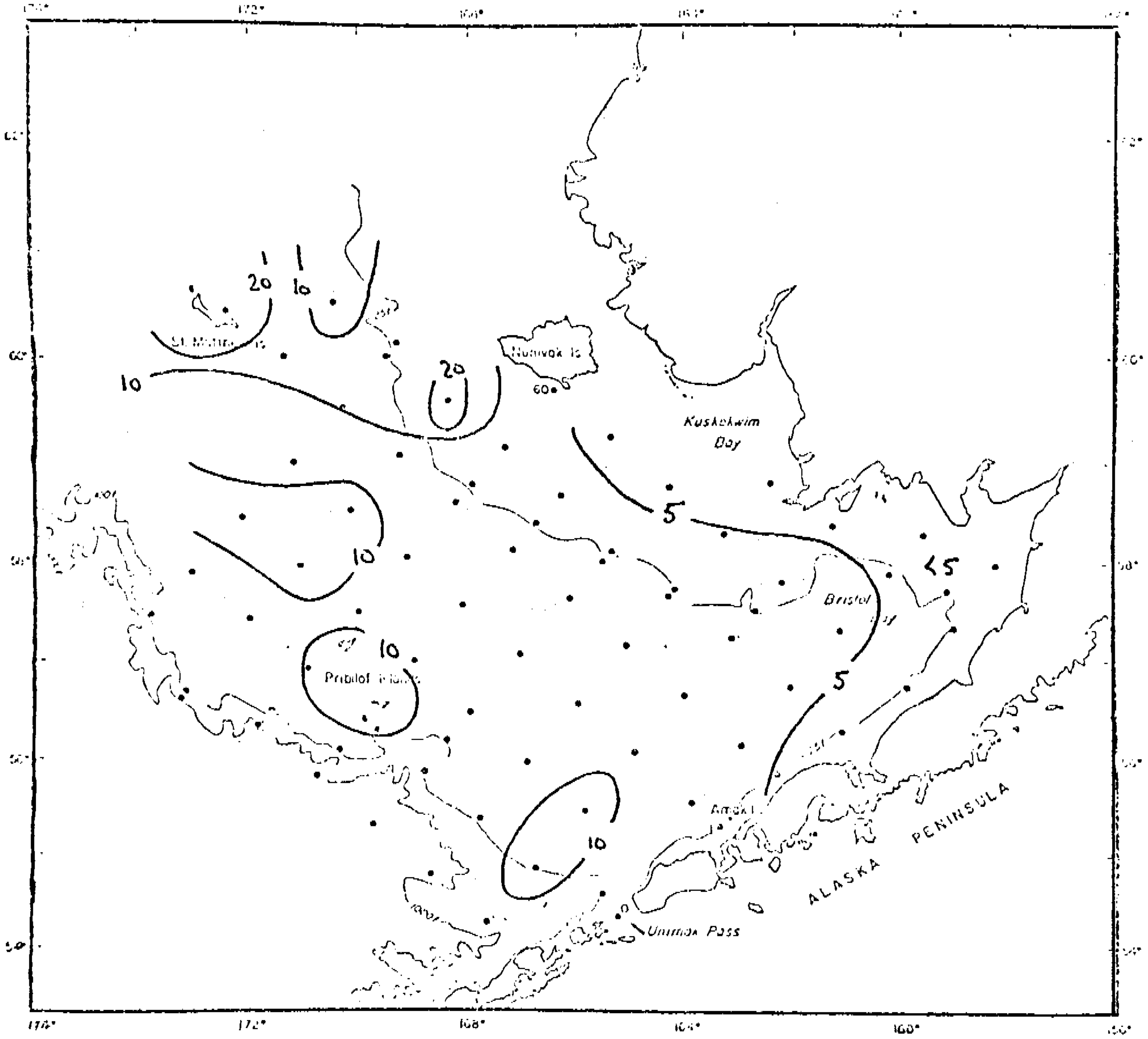

Figure 26. S. Bering Sea. Weight percent of clay sized surficial sediment.

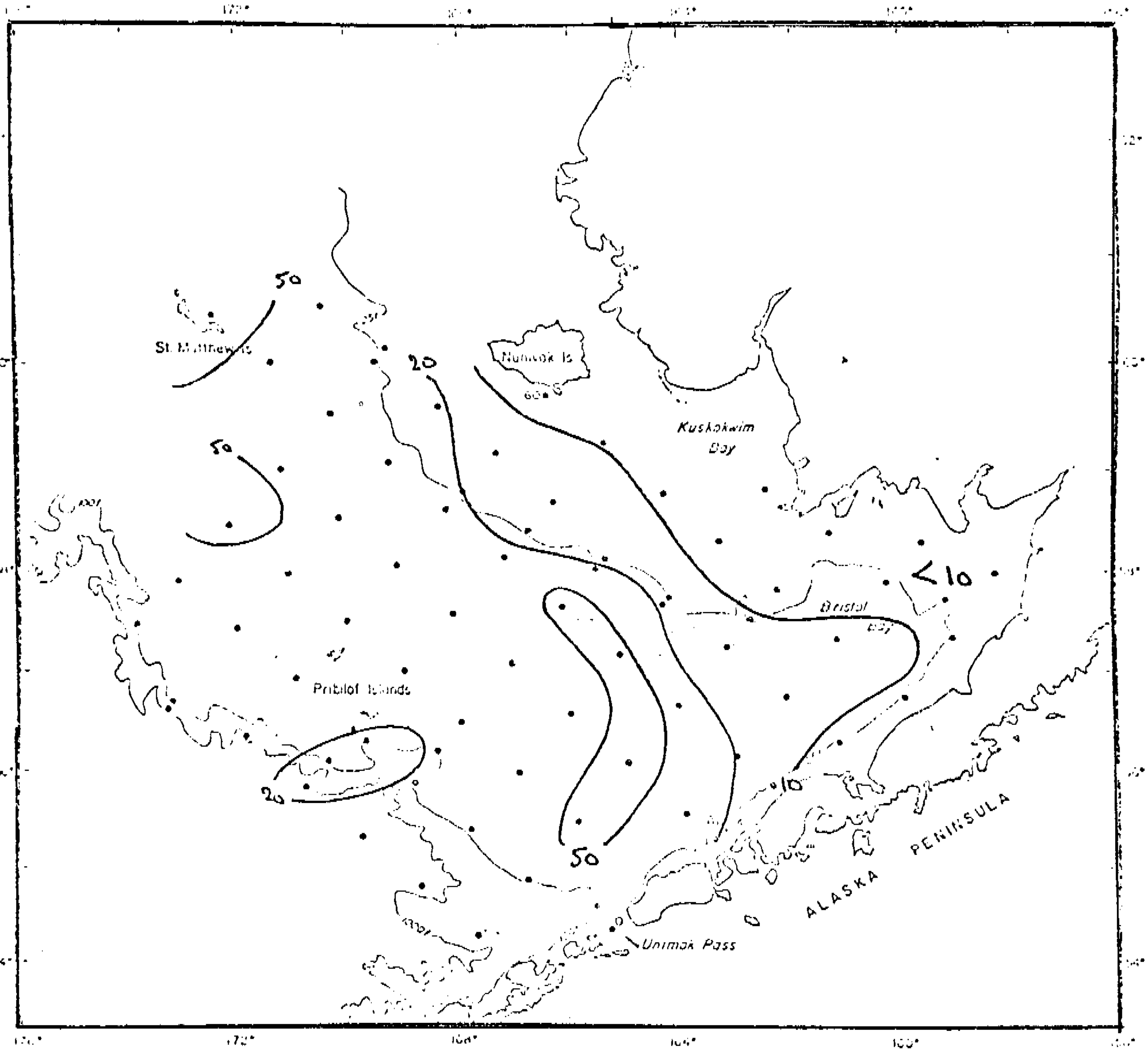

Figure 27. S. Bering Sea. Weight percent of mud sized surficial sediment.

TABLE XLIII

S. BERING SEA

O.S.S. *Discoverer* - June 1975
Summary of heavy metal contents of sediment extracts
(μg/g) and % mud (silt & clay)

Station	Mud (%)	Ni	Zn	Fe	Mn
6	2.4	<2.5	6.4		
8	0.2	6.4	21.3		
10	19.1	<2.5	7.2		
12		<2.5	12.2		
13	40.0	3.0	9.3		
14	11.8	2.5	9.5		
17	63.6	<2.5	12.2	1920	26.0
19	40.7	<2.5	6.1	1900	26.0
21	10.6	<2.5	17.0		
26	14.2	<2.5	6.8		
28	46.6	3.0	9.9	1850	22.7
30		7.3	23.9		
31	23.1	<2.5	7.1	637	9.0
41	3.1	<2.5	6.4	1466	22.7
43	14.7	2.5	6.3		
44	14.9	<2.5	5.9	1040	16.2
56	37.6	8.2	19.3		
57	19.2	<2.5	6.8		
59	16.8	<2.5	4.8	1555	18.2
60	5.8	<2.5	12.0		

TABLE XLIII (Continued)

Station	Mud (%)	Ni	Zn	Fe	Mn
62	25.3	<2.5	9.7		
63	49.5	<2.5	13.3	1756	27.3
64	43.5	<2.5	12.0	1350	20.9
65	40.4	<2.5	10.5	915	18.8
69	41.9	<2.5	12.5	985	21.3

TABLE XLIV

S. BERING SEA

Discoverer, 2-19 June 1975
A. S. Naidu, Analyst
Clay mineralogy (weighted peak area percents)

Station No.	Expandable component[a]	Illite	Kaolinite	Chlorite
16	40	22	5	33
17	41	29	3	27
18	36	35	5	24
30	31	29	3	37
36	32	28	3	35
37	16	46	4	34
66	31	41	3	25

[a] See text for definition.

TABLE XLV

NORTON SOUND

OSS *Discoverer* - September 1976

Sediment Size Fractionation Data (%)

Station #	Clay	Sand	Gravel
N 1	22.11	77.83	.05
2	8.69	91.03	.28
3	44.46	55.17	.37
4	87.04	12.96	0.
5	64.30	35.70	0.
6	86.42	13.58	0.
7	17.14	82.51	.35
8	64.29	34.91	.79
9	89.03	10.41	.56
10	16.26	83.70	.03
11	19.35	80.63	.02
12	56.79	43.21	0.
12D	59.52	39.56	.92
13	81.87	18.12	.02
14	94.64	4.98	.37
15	81.89	18.09	.01
16	19.35	80.63	.02
17	85.61	13.08	1.31
18	91.39	8.59	.01
19	40.79	58.96	.24
20	35.18	63.92	.90
21	21.52	78.48	0.
22	94.53	5.43	0.03
23	43.75	54.95	1.29
24	16.83	83.09	.07
25	13.05	71.40	15.55
26	17.56	67.29	15.15
27	14.08	85.21	.71
28	7.04	82.65	10.31
28A	14.84	71.28	13.88
29	60.97	38.86	.17
30	34.60	56.21	9.18

TABLE XLVI

CHUKCHI SEA

OSS *Discoverer* - September 1976

Sediment Size Fractionation Data (%)

Station #	Clay	Sand	Gravel
C 1	2.82	9.31	87.87
2	27.71	54.62	17.67
3	50.97	49.02	.01
4	6.66	93.33	.01
5	85.71	14.21	.08
6	96.05	3.64	.31
7	11.39	85.06	3.54
7A	69.21	30.73	.06
8	78.47	21.53	0
9	68.89	31.02	.09
10	5.89	94.11	0
#2	9.19	90.79	.01
11	86.93	12.99	.08
12	88.12	11.88	0
13	98.98	0.84	0.18
14	92.78	7.13	.09
15	34.52	65.29	.19
16	46.75	52.37	.88
17	20.51	62.52	16.97
18	32.69	22.44	44.86
19	71.27	28.59	0.14
20	6.62	92.94	.44
21	92.72	7.26	.02
22	81.70	18.15	.15
23	3.83	95.74	.43
24	58.42	40.75	.83
25	74.49	25.44	.07
26	25.30	74.47	.23
27	7.38	91.35	1.27
28	24.01	14.39	61.59
29	28.41	58.60	12.99
30	44.87	55.10	.03
31	8.01	91.53	.46

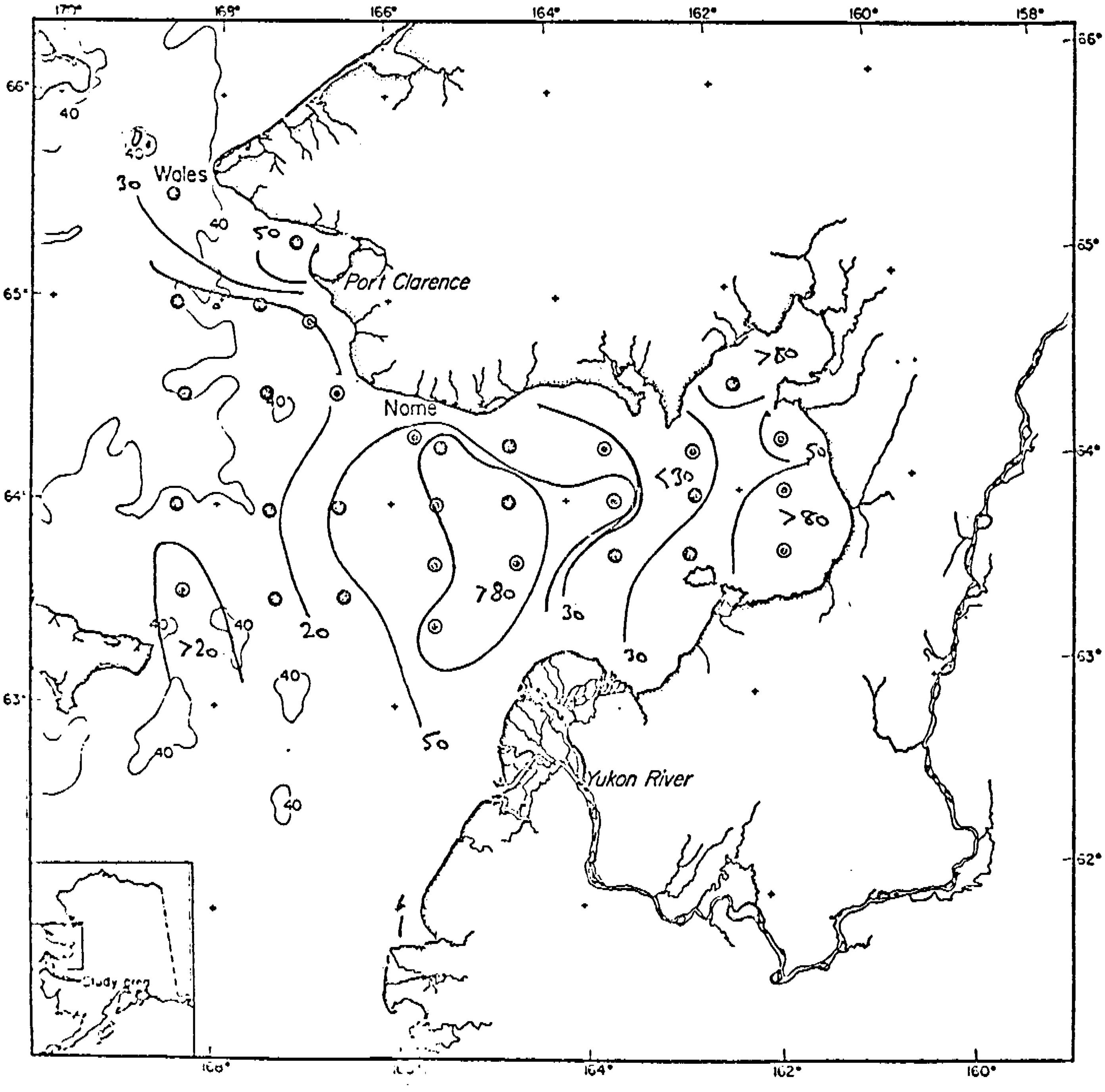

Figure 28. Norton Sound. Weight percent of clay sized surficial sediment.

illite and chlorite dominate the <2 μm sediment fraction. Acid extractable heavy metal contents from total sediment samples from these areas are given in Tables XLVII and XLVIII. Again, these concentrations are less than for Gulf sediments. Close correlations of the extractable contents with grain size fineness are evident for iron and nickel in particular and also for zinc and copper but not for manganese, as shown in Table IL. Such relationships would be expected.

The benthic biota is of prime concern with regard to the uptake - natural and pollution enhanced - of heavy metals, as noted elsewhere. We have received far too few specimens for analysis to permit any broad generalizations, neither do we have detailed information to tie together the coexistance of particular communities with specific substrate types and the resulting heavy metal transfers. A generalized picture is beginning to emerge of particularly rich productivity zones possibly linked with broadly defined depositional facies, however; in future years we will be pursuing in more detail the detailed status and dynamic geochemical conditions which give rise to productivity "hot spots" in this area which are of tremendous commercial potential. Copper concentrations in Bering Sea tanner crab (Table L) are generally somewhat lower than in the Gulf but not significantly so. We would wish here to flag our data for *Neptunea*, the giant snail. Table LI illustrates random heavy metal contents for both whole organisms (tissue) and the digestive tract. Concentrations of Cd, Cu and Zn are very high (far higher than could be explained by sediment incorporation). Since these animals are used for food it would seem desirable to investigate this and other benthic detritivores used for food in more detail.

Tables LII and LIII give intertidal *Mytilus* and *Fucus* heavy metal contents. These few data sets appear to be comparable with those for the same species from the Gulf shelf areas and no anomolies are apparent.

TABLE XLVII

NORTON SOUND

OSS *Discoverer* - September 1976

Heavy metal contents of sediment extracts (μg/g) and clay + silt %

#	Clay/silt (%)	Cd	Cu	Ni	Zn	Fe	Mn
1	22.1	<0.1	<0.3	<1.3	6.2	746	8
4	87.0	<0.1	0.5	2.5	5.0	3050	48
5	64.3	<0.1	0.5	2.9	5.0	2843	86
6	86.4	<0.1	2.0	3.3	5.7	3084	121
9	89.0	<0.1	1.1	4.3	8.0	4250	79
12D	59.5	<0.1	0.6	1.4	5.1	1609	230
13	81.9	<0.1	0.5	1.8	6.0	2086	283
15	81.9	<0.1	<0.3	<1.3	5.1	1779	75
17	85.6	0.1	2.2	4.2	9.1	2961	193
20	35.2	<0.1	<0.3	<1.3	3.5	966	58
21	21.5	<0.1	0.3	<1.3	3.5	1219	52
23	43.8	<0.1	0.6	1.8	6.6	2066	70
26	17.6	<0.1	<0.3	<1.3	2.5	565	60
28A	14.8	<0.1	<0.3	<1.3	2.5	745	20

TABLE XLVIII

CHUKCHI SEA

OSS *Discoverer* - September 1976

Heavy metal contents of sediment extracts (μg/g) and clay + silt contents (%)

#	Clay/silt (%)	Cd	Cu	Ni	Zn	Fe	Mn
3	51.0	<0.1	<0.3	1.6	3.8	1275	11
5	85.7	<0.1	0.6	1.8	3.7	1489	20
6	96.1	<0.1	<0.3	1.4	6.0	2134	134
7	11.4	<0.1	0.4	1.4	3.5	912	12
7A	69.2	<0.1	0.6	1.8	4.6	2283	54
9	68.9	<0.1	<0.3	1.3	2.6	948	24
10	5.9	<0.1	<0.3	<1.3	2.6	620	25
12	88.1	<0.1	<0.3	1.8	3.4	1197	6
13	99.0	<0.1	0.4	1.8	3.7	1589	10
14	92.8	<0.1	0.3	1.8	3.9	1490	13
15	34.5	<0.1	0.3	<1.3	3.3	1223	29
16	46.8	<0.1	<0.3	1.3	3.4	967	5
19	71.3	<0.1	<0.3	1.3	3.5	1272	22
20	6.6	<0.1	0.3	<1.3	2.8	825	29
22	81.7	<0.1	0.3	1.4	4.3	1560	16
23	3.8	<0.1	0.3	<1.3	0.9	298	2
24	58.4	<0.1	0.3	1.9	3.9	1514	10
25	74.5	<0.1	0.3	1.3	3.7	1343	17
29	28.4	<0.1	0.3	<1.3	3.8	1015	10

TABLE IL

NORTON SOUND

Discoverer - September 1976

Heavy metal extract data and grain size correlation coefficients

	S + C	Fe	Mn	Zn	Ni	Cu
Silt and Clay		0.86	0.53	0.67	0.73	0.62
Fe			0.27	0.71	0.98	0.84
Zn					0.76	0.84
Ni						0.85

CHUKCHI SEA

Discoverer - September 1976

Heavy metal extract data and grain size correlation coefficients

	S + C	Fe	Mn	Zn	Ni	Cu
Silt and Clay		0.75	0.27	0.63	0.80	-
Fe			0.58	0.89	-	-

TABLE L

S. BERING SEA

Miller Freeman - April 1976
Heavy metal contents of tanner crab.
(μg/g dry weight)

Sample #	Cd	Cu	Ni	Zn
3	<1.3	27.7	<1.3	157
7	"	20.1	"	104
9	"	23.9	"	100
10	"	61.3	"	111
12	"	36.7	"	117
14	1.8	40.0	"	135
16	<1.3	30.3	"	138
20	"	29.1	"	113
26	1.3	38.8	"	188
29	<1.3	25.0	"	182
32	"	20.4	"	117
33	"	27.5	"	169
37	3.8	20.4	"	158
40	"	21.3	"	109
48	"	21.4	"	155

TABLE LI

S. BERING SEA

Miller Freeman collection - April 1-16, 1976

Heavy metal contents of *Neptunea* (μg/g dry weight).

A. Tissue

Sample No.	Cd	Cu	Ni	Zn
15	13.0	215.9	<0.63	72.8
19	5.0	127.0	<0.63	85.9
22	32.0	241.3	0.92	133.1
31	<1.3	111.2	0.70	56.8
50	2.5	155.8	0.63	84.8

B. Digestive gland and reproductive organ

Sample No.	Cd	Cu	Ni	Zn
15	292.9	1495	0.93	1263
19	155.0	460	8.50	1325
22	200.0	875	4.63	275
31	65.0	140	1.88	350
50	280.0	6200	2.13	7000

TABLE LII

S. BERING SEA

Heavy metal contents of *Mytilus* samples (μg/g dry weight)
Mean of duplicates

Locality	Cd	Cu	Ni	Zn
Cape Lupin (Unimak Is.)	7.3	9.8	0.8	90
Sennett Point (Unimak Is.)	5.0	10.8	1.8	130
Eider Point (Unalaska)	4.0	9.8	1.3	122
Makushin Bay	6.0	6.0	1.4	81
Otter Island	4.6	6.0	1.8	156

Summer 1976 collection.

TABLE LIII

S. BERING SEA

Heavy metal contents of *Fucus* samples (µg/g dry weight)
Mean of duplicates

Locality	Cd	Cu	Ni	Zn
Cape Lupin (Unimak)	6.4	2.0	11.0	22
Sennett Point (Unimak)	5.3	2.0	3.2	17
Eider Point (Unalaska)	5.5	1.5	4.9	17
Makushin Bay	3.8	0.8	7.1	10
Otter Island	3.1	5.0	5.1	8

Summer 1976 collection.

Our most complete set of Bering Sea biota samples (which were collected especially for heavy metal analysis) are muscle and organ samples from the seal specimens collected on two cruises at the localities shown previously in Figure 12. The original intent of this sub-project was to look for statistical differences between the contents of four separate seal species which were thought to have distinctive feeding habits. Our data are largely for ribbon, spotted and bearded seals (see species data in Tables VII and IX) which were initially considered to feed predominantly on fish and benthos, fish, and invertebrate benthos, respectively. Unfortunately, it was found to be not possible to obtain representative food species at the time of collection of mammals. Nor were stomach contents suitable for either identification or analysis; in many cases it was found that the sacrificed samples had starved for a number of days. The biological investigators also found that these mammals tended to be opportunist feeders and would eat what was available and only tend to differentiate diet with species where there was adequate choice so that marked differences in heavy metal contents as a reflection of transfer from a particular type of food could not be expected. Nevertheless, some possible trends are indicated.

The heavy metal contents are given in Tables LIV and LV which are means of duplicate determinations (hence the spread listed gives these individual values). Accuracy and precision data relating to this batch of numbers are given in Table LVI. The following general characteristics are apparent (but with numerous exceptions):

Cadmium

a) Concentrations in the kidneys of ribbon seals greater than in spotted or bearded.

b) Higher cadmium contents in the muscle tissue of bearded seals than in ribbon or spotted seals.

TABLE LIV

BERING SEA

O.S.S. *Surveyor* 31 March - 27 April 1977

Heavy metal contents of seal tissue (μg/g dry weight)

Sample	Species	Tissue	Cd[a]	Ni[a]	Cu[a]	Zn[a]
01	Rib	muscle	0.13 ± 0.01	2.5 ± 0.4	6.7 ± 0.5	37 ± 12
		liver	6.4 ± 0.1	2.6 ± 0.9	16.5 ± 0.2	169 ± 7
		kidney	53.0 ± 0.3	2.8 ± 0.2	19.4 ± 0.1	149 ± 1
02	Rib	muscle	0.3 (c)	1.3 (c)	4.4 ± 0.6	50 ± 0
		liver	8.7 ± 1.2	1.3 (c)	16.5 ± 3.5	8 ± 2
		kidney	20.1 ± 4.5	0.5 ± 0	16.5 ± 3.5	102 ± 22
03	Rib	muscle	0.25 ± 0	8.3 ± 1.0	5.5 ± 0	54 ± 2
		liver	6.4 ± 0.1	2.2 ± 0.4	26.9 ± 1.3	140 ± 15
		kidney	34.5 (c)	3.0 (c)	16.0 (c)	98 (c)
04	S	muscle	0.14 ± 0.01	3.0 ± 0.2	6.7 ± 1.3	51 ± 9
		liver	0.4 ± 0.1	2.5 ± 0.2	25.0 ± 2.5	116 ± 51
		kidney	16.7 ± 0.2	2.4 ± 0.4	44 ±13	113 ± 23
05	B	muscle	0.8 ± 0.1	2.8 ± 0.3	7 ± 2	175 ± 25
		liver	21.0 ± 0.5	1.3 ± 0.1	36.5 (c)	182 ± 2
		kidney	16.0 ± 2.0	2.0 ± 0.1	28.5 ± 0	163 ± 3
06	Rib	muscle	0.47 ± 0.01	5.8 ± 0	6.8 ± 0.8	18 ± 6
		liver	11.4 ± 0.1	0.9 ± 0.2	29.0 ± 2.5	100 ± 10
		kidney	33.4 ± 0	1.2 ± 0.2	17.5 ± 0.3	48 ± 0
07	B	muscle	0.57 ± 0.04	2.8 ± 0.2	<5 (b)	147 ± 20
		liver	22.2 ± 1.3	0.8 ±	22.8 ± 0.2	170 ± 17
		kidney	22.5 ± 2.0	1.3 ± 0.3	40 ± 6	160 ± 15
08	B	muscle	1.26 ± 0	1.2 ± 0.1	7.6 ± 0	40 ± 1
		liver	41.1 ± 0.9	0.5 ± 0	44.1 ± 2.4	87 ± 3
		kidney	17.4 ± 0.1	1.5 ± 0.1	28.1 ± 0.6	110 ± 1
10	S	muscle	1.5 ± 1.0	2.4 ± 0.2	11 ± 3	52.5± 0
		liver	0.6 ± 0.1	8.1 ± 1.6	18 ± 4	213 ± 7
		kidney	44.3 ± 0.7	<1.0 (b)	24.5 (c)	183 (c)
11	Rib	muscle	0.24 ± 0.02	<0.5 (b)	16.5 ± 3.5	140 ± 5
		liver	35 ±15	<0.5 (b)	13.8 ± 1.2	15 ± 10
		kidney	16 (c)	<0.5 (b)	19 ± 6	8 ± 3

TABLE LIV (Continued)

Sample	Species	Tissue	Cd[a]	Ni[a]	Cu[a]	Zn[a]
16	B	muscle	1.13 ± 0.07	4.8 ± 0.2	6.9 ± 0.6	60 ± 10
		liver	5.3 ± 0.6	5.4 ± 1.1	37.6 ± 1.6	228 ± 3
		kidney	108.7 ± 0.5	6.2 ± 0.2	34.7 ± 0.2	110 ± 20
17	Walrus	muscle	1.50 ± 0.25	2.4 ± 0.5	6.3 ± 1.3	43 ± 8
		liver	26.0 ± 1.0	1.6 ± 0.3	41.6 ± 0.4	99 ± 1
		kidney	26.5 ± 1.0	<1.0 (b)	27.7 ± 0	96 ± 1
28	S	muscle	0.11 ± 0.01	<0.5 (b)	6.4 ± 0.05	68 ± 1
		liver	4.5 ± 0.05	<0.5 (b)	16.4 ± 0.1	136 ± 1
		kidney	– –	– –	– –	– –
29	Rib	muscle	0.70 ± 0.03	<0.5 (b)	1.7 ± 0	74 ± 2
		liver	17.0 ± 0.3	<0.5 (b)	5.2 ± 1.4	130 ± 3
		kidney	37 ± 5	<0.5 (b)	5.2 ± 1.3	92 ± 14
30	S	muscle	0.16 ± 0.04	<0.5 (b)	4.0 ± 0.1	133 ± 0
		liver	7.3 ± 0.2	<0.5 (b)	18.5 ± 0.2	160 ± 0
		kidney	34 ± 5	<0.5 (b)	15 ± 2.5	120 ± 17
32	S	muscle	0.17 ± 0.01	<0.5 (b)	1.1 ± 0.1	62 ± 9
		liver	15.9 ± 0.8	<0.5 (b)	17.1 ± 0.9	125 ± 23
		kidney	49 ± 7	<0.5 (b)	4 ± 2.5	110 ± 32

a = mean of duplicate determinations
b = duplicate determinations
c = single determinations

TABLE LV

BERING SEA

O.S.S. *Discoverer* 25 May - 5 June 1977

Heavy metal contents of seal tissue (μg/g dry weight)

Sample	Species	Tissue	Cd[a]	Ni[a]	Cu[a]	Zn[a]
01	Rib	muscle	0.29 ± 0.04	0.5 ± 0.1	4.6 ± 0.1	96 ± 5
		liver	3.2 ± 0.9	<0.5 (b)	6 ± 3	185 ± 15
		kidney	<0.3 (b)	1.3 ± 0.5	10 ± 1	197 ± 6
02	S	muscle	1.3 (c)	<0.5 (b)	3.9 ± 0.5	18.2 ± 1.1
		liver	2.48 ± 0.02	<0.5 (b)	11 ± 3	23.3 ± 0.2
		kidney	<0.5 (c)	<0.5 (b)	25.5 ± 0	22 ± 2
03	S	muscle	0.29 ± 0.07	2 ± 1	7.6 ± 0.8	87 ± 7
		liver	1.85 ± 0.15	2.5 ± 0	16.5 ± 0.1	114 ± 1
		kidney	11.0 (c)	1.4 (c)	24.0 (c)	93 ± 25
05	S	muscle	0.6 (c)	<0.5 (b)	2.2 ± 0.7	7.5 ± 1
		liver	0.99 ± 0.01	<0.5 (b)	2.3 ± 0.1	10 ± 1
		kidney	<0.5 (c)	<0.5 (b)	23 ± 3	13 ± 1
08	S	muscle	0.08 ± 0	<0.5 (b)	6.5 ± 0.5	62 ± 3
		liver	1.9 ± 0.4	<0.5 (b)	44.3 ± 0.3	101 ± 15
		kidney	1.52 ± 0.02	<0.5 (b)	29 ± 3	83 ± 3
10	S	muscle	0.24 ± 0	2.4 ± 0	7.1 ± 0.9	123 ± 2
		liver	2.6 ± 0.4	1.8 ± 0.2	20.3 ± 0	109 ± 5
		kidney	11 ± 4	0.9 ± 0.1	12 ± 3	103 ± 9
11	Ring	muscle	0.19 ± 0.01	0.6 ± 0.1	9.5 ± 0	135 ± 0
		liver	5.0 (c)	<0.5 (b)	25 (c)	72 ± 2
		kidney	2.52 ± 0.04	0.7 ± 0.1	10 (c)	227 ± 13
15	S	muscle	0.17 ± 0.05	1.4 ± 0.8	6.9 ± 0.1	80 ± 1
		liver	3.1 ± 0.4	2.1 ± 0.2	18.5 ± 1.5	134 ± 9
		kidney	13.1 ± 0.1	3.8 ± 0.3	16.1 ± 0.1	123 ± 1
07	Rib	muscle	0.27 ± 0.01	<0.5 (b)	3.3 ± 0.7	116 ± 7
		liver	3.0 ± 0.2	17.5 ± 0	2.5 (c)	115 ± 5
		kidney	5.5 ± 0	<0.5 (b)	10 ± 1	138 ± 3

a = mean of duplicate determinations
b = duplicate determinations
c = single determinations

TABLE LVI

BERING SEA

Marine mammal analysis program - precision and accuracy
(μg/g dry weight ± one standard deviation)

a. NBS Standard # 1571 orchard leaves.

Element	n	This Study	NBS Certified
Cd	3	0.15 ± 0.06	0.11 ± 0.02
Ni	4	1.4 ± 0.03	1.3 ± 0.2
Cu	7	10.5 ± 3	12 ± 1
Zn	7	25 ± 5	25 ± 3

b. NBS Standard # 1577 bovine liver.

Element	n	This Study	NBS Certified
Cd	3	0.31 ± 0.07	0.27 ± 0.04
Ni	4	0.9 ± 0.08	--
Cu	3	150 ± 30	193 ± 10
Zn	8	120 ± 20	130 ± 10

c) Liver contents of spotted seals relatively low.

d) Liver cadmium contents of bearded seals relatively high.

Nickel - muscle contents of this metal generally higher than liver than liver or kidneys.

Copper - contents of spotted seal kidneys generally higher than liver but the reverse for ribbon and bearded seals.

Zinc

a) Muscle contents of bearded (and possibly spotted) seals higher than ribbon seals.

b) Concentration of zinc in all liver generally higher than in kidneys.

It appears likely that the spotted seals have the lowest overall metal contents and, yet more tentatively, the bearded the highest. The former are considered to be largely consumers of fin fish, whereas the bearded seals consume large quantities of benthic invertebrates. Since the benthos concentrates metals more than pelagic communities this possible trend is what we initially expected. Clearly more positive correlations will require not only a considerably large number of specimens of one specific species but also food species or fresh stomach contents. The clam-walrus food link is yet less ambiguous and has been flagged by us previously, but in a study conducted in 1972, the cadmium contents of walrus tissue collected south of St. Lawrence Island was found to be quite low; in the 2-4 $\mu g/\ell$ range. The single sample included in this present study gives values comparable with those for seals (but not notably higher). In view of the recent advances in analytical technique the earlier data must be suspect.

With regard to the liver and kidney contents, there appears to be no correlation with age; presumably the residence time in these organs is relatively short and concentrations probably reflect recent eating habits. For the muscle tissue however, there is a suspicion of increasing contents (see especially zinc) with age. It is obvious, however, that we have available to us far too few individuals of any one species or age group to permit anything approaching a rigorous statistical analysis. The cadmium contents are generally surprisingly high. This is a highly toxic metal and it would seem advisable for liver and kidneys of these mammals not to form a regular part of any human diet. (See also Burrell, 1978, in Appendix III).

Beaufort Sea

A summary of the Beaufort Sea environment data is given as Appendix II.

Natural Flux of Heavy Metals in Alaskan Fjord Estuaries

Trace heavy metals behave non-conservatively in the marine environment. Some metals flocculate or co-precipitate as soluble complexes become unstable in saline waters, while others appear to be taken up by organisms or scavenged by various physical-chemical process by biota and inorganic solid phases. The net result is transport and accumulation in the deposited sediments with natural soluble concentrations in seawater being maintained at levels generally far below those predicted thermodynamically.

At the sediment water interface various physio-chemical and biological transformation reactions may occur such that metals may be remobilized and made available for diffusion from elevated interstitial water concentrations back into the water column. We have previously (e.g., Heggie and Burrell, in press) documented this general sequence for copper. Details of the various processes are mostly unknown, however. Least understood is the nature of the (presumably largely microbially mediated) reactions of the interface: this is the basic focus of the work reported in the following section of this report. But also scavenging and reactions partitioning metals onto the settling solid phases are not understood to any great extent. The fjord-estuaries of S.E. and S. Central Alaska provide ideal environments to pursue this line of research because the intra-sill deep basins are environments which may retain quasi-stagnant bodies of water at certain times of the year such that gradients at the base of the column may be observed and correlated with physical and chemical parameters. These are all natural reactions and fluxes; the importance to the OCS program lies in the potentiality for perturbing the natural order *via* massive doses of pollution.

A classification of bottom water circulations within Alaskan fjords has been given by Muench and Heggie (1977). For the present program we have directed our field efforts to Yakutat and Resurrection Bays which serve as suitable specific study sites for the N.E. Gulf and Lower Cook Inlet lease areas, respectively. We have previously described the oceanographic characteristics of Resurrection Bay in some detail (Heggie *et al.*, 1977; Heggie and Burrell, in press). Work in this inlet under the auspices of the OCS program has only just begun and no data will be reported in this report. Yakutat Bay is a complex multi-silled fjord as shown in Figure 30 for the transect of Figure 29. Based on the sill-height classification referenced above it would be expected that deep water replacement would occur in (late) oceanographic winter.

The object of the present program was, firstly to determine the general seasonal hydrographic regimes pertaining within the basins, and then to research sediment-water column exchanges in detail within one (or more) basins with particular reference to the partitioning of heavy metals onto inorganic or biogenic particulate sediment. At the present time we have made chemical and physical observations in April, July and September and have looked at copper, vanadium, manganese and cadmium distributions. Most of the data (see Appendix VI) has not yet been analyzed in any detail and only preliminary interpretations can be given at this time. One major difficulty with this study site is the absence of good bathymetric coverage. The transect shown in Figure 30 is intended to cross the sills at their lowest points. However, a preliminary interpretation of the hydrographic data has required, for example, assumption that the effective barrier between the basins represented by stations YAK-3 and YAK-5 should be increased to within, say, 50-60 m from the surface. Time did not permit occupation of more than one station per basin so that we have no feeling for property slopes within each basin. Taking into consideration the extreme vertical exageration of Figure 29 it seems likely that the

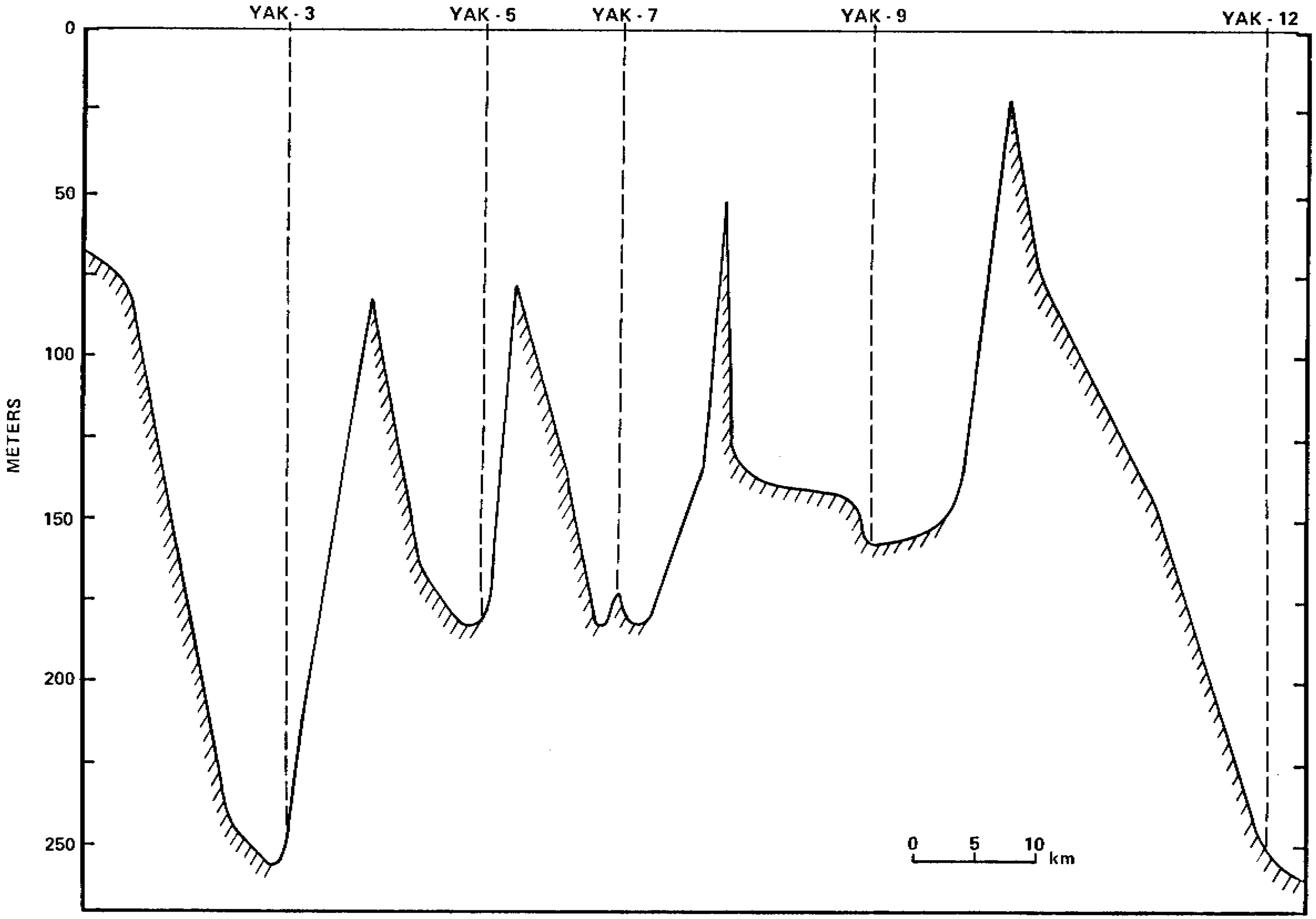

Figure 29. Longitudinal section of Yakutat Bay showing standard stations (section line shown in Figure 30).

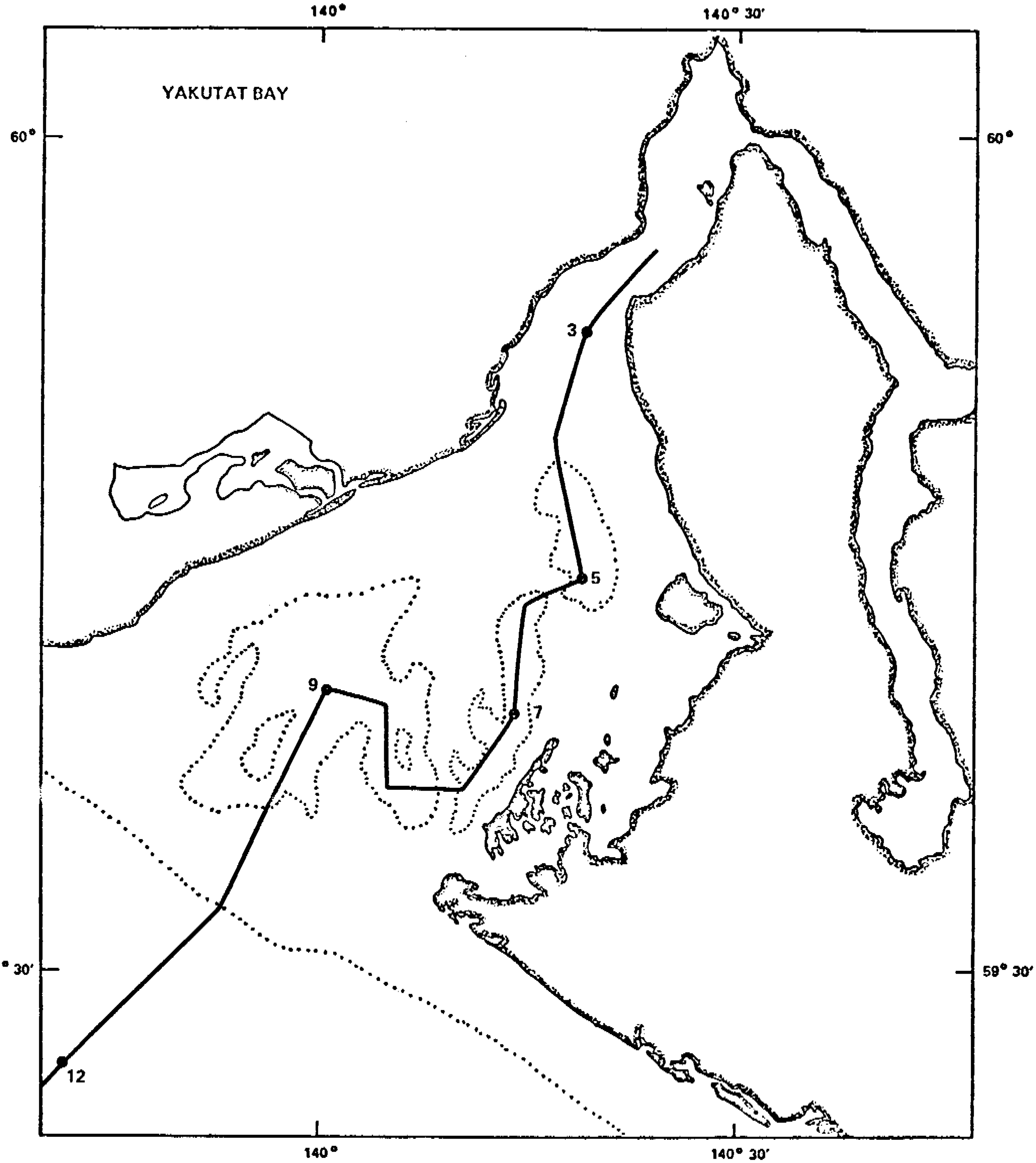

Figure 30. Yakutat Bay showing principal fjord basins, standard hydrographic stations and the line of the longitudinal section of Figure 29.

sharp divisions shown between adjacent basins are artifacts. They serve, however, to emphasize the mean properties of the water in each basin.

Density distributions for April are shown in Figure 31. Given the relatively shallow entrance sill, flushing of the intrabasin waters would be expected at about this time of year, and this seems to be the case. For this particular data set (see also salinity distributions of Fig. 32) it appears, in fact, that replacement of the deep waters of the outer three basins is in progress but that the inner basin is largely unaffected, suggesting that the height of the enclosing barrier is not as depicted from the scant bathymetric data.

Figure 33 shows vertical profiles for dissolved and particulate organic carbon, particulate aluminum and total suspended load at this time at station YAK-7. There is an increase in total suspended solids at the base of the water column and large (offset) maxima for both POC and DOC just above the bottom. All these may be indications of advective movements at depth in this basin consequent upon wholesale replacement by extra-fjord shelf waters.

In July, the deep waters of the outer two basins are stratified and contain their seasonally maximum density water (Fig. 34). At the inner basins, however, and particularly that represented by station YAK-3, the water below sill depth shows considerable homogeneity as shown by the temperature structure of Figure 35. This latter figure also illustrates a core of cold water in the surface layers originating from the glacial runoff further up-fjord. It is apparent that the deep water of the inner basin is affected by this distinctive upstream water since the denser bottom water is cold but has, in fact, a slightly lower salinity than that higher in the column (Fig. 36).

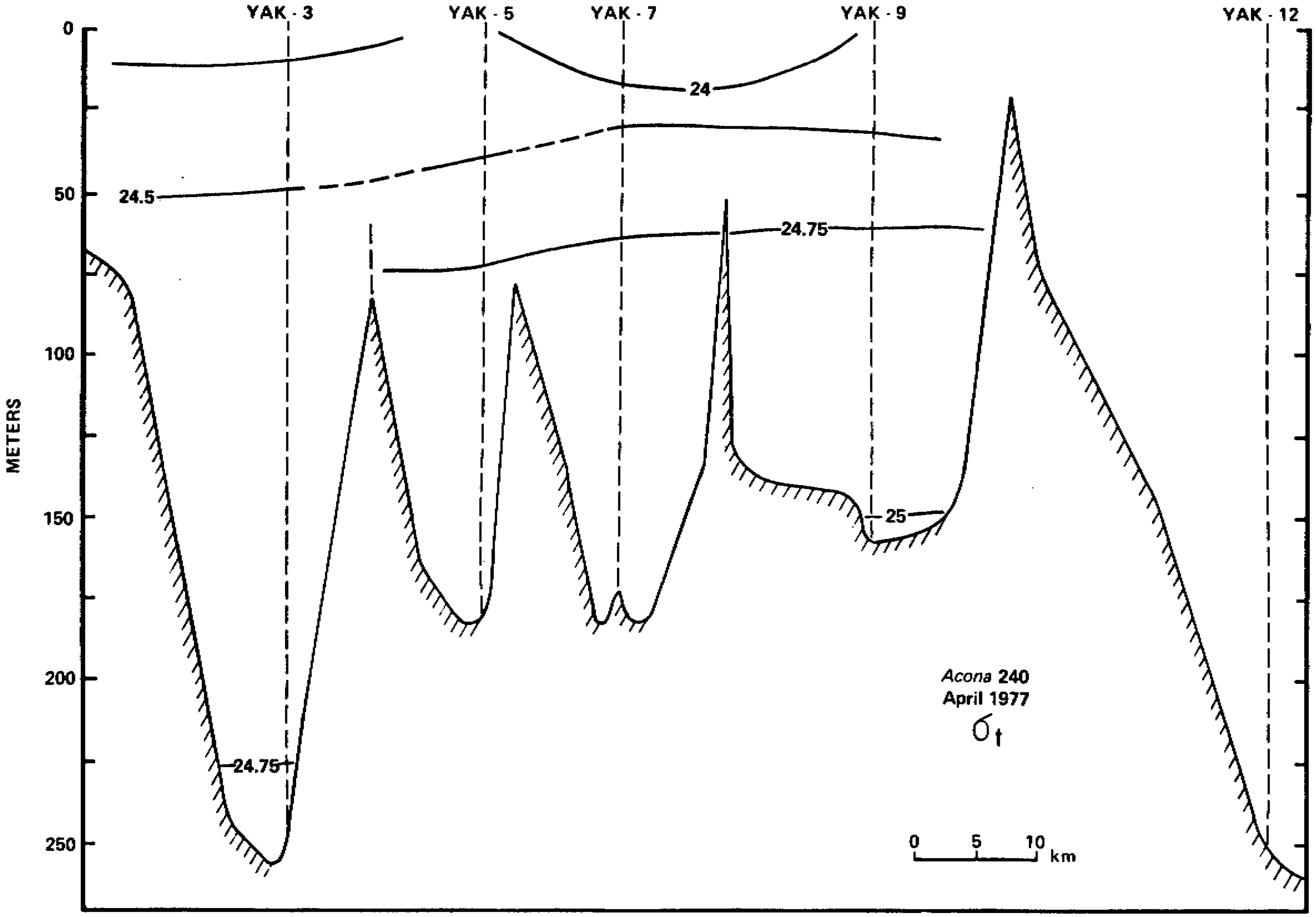

Figure 31. Density distribution in Yakutat Bay, April 1977 (*Acona* 240).

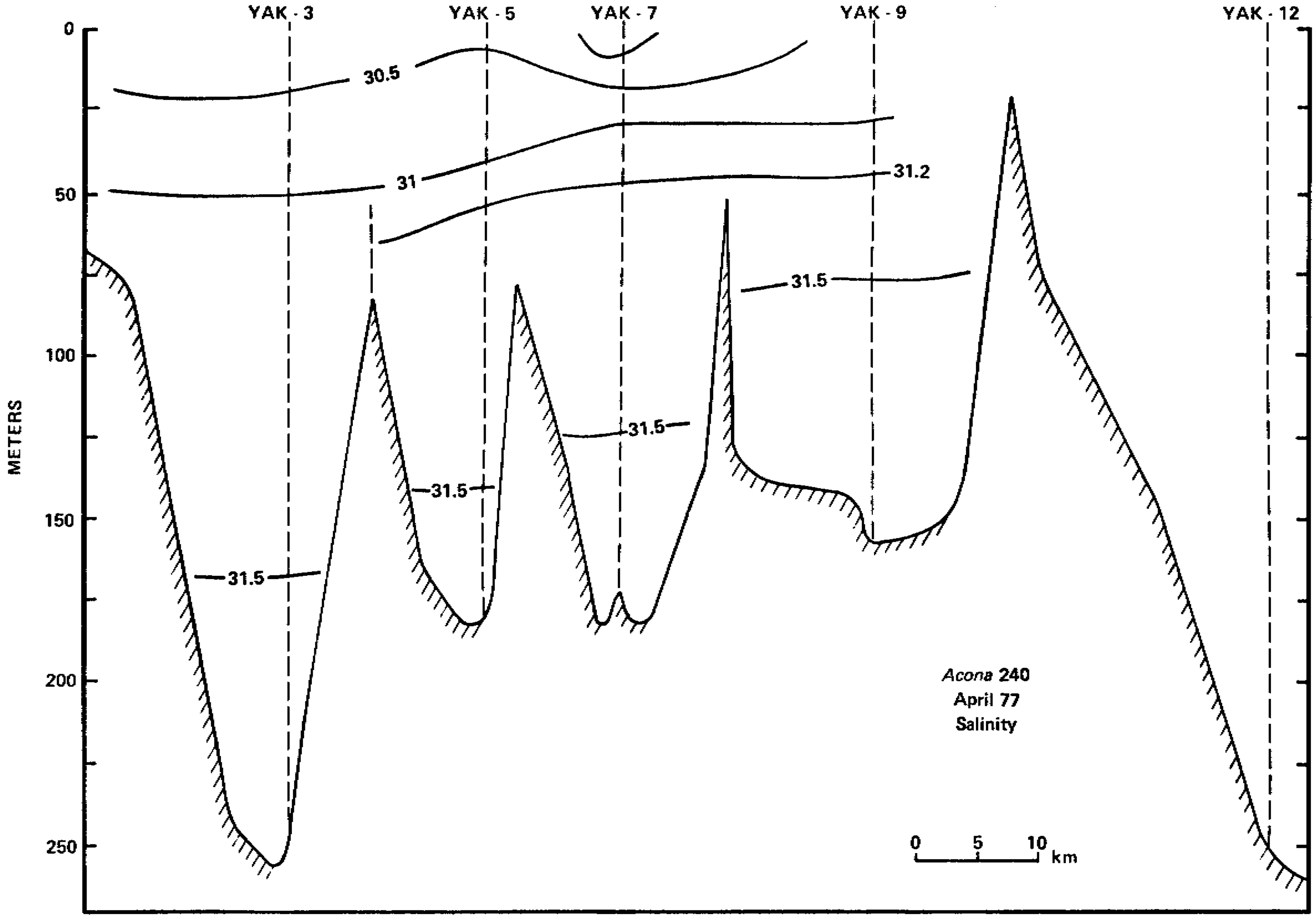

Figure 32. Salinity distribution in Yakutat Bay, April 1977 (*Acona* 240).

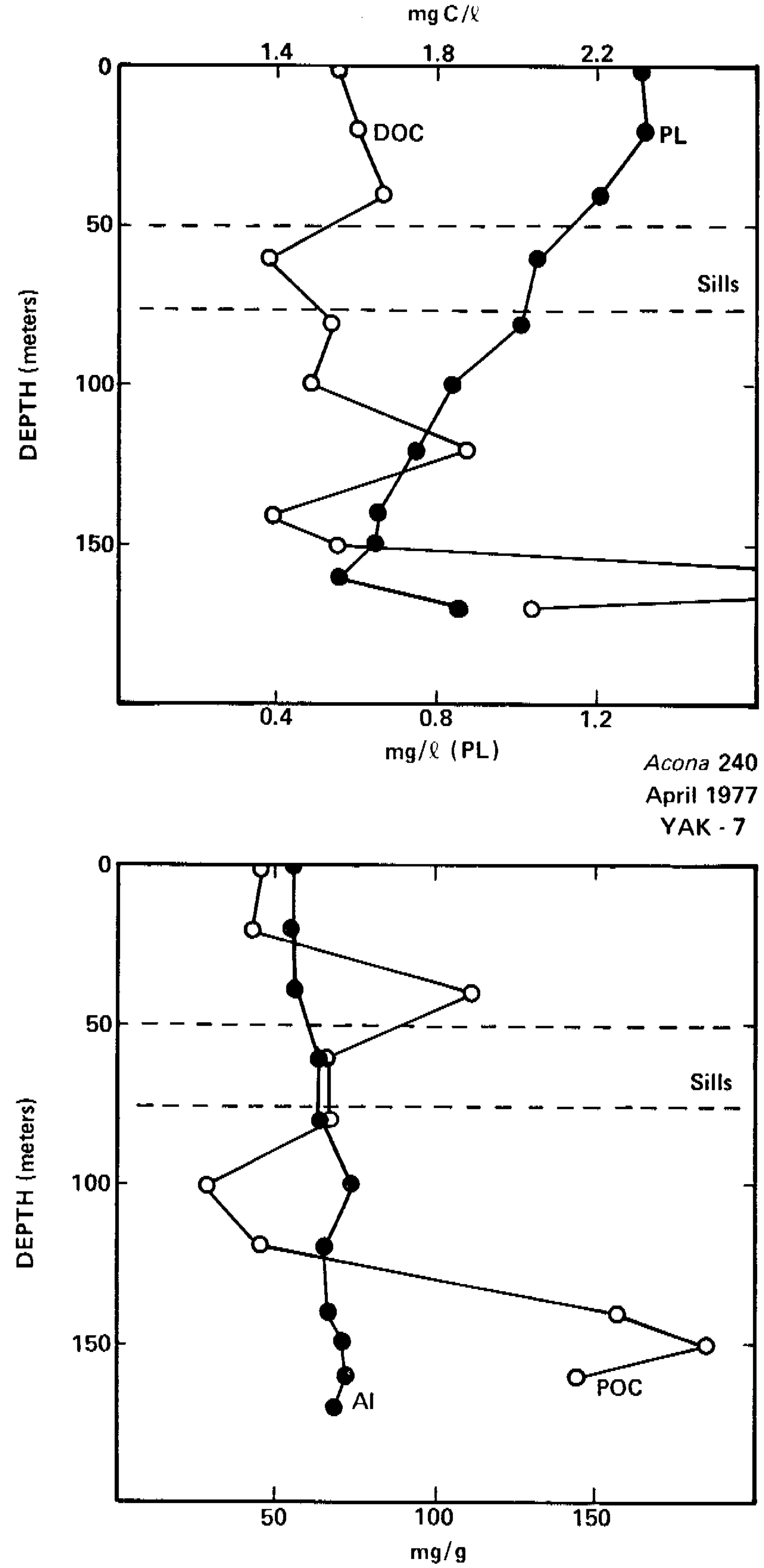

Figure 33. DOC, POC, particulate aluminum and total suspended load profiles at Station YAK-7, Yakutat Bay, April 1977.

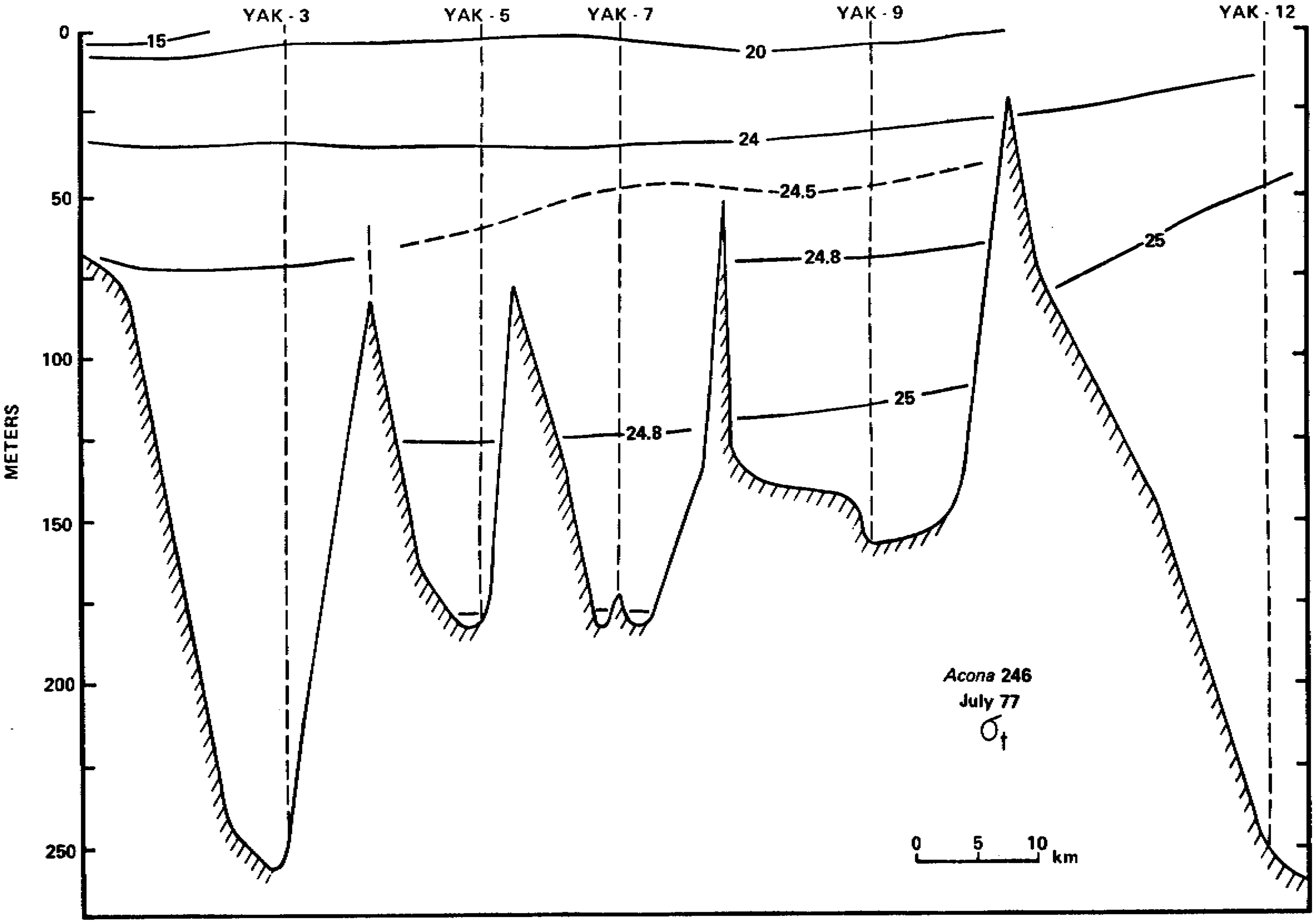

Figure 34. Density distribution in Yakutat Bay, July 1977 (*Acona* 246).

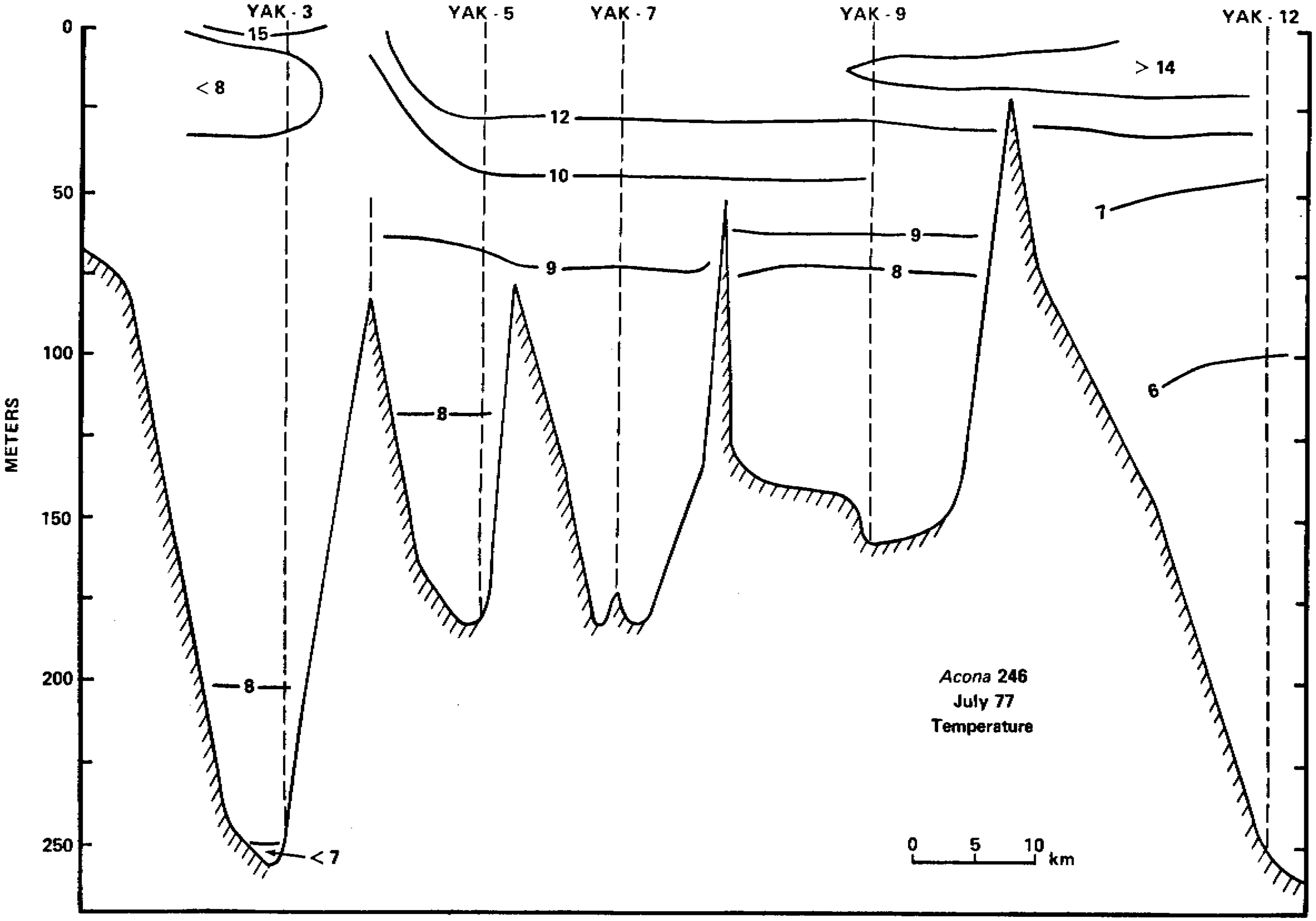

Figure 35. Temperature distribution in Yakutat Bay, July 1977 (*Acona* 246).

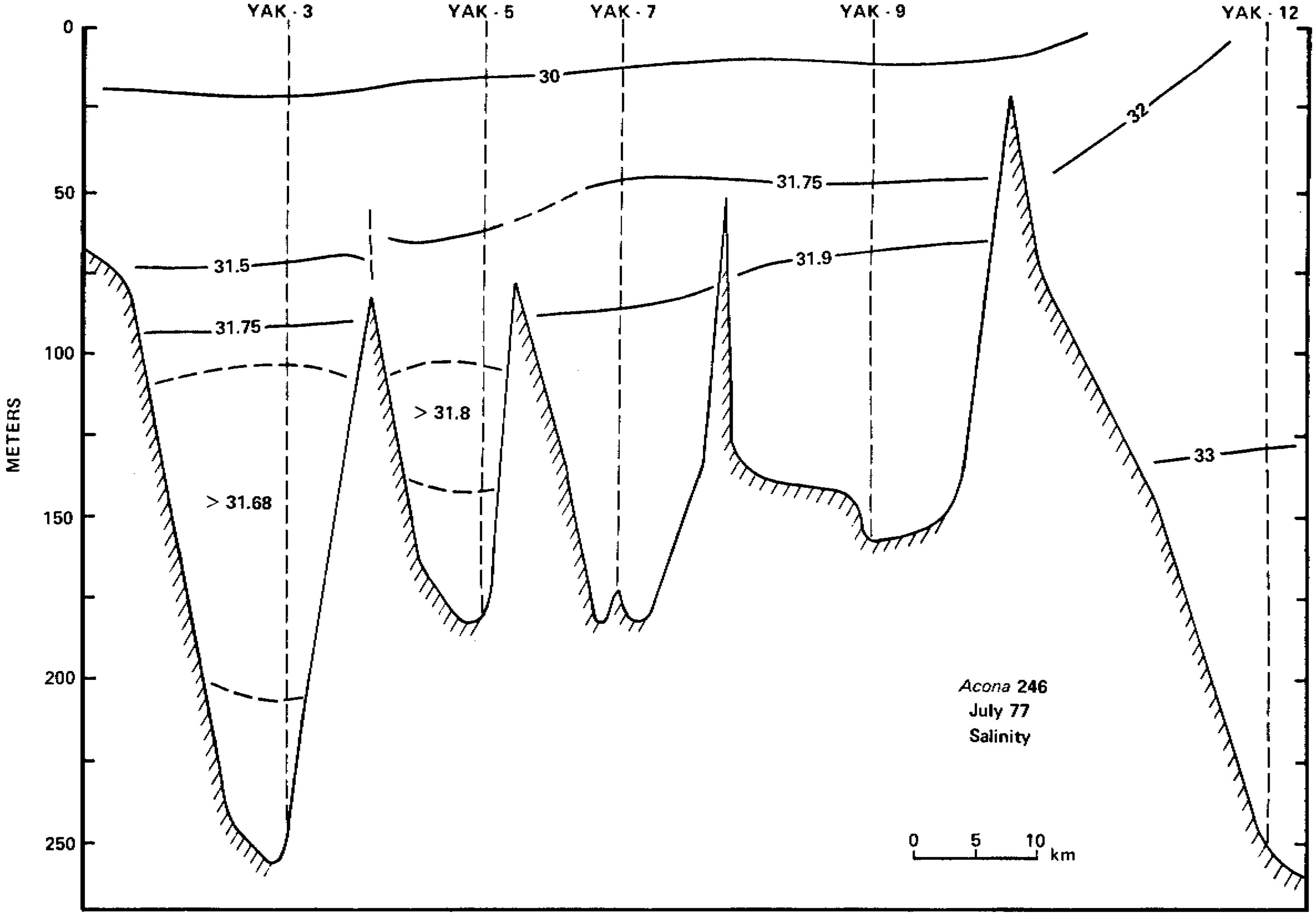

Figure 36. Salinity distribution in Yakutat Bay, July 1977 (*Acona* 246).

Investigation of the basin chemistry at this time was confined to Stations YAK-7 and 9, which, as noted above, contain dense shelf water which appeared to be emplaced in April. We do not, unfortunately, know the density of the extra-fjord water at the outermost sill in late oceanographic winter. By July this latter has a value reduced to around 24 by September. Based on our fjord investigations elsewhere it seems reasonable to suggest that the YAK-9 outermost basin is not reflushed (at least at depth) during the summer and that since the April replacement the base of the water column has not been subjected to major advection flow. Particulate load, aluminum and organic carbon distributions for Station YAK-9 is shown in Figure 37. For YAK-9 there is an approximately constant increase in total particulate load from sill height to the bottom. As would be expected, there is a large amount of particulate organic material in the surface waters but no significant gradient, at this early summer season, at depth. The distribution of dissolved organic carbon in this basin at this time (not shown here) similarly shows a surface maximum (>1 mg c/ℓ) and uniformly low concentrations (0.12 - 0.21 mg C/ℓ) below sill height.

We are less sure of the advective stability of the deep waters in the YAK-7 basin. As may be seen from Figure 34, the density structure is very similar to the YAK-5 basin and there also appears to be a very slight decrease in salinity at the bottom. Figure 38 illustrates the distributions of the same particulate parameters of Figure 37 for this basin. In this case there appears to be a significant increase in both total particulate load and particulate organic carbon adjacent to the sediment surface. If this is an indication of resuspension of deposited material then it is of interest to note that the bulk of this material appears to be organic detritus rather than aluminosilicates (as given by the particulate aluminum distribution). This would be

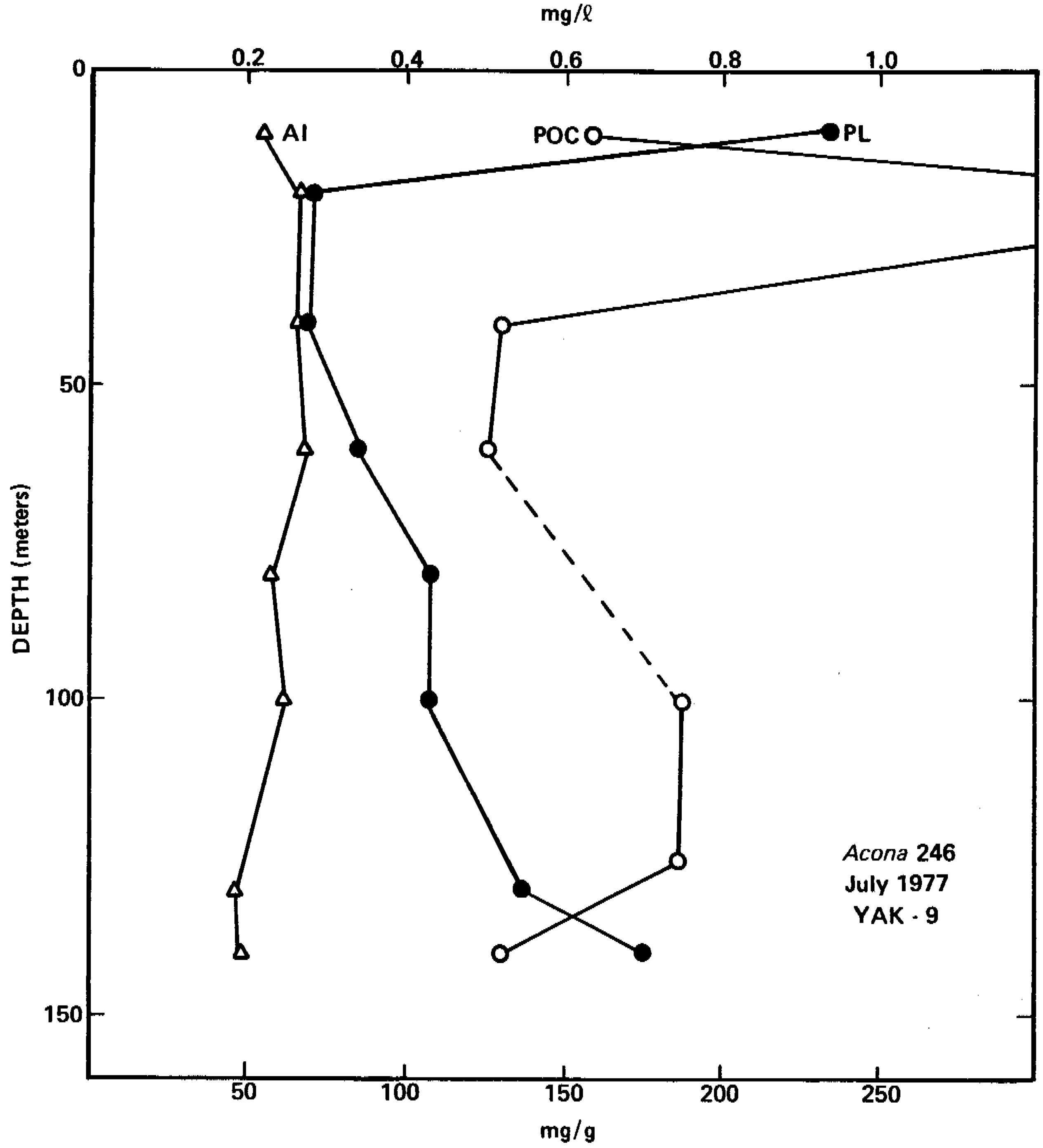

Figure 37. POC, particulate aluminum and total suspended load profiles at Station YAK-9, Yakutat Bay, July 1977.

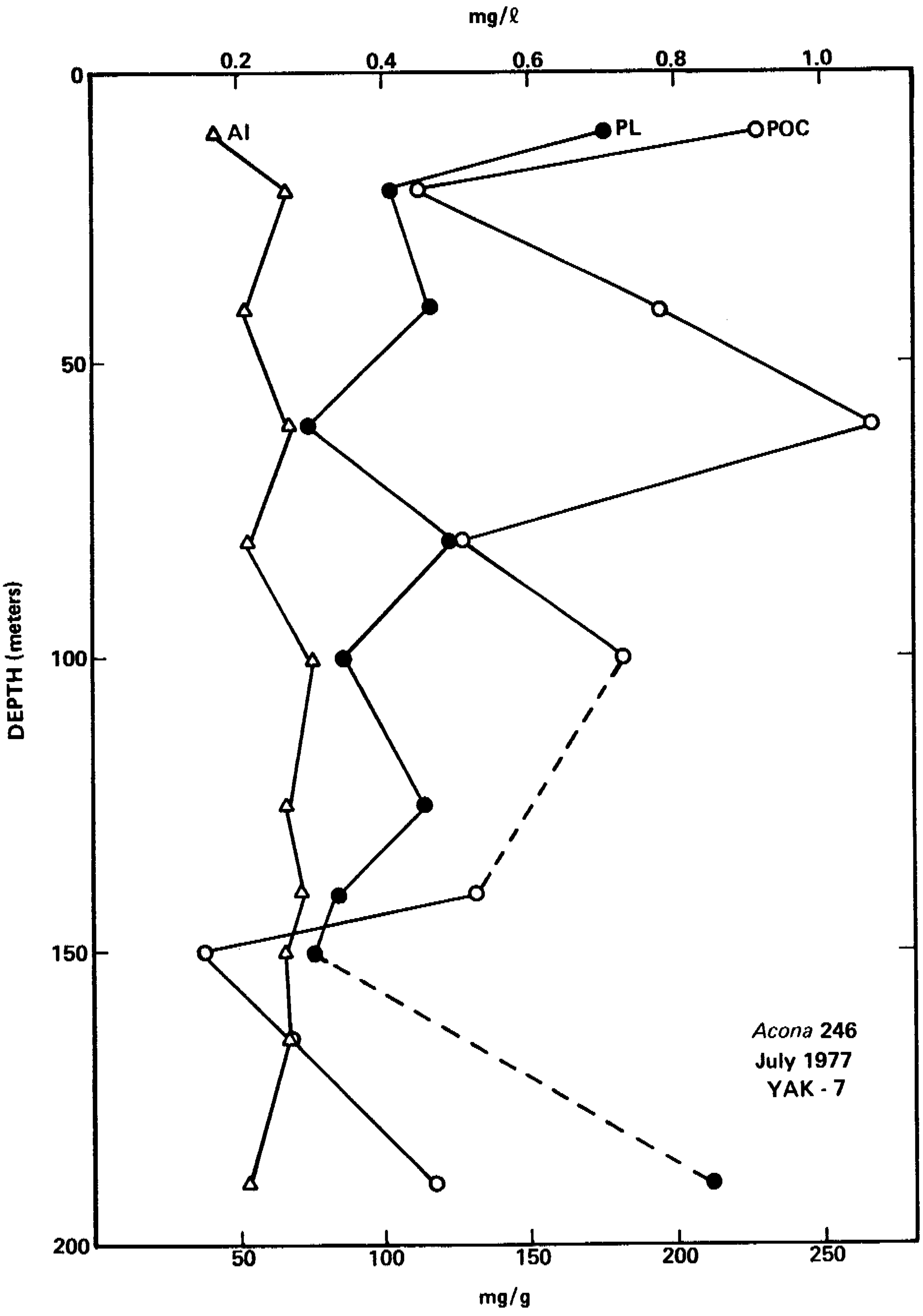

Figure 38. POC, particulate aluminum and total suspended load profiles at Station YAK-7, Yakutat Bay, July 1977.

expected since deposition of glacial till sediment would have ceased during the winter months. Above these bottom maxima there is a positive gradient in both POC and total load directed towards the surface waters.

The vertical distributions of soluble vanadium and manganese (filtered at 0.4 μm) at Stations YAK-7 and YAK-9 are given in Table LVII and Figures 39 and 40. Vanadium shows a constant soluble concentration from surface to bottom but for manganese there are pronounced positive gradients directed for the base of the water column into the sediment. Further, concentrations of manganese are enhanced at Station YAK-9 compared with YAK-7. It is possible that we are here observing colloidal or other particulate forms of manganese smaller than the membrane cut-off size (nominally 0.4 μm) and further work will be required to resolve the chemical speciation of this element. These preliminary data show again, however, that important fluxes of heavy metals occur at the sediment-water interface.

Density and salinity distributions within the Yakutat Bay basins in September are shown in Figures 41 and 42. In the outermost basin (YAK-9) the bottom water is warm (>7°C), saline (>31.7°/₀₀) and stratified. The density adjacent to the bottom has decreased somewhat from July (>25 to 24.85), as also has the salinity (31.97 to 31.74 °/₀₀), and this is consistent with eddy diffusion mixing. However, the bottom temperature (not shown) has also decreased. At the inner station (YAK-3) the bottom water has both <5°C and <31.7 and the character of this water is clearly dictated by the cold and dilute glacial run-off which is at a maximum at this time of year. Further evidence of this is given by the dissolved oxygen distributions of Figure 43; high oxygen water (>6.4 ml/ℓ) is present at depth in this basin. Conditions in the center two basins represented by Stations YAK-5 and YAK-7 at this time of year are more ambigious, given our limited data base. Cold

TABLE LVII

N. E. GULF OF ALASKA (YAKUTAT BAY)

R/V *Acona* Cruise No. 246 - July 1977
Soluble heavy metal contents (μg/kg)
H. V. Weiss, Analyst

Depth (m)	Vanadium		Manganese	
	Station 7	Station 9	Station 7	Station 9
10	1.40	1.30	0.56	0.77
20	1.48	1.40	0.89	0.63
40	1.44	1.50	0.56	0.46
60	1.50	1.43	0.57	1.03
80	1.40	1.53	0.77	1.30
100	1.54	1.40	0.93	1.44
120	1.42	1.42	1.26	2.75
130		1.42		3.04
160	1.43	1.44	1.49	4.32
150		1.53		6.75
160	1.39		2.66	
170	1.43		6.43	

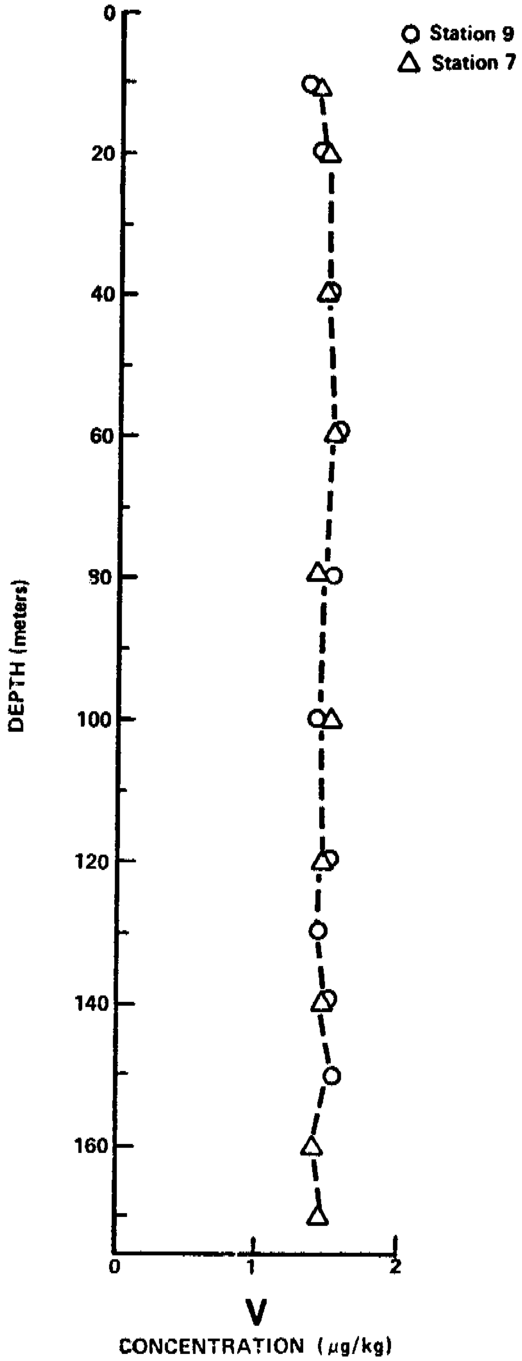

Figure 39. Soluble (0.4 µm) vanadium at Stations YAK-7 and -9, Yakutat Bay, July 1977 (*Acona* 246).

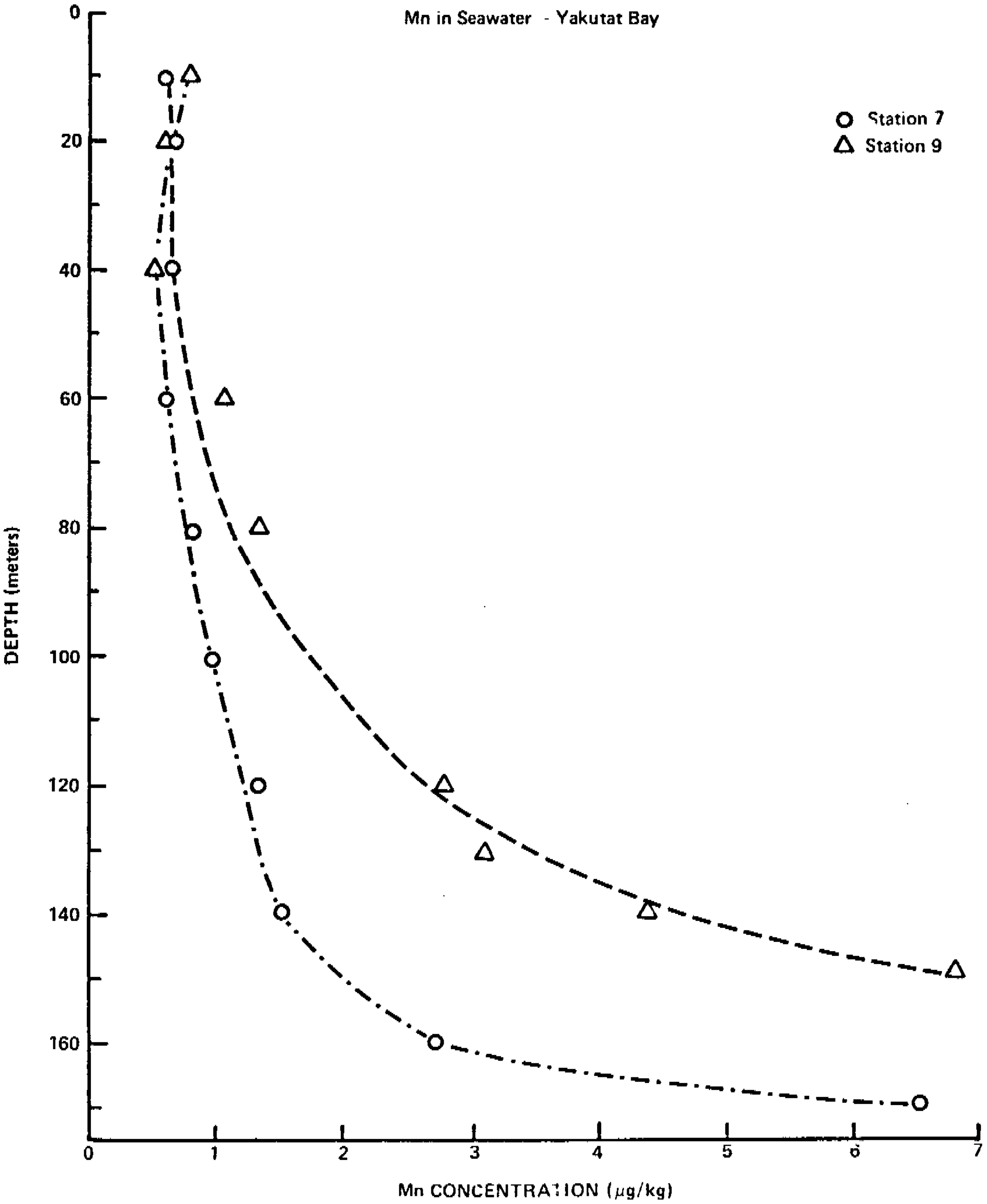

Figure 40. Soluble (0.4 μm) manganese at Stations YAK-7 and -9, Yakutat Bay, July 1977 (*Acona*).

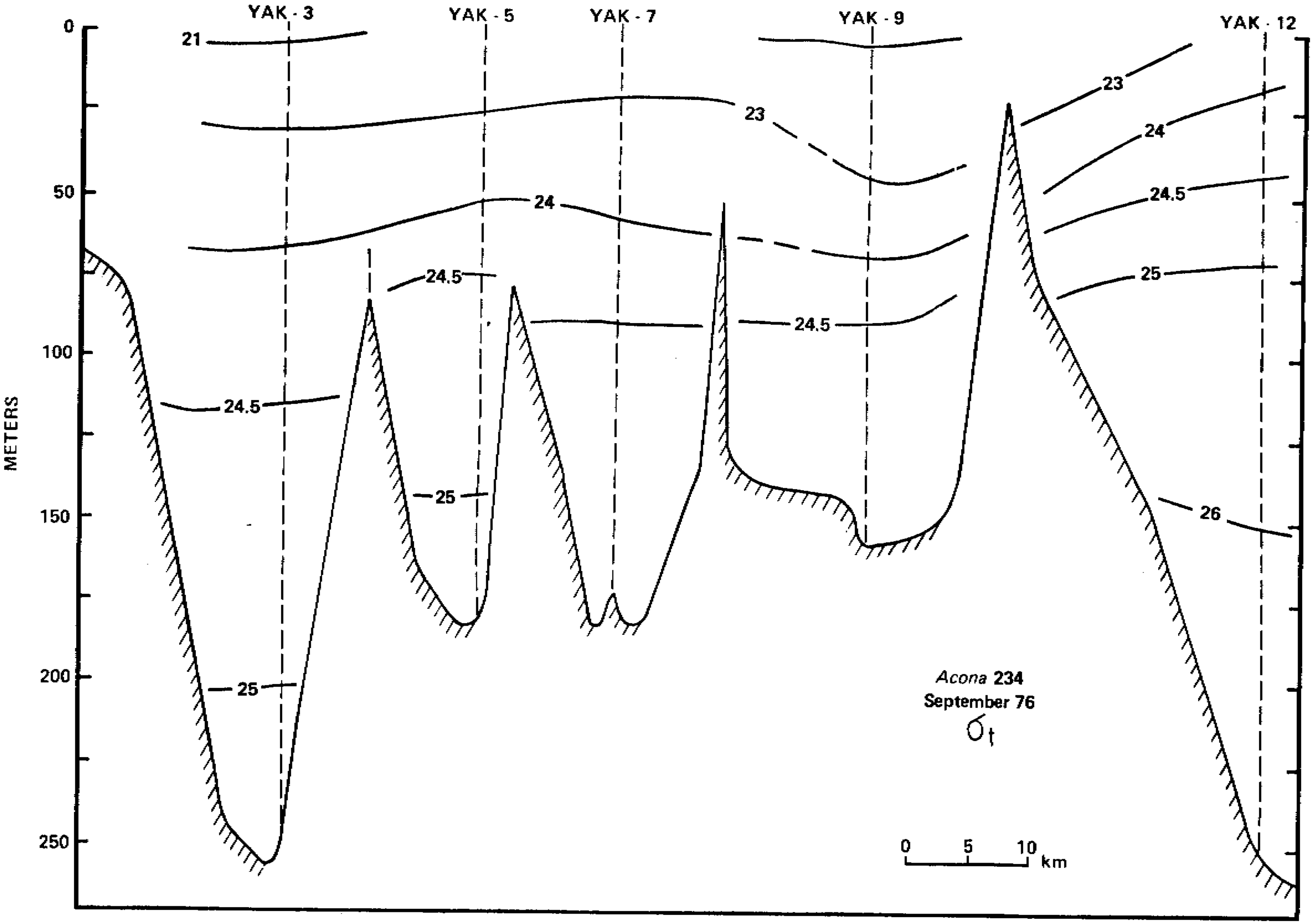

Figure 41. Density distribution in Yakutat Bay, September 1976 (*Acona* 234).

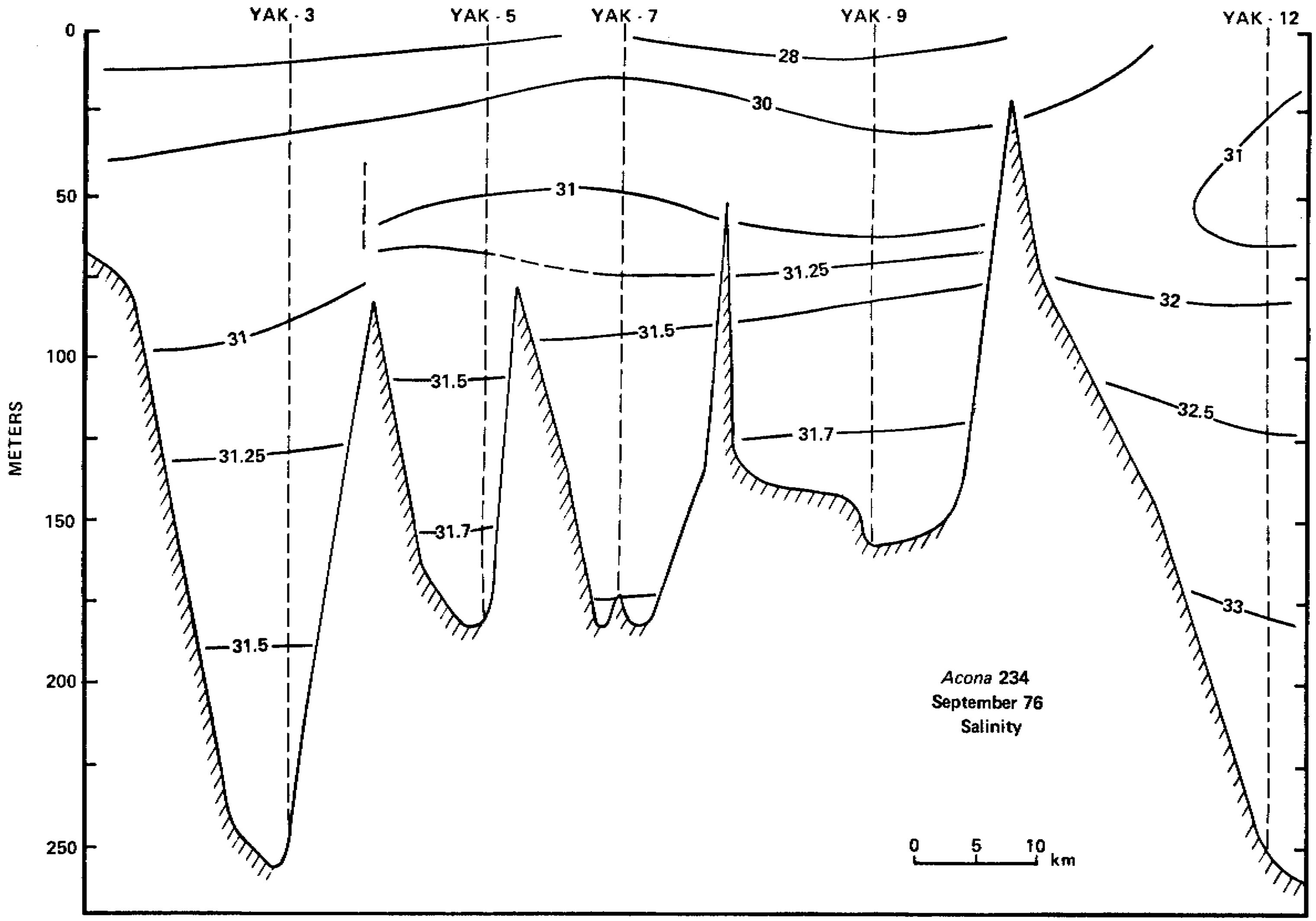

Figure 42. Salinity distribution in Yakutat Bay, September 1976 (*Acona* 234).

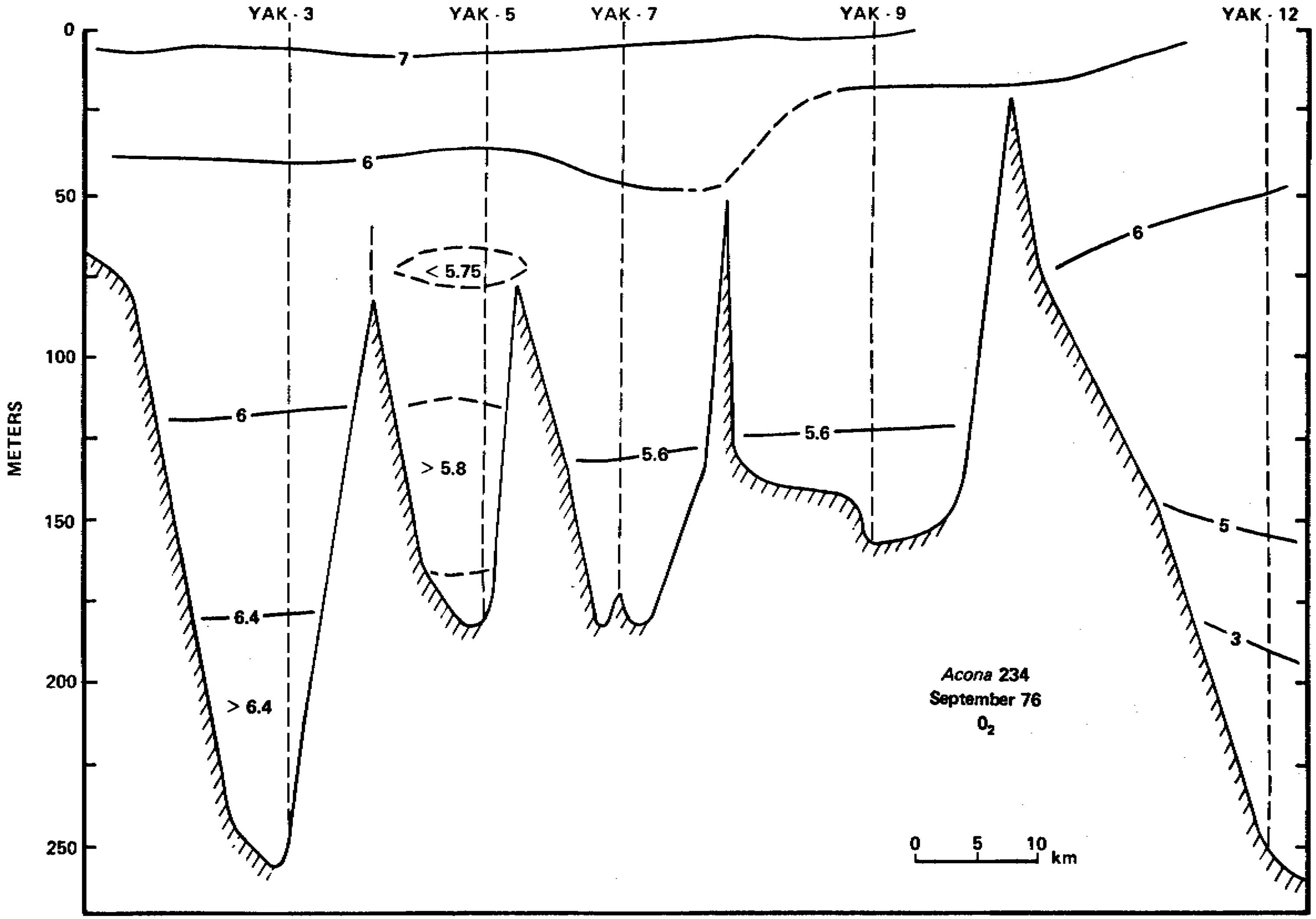

Figure 43. Oxygen distribution in Yakutat Bay, September 1976 (*Acona* 234).

water is present at depth in the YAK-5 basin and an oxygen maxima (>5.8 ml/ℓ) occur at depth. The YAK-7 basin shows characteristics intermediate between the two extremes; there is a suspicion of an oxygen maxima and the bottom water is less saline than that in the YAK-5 basin, but the temperature (>8°C) is higher even than that recorded in the outermost basin.

This is a very preliminary interpretation of the hydrography and chemistry of the Yakutat Bay estuary and subject to revision as more data are acquired. Nutrient distributions at the above three seasons are included in this report in Appendix VI but have not been analyzed in any detail as yet.

Aquaria Experiments of Food Chain Transfers of Heavy Metals

Elsewhere in this report we have shown: (1) that the sediments constitute the major heavy metal reservoir in the marine environment; (2) that Alaskan shelf waters support a rich and varied population of deposit-feeding benthos; (3) that these latter organisms directly feed the (commercially highly important) crab communities; (4) that the overall metal contents of the deposit-feeding infauna are generally higher than those of crab but that these latter organisms also show elevated concentrations when compared with pelagic biota. (See also Weihs and Burrell, 1978, in Appendix III).

It is well known that organisms generally receive the bulk of their heavy metal contents *via* ingestion. In spite of this, most aquaria experiments on metal uptake and release add tracers in soluble form directly to the water. One primary aim of the experiments, whose preliminary initial results are described here, was to research ways in which metals might more realistically be transferred to deposit-feeding benthic organisms. Since recent advances in benthic ecology (e.g., McCave, 1976) have flagged the major importance of bacteria as a detritivore food source, it was considered that this food link should be investigated as being of prime importance in transferring pollutant chemicals, in this case heavy metals, from the sediments into the marine food web.

It has been noted above and elsewhere that chemical pollutants added to the marine environment are transferred to, and immobilized in, the sediments. However, the sediment-seawater interface region is one of high energy, of complex biological activity and of important gradients in physical and chemical processes. Increasingly it is being shown that, in particular, heavy metals may be chemically transformed into more mobile species and hence transported back into the water column (down the concentration gradient). Our researches outlined in a previous section of this report on such fluxes of metals from the sediments into the deep Alaskan estuarine waters is, we believe, a useful contribution to this new and important field of chemical oceanography. It would seem reasonable to suppose that certain chemical forms of heavy metals present in the surface sediments would be amenable to uptake by the indigenous bacteria. Further, it is commonly supposed that the transformation remobilization mechanisms are likely to be microbially mediated. An extension of this argument proposed at the time of the initiation of the OCS heavy metal program is that oil pollution may stimulate or inhibit natural microbial activity and hence materially perturb the natural transport of toxic metals into the food web.

The laboratory procedures employed for the initial batch of experiments have been described in Section V of this report. It should be noted that this was a "single injection" rather than a continuously maintained impingement experiment. The aquaria conditions were chosen to facilitate later research on the transfer of metals from the clams to commerically important crab species under "Alaskan conditions".

The 0.1 ppm cadmium enriched bacterial population readily concentrated this metal from the growth medium as shown in Table LVIII; within 48 hours the cell pellet content (w/dry weight) had reached 5 x 10^3 the initial concentration (w/v) in solution. After this point as the solution became progressively depleted (Fig. 44) cell pellet samples showed diminishing contents. This initial period appears to correspond to the growth stage when the total cell mass is increasing exponentially. After 160 hours the medium showed

TABLE LVIII

UPTAKE OF CADMIUM BY HETEROGENEOUS MARINE BACTERIA POPULATION FROM A MEDIUM INITIALLY CONTAINING 0.1 mg Cd/ℓ

Time (hrs)	Medium Cd (ppm)	Cadmium (μg/g dry weight) Control	Sample
0	0.1		
24		nd	450
48		1.6	500
65		1.0	30
81		0.3	11
108		0.6	18
133		4.0	13
161	nd	1.0	8

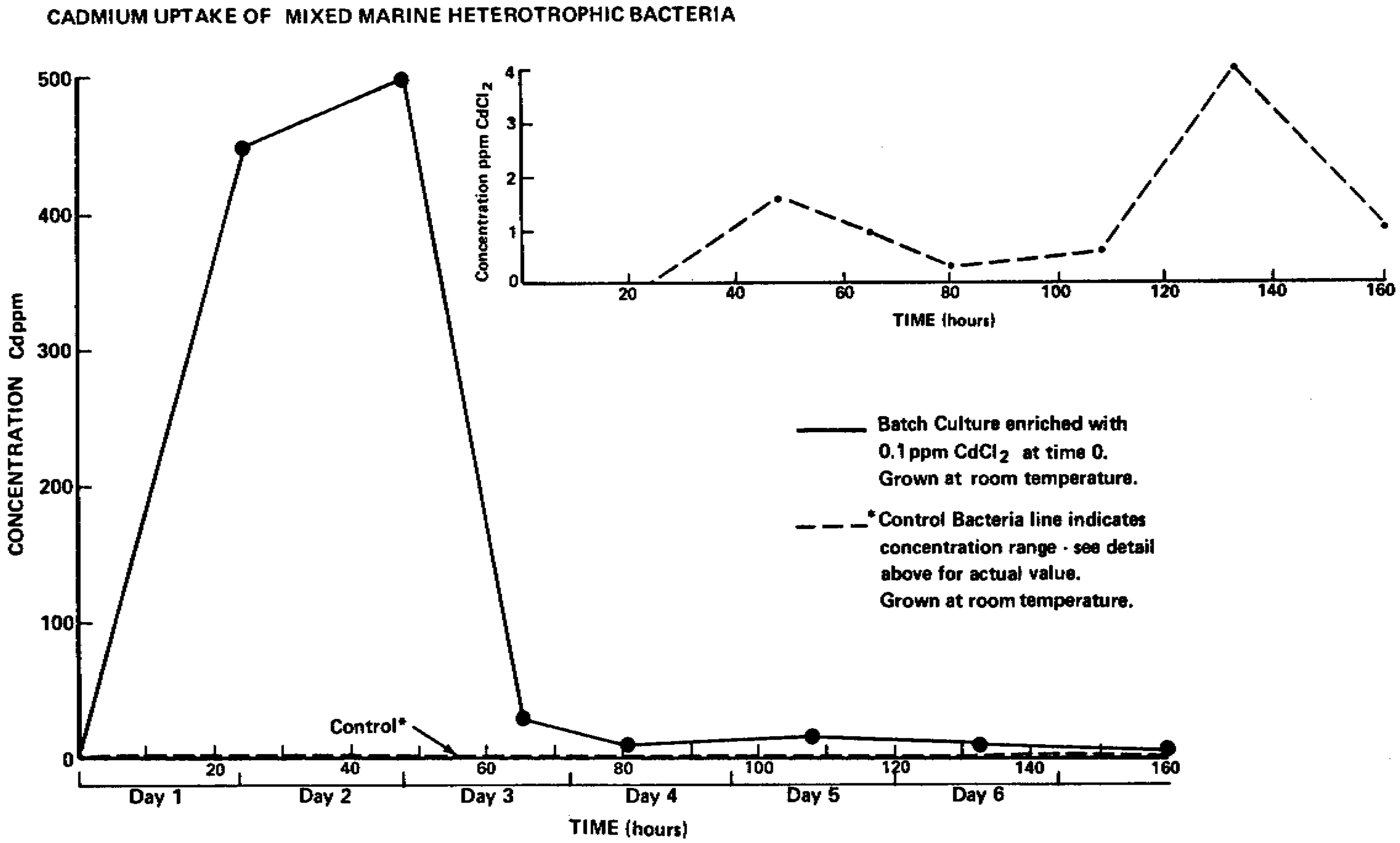

Figure 44. Uptake of cadmium by natural heterogeneous marine bacteria population.

nondetectable levels of cadmium and the cell pellet contents approached those of the controls. We presume that much cell debris was present at this time but there is no evidence for massive return of the pollutant metal back into solution.

To research the transfer of cadmium from bacteria to *Macoma baltica*, these latter organisms were starved for a period and added to an autoclaved substrate. A cadmium enriched bacteria population was then grown on the sediment habitat surface. The cell pellet initiating this culture was taken from day 7 of the above described experiment and had at that time, a cadmium content of 7 ppm. This would have been rapidly diluted with growth of the population. A difficulty encountered here was that *Macoma baltica* does not feed for prolonged periods during the winter so that ingestion was not assured. However, after two weeks the test clams had a cadmium content approaching that of the original bacteria (7-9 μg/g dry weight), a remarkable uptake from a source which is being progressively diluted. After a further two week period the content of sacrificed test organisms had dropped to 5 μg/g showing that the residence time of this metal in *Macoma* is quite short.

Further experiments are currently in progress to determine the effects of temperature, varied cadmium concentration sources, growth factors and chemical conditions of bioavailability. We have as yet no positive evidence that the presence of oil components affects the trophic transfer of metals. Table LIX shows the contents of cadmium, nickel, copper and zinc in a series of *Macoma baltica* samples which had been exposed to two different constant concentrations of oil for a period of 182 days. These data are for composite samples so we have no check on between-sample accuracy. The heavily oiled sample appears to have concentrated zinc, in particular, but the trends are non-systematic. One difficulty here is that we know that the condition of

TABLE LIX

HEAVY METAL CONTENTS OF COMPOSITE *MACOMA BALTICA* SAMPLES EXPOSED TO TWO LEVELS OF CRUDE OIL FOR 182 DAYS

Oil Concentration (ppm)	Metal Contents µg/g dry weight			
	Cd	Ni	Cu	Zn
Control	2.5	0.4	33	417
0.05	1.2	0.5	38	308
0.3	2.6	0.3	38	729

the clams changed drastically over the course of the experiment. It might by supposed that this would produce an apparent general increase in the concentration of "stored" metals as the total organic weight per individual diminished with time. At any rate, nothing definitive can be concluded from these initial values but it would seem prudent to continue this line of research.

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APPENDIX I

SELENIUM AND CHROMIUM IN THE ALASKAN SHELF ENVIRONMENT AND THEIR GAS CHROMATOGRAPHIC ANALYSIS

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SELENIUM AND CHROMIUM IN THE ALASKAN SHELF ENVIRONMENT AND THEIR GAS CHROMATOGRAPHIC ANALYSIS

I. Introduction

A. General

The elements selenium and chromium fall into the category of being essential to biological systems and yet toxic to them if the concentrations exceed very low limits. While both elements are readily detectable in sediments and biological tissue, they are very dilute in seawater. Aside from radioactivity and gas chromatographic methods, selenium and chromium species would have to be preconcentrated from seawater before normal survey work by atomic absorption could be achieved. Proper storage procedures for selenium have never been published.

B. Selenium

Selenium is found in biological systems in a form similar to sulfur in proteinaceous material. The distribution between different biota species varies considerably, and the concentration within specific organs is dramatic. In general, whole marine organisms will have selenium concentrations on the order of tenths of a part per million, whereas selected organs such as the liver, skin and some eyes, may have concentration well over one hundred parts per million.

The principle species of selenium in seawater is selenite with concentrations on the order of fifty to five hundred ppb; most commonly at the low end of the range.

Sediments can be expected to hold selenium in highly variable quantity, more in anoxic sediments, and most probably as a metal selenide. The concentration range should be on the order of <0.1 to 10 mg/ℓ.

The toxicity potential due to selenium does not appear to be a factor for concern in normal marine environments. It is of interest, however, because petroleum does contain variable small nontoxic quantities of it, like sulfur, which may indicate the presence of hydrocarbons. Furthermore, petroleum contaminated sediments will become reduced in nature, and can be expected to cause the accumulation of selenium as the selenide.

There is a known 1:1 correlation between selenium and mercury content of marine organisms. Furthermore, it is known that the selenium content affords protection from some of the toxic factors of mercury.

C. Chromium

Chromium is found in highly variable quanties in most marine organisms. It is of greater importance to animals than to plants, and is probably associated with enzymes. Chromium is found in "not detectable" to a few hundred micrograms/kg in fishes. Some invertebrates (clams and *crassostrea*), especially if taken near a source, may contain 10-40 mg/kg of chromium which in an enrichment factor of more than 10^4 over seawater at about 0.3 μg/ℓ.

Clean sediments contain 10-100 mg chromium/kg on a whole sediment basis. Extractable loads are about an order of magnitude less.

The toxicity of chromium in seawater depends upon its oxidation state. While the hexavalent state is both the common form in seawater and the species to cause disease, it is not in sufficient quantity in seawater to cause observable problems. The 0.3 μg/kg average seawater concentration is about 10^3 less than threshold toxicity factors for species such as *Macrocystis* and *Neris* sp.

Chromium is found in petroleum, and is used as one of several indicator elements. The concentration of chromium in petroleum is less than toxicity levels, but there is the possibility that oil induced resolublization of sediment loads could raise the concentration in local seawaters to the threshold toxicity values for a short period of time.

II. Gas Chromatographic Analysis of Selenium and Chromium

A. General

If a compound or element is volatile, or can be made into a volatile compound, number of detectors exist for gas chromatography to detect them. Aside from using atomic absorption or mass spectrophotometers as detectors, at least two compact detectors, electron capture and microwave, are available to detect selenium and chromium in the concentrations found in seawater. The electron capture detector is readily obtainable, provided necessary licensing of the radioactive source has been secured. The detector has the advantages of sensitivity for electronegative compounds on the order of 10^{-14} g and insensitivity to common compounds such as nitrogen or light petroleum solvents used to introduce the sample to the system. The major disadvantage lies in its strength. That is, scrupulous cleanliness procedures must be employed at all times to keep out of the system trace electronegative contaminants such as halogenated compounds, oxygen or polymers of compounds to be studied.

The microwave detector has nearly the same sensitivity as the electron capture detector, and is superior in that specific element frequencies can be dialed into the system so that contamination interference can be minimized. The disadvantage is that no single package is available on the market. The investigator must obtain a source, a monochrometer, and usually machine his own variable detector or cavity before it can be employed.

Gas chromatographs are proven sea-going instrumentation for a large variety of analytical work, require little space, no ventilation hoods, and can complete an analysis of several components in minutes.

B. Selenium

Because of the low concentrations and lability, of selenium compounds it is almost mandatory that such analyses be accomplished at the collection site rather than involve a storage procedure. Proper storage procedures for this compound have never been studied with any detail. It is known however, that it is rapidly lost from samples.

The principle species of selenium in seawater is selenite which is the form required to produce the volatile piazselenol compounds which can be detected by gas chromatographic detectors (or by colorimeters if the concentration were high enough).

A single aromatic solvent extraction will quantitatively enrich the component in the organic layer by a factor of 10^3, thus bringing it into the detection limits for a few microliter subsamples. The principle interferences are nitrates and decomposition products of the reagent. The presence of these compounds can interfere unless the analysis is completed as quickly as possible. The other problem is that neither the piazselenol nor the reagent, particularly the nitro system are stable for more than a few days. Thus, again, it is mandatory that the analysis be completed in the same day as the collection.

C. Chromium

The analysis of chromium by gas chromatography is a relatively simple matter. The chelate compound is very stable and may be stored for an

TABLE I

BEAUFORT SEA
T. A. Gosink, Analyst
Archived Sediment Samples (see Annual Report)

Chromium contents of sediment extracts
(mg/kg; 2 or 3 analyses per sample).

Station No.	Depth (m)	Cr (mg/kg)
72AER129	-	2.5
GLA27	-	1.3
PDB7431	-	1.4
GLA7144	-	1.7
72AER137	-	1.0
72AJT8	-	2.1
GLA7171	-	3.2
72AER166	-	1.4
GLA7180	-	1.9
GLA7129	-	2.7
GLA7163	-	3.0
71AER15	-	1.5
70BS22	-	1.6
GLA7172	-	2.7
GLA711	-	1.5
GLA7118	-	2.1
GLA7184	-	2.7
GLA718	-	3.5
GLA7125	-	1.4
72AJT6	-	0.7
BSS88	-	1.8
PDB7439	-	1.5
72AJT2	-	1.3
GLA715	-	2.5
GLA7123	-	2.2
72AJT5	-	1.5
GLA7112	-	6.5

TABLE I

(Continued)

Station No.	Depth (m)	Cr (mg/kg)
PDB7434	-	1.7
72AGR168	-	1.8
GLA7119	-	3.0
PDB39	-	1.9
PDB34D	-	2.0
BSS62	-	2.3
GLA7178	-	3.0
PDB743	-	4.0
GLA7174	-	2.3
72AER134	-	5.0
BSS80a	-	2.3
GLA7180b	-	3.0
GLA7180c	-	1.3

TABLE II

BEAUFORT SEA

Archived samples*

T. A. Gosink, Analyst

Chromium contents of sediment extracts (mg/kg).

Station No.	Cr
71 AJ T-5 (31)	1.34
GLA 71-19 (4)	2.68
BSS-83 (30)	2.09
GLA 71-3 (44)	2.30
71 AJ T-20 (33)	1.50
PDB74-43 (3)	0.92

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*Archived samples provided by A. S. Naidu, see 1975-1976 Annual Report for localities. Hydroxyl amine - acetic acid extracts.

TABLE III

BEAUFORT SEA

Glacier Leg II 23 August - 3 September, 1976

T. A. Gosink, Analyst

Selenium and chromium contents of surface sediment extracts (μg/g).

Station	Cr	Se
3	ND	0.29
4	-	0.41
5	-	0.27
6	Tr	0.20
7	ND	0.47
8	ND	0.04
9	0.03	0.15
10	ND	0.43
12	-	0.24

ND = not detected above blank level

TABLE IV

BEAUFORT SEA
C.G.C. *Glacier* 23 August - 3 September 1976
T. A. Gosink, Analyst

Cr and Se in untreated and filtered (0.4 µm) water (µg/ℓ).

			µg/ℓ		µg/ℓ	
Sta.	Sta. Depth(m)	Sample Depth(m)	Cr(total)	Cr(filtrate)	Se(total)	Se(filtrate)
A	24	0	Tr	ND	ND	ND
		20	ND	Tr	ND	ND
A'		0	Tr	ND	Tr	ND
		20	Tr	ND	Tr	ND
A"		0	-	-	0.56	-
		20	-	-	ND	-
B	-	0	0.24	ND	0.22	0.02
		(20)	0.12	ND	ND	ND
C	-	0	0.42	Contaminated	Tr	ND
		(20)	0.44	Contaminated	ND	ND
D	32	0	1.8	Contaminated	0.09	ND
		20	1.5	Contaminated	Tr	ND
Y	175	0	ND	ND	ND	ND
	-	130	0.16	ND	ND	ND
3	-	0	1.12	0.68	ND	ND
		20	0.8	0.76	ND	ND
4	49	0	2.1	0.56	0.15	ND
		45	1.9	1.2	ND	ND
5	-	0	0.8	Tr	ND	ND
		65	0.66	Tr	ND	ND
7	1900	0	0.8	0.24	Tr	Tr
		500	0.6	0.48	Tr	Contaminated
11	25	0	0.92	0.24	1.12	0.16
		20	ND	ND	Tr	ND
12	25	0	0.6	ND	1.1	ND
		22	ND	ND	0.4	ND

TABLE IV

(Continued)

Chronological Order of Sampling:

A, A' and A"	24 August
12	25 August
11	26 August
B	27 August
C	29 August
7	29 August
5	30 August
4	31 August
3	1 September
D	2 September
Y	2 September

Cr ND = not detected above blank level or < 0.05 μg/ℓ
Tr = trace = < 0.1 μg/ℓ

Se ND = not detected
Tr = trace = < 0.01 μg/ℓ

values were <2 ppb. Raw water values were slightly higher (factors of 1 to 4) with samples nearer coastal influence showing the highest values.

Sediments - Numerous surface sediment analyses have been reported in the range of 0.2 to 6 ppm. Most analyses are around 1-2 ppm. A few are below the 0.2 ppm level.

Biota - Samples were not received.

Data for chromium and selenium Beaufort Sea area are to be found in Tables I-IV. The data for the S. Bering Sea area are in Tables V-IX. The data for the Gulf of Alaska are in Tables X-XIV.

IV. Conclusions

The only unusual character to these analyses are the water samples which are lower than average values for both selenium and chromium, particularly the former. Surface sediment and biological materials appear normal.

Chromium shows a completely normal clean environment picture, with the water on the low side of average. Coastal sediment has some influence on raising the water column values slightly.

Selenium also shows a clean environment. The water column is particularly devoid of selenium except surface waters when copious biological material is present.

TABLE V

SOLUBLE Cr DATA FOR BERING SEA (μg/ℓ)

(*Discoverer* Leg III Sept. 25-Oct. 3)
Filtered Samples at 0.45 μ

Station No.	Depth (m)	Filtered	Unfiltered
48	3	0.29	0.69
	150		0.14
51	3		0.16
	1500	0.14	
54	3	0.15	4.2
	98		0.07
66	134		0.30
65			14
56	61		0.04
59	3	0.02	0.14
	33	0.12	0.11
41	3	0.73	
	28	Tr	
24	3	0.37	
	40	Tr	
8	3	0.30	
	18	0.27	
12	3	0.06	
	76	0.13	
35	3		0.22
	155		0.07
19	71	0.14	
46	65	0.92	
37	3	0.59	
	70	0.08	
17	114	Tr	

TABLE VI

S. BERING SEA

Total chromium contents of particulate sediment (μg/ℓ co-existing water; particulate material defined by 0.45 μ membrane filter)
Discoverer September 13-October 3, 1975

Stations	Depths (m)	Cr (μg/ℓ)*
8	3	Tr
	18	n.d.
12	3	n.d.
	76	n.d.
17	3	Tr
19	3	n.d.
	71	n.d.
24	3	n.d.
	40	0.14
41	3	0.36
	28	n.d.
46	3	0.12
54	3	n.d.
59	3	0.2
	33	n.d.
PMEL 46	3	n.d.
Off Nelson Lagoon		Tr
Izembeck Lagoon		n.d.

* n.d. - not detectable above background
Tr - 0.04 - 0.10 μg/ℓ above background

TABLE VII

S. BERING SEA
Discoverer 2-19 June 1975
T. A. Gosink, Analyst

Chromium contents of sediment extracts.

Station No.	Depth (m)	Cr (mg/kg)
24	-	2.5
28	-	1.5
41	-	0.6
46	-	1.7
59	-	0.9
59	-	1.6
64	-	2.8
65	-	2.9

TABLE VIII

S. BERING SEA

Discoverer Leg III 25 September - 3 October, 1975

T. A. Gosink, Analyst

Selenium, chromium and aluminium contents of surface sediment extracts (μg/g).

Station	Se	Cr	Al
8	0.02	0.4	92
17	ND	ND	342
19	ND	ND	178
24	0.01	ND	103
35	0.09	0.4	102
40	ND	ND	ND
43	ND	1.7	55
46	ND	0.5	84
51	ND	0.9	122
54	0.02, 0.03	0.3	211
56	ND	ND	60
65	ND	1.9	138

ND = not detected

TABLE IX

S. BERING SEA

Miller Freeman Cruise 19 August - 3 September, 1975

Samples collected by M. Hoberg, T. A. Gosink, Analyst

Selenium contents of biota (mg/kg dry weight).

Station		Specimen Identification	Se (ppm)
1.	59°41'N 171°15'W	*Spirontocaris* sp.	0.21
2.	59°60'N 171°17'W	*Spirontocaris* sp.	0.71
3.	59°20'N 171°50'W	Wattled eelpout (eyes)	0.48
4.	59°20'N 171°50'W	Wattled eelpout (skin)	1.08
5.	58°30'N 170°14'W	Kelp	0.45
6.	58°00'N 170°16'W	Kelp	0.44
7.	60°00'N 168°40'W	King salmon (liver)	11.1
8.	60°00'N 168°40'W	Pollock (eyes)	0.08, 0.37
9.	60°00'N 168°40'W	Pollock (skin)	0.58
10.	59°20'N 171°48'W	*Chionoecetes opilio* (meat)	ND
11.	60°00'N 169°17'W	Agarum cribosum	0.38
12.	57°41'N 169°35'W	Capelin (whole)	1.29

ND = not detected

TABLE X

N.W. GULF OF ALASKA

Soluble Se (ng/ℓ) and Cr (μg/ℓ) *Discoverer* Leg IV
October 8-16, 1975
(Filtered samples at 0.45 μ)

Station No.	Depth (m)	Se (ng/ℓ)	Cr (μg/ℓ)
156	3	2.8	--
	125	4.0	
158	100	Tr	
159	3	0.8	
148	3	5.2	
	100	n.d.	
160	3	n.d.	
	135	n.d.	
137	3	4.4	
	95	n.d.	
133	3	n.d.	7.64
	70	n.d.	5.64
124	3	n.d.	n.d.
	105	n.d.	0.06
119	3	n.d.	0.23
	200	n.d.	n.d.
101	3	n.d.	
	85	n.d.	n.d.

TABLE XI

N.W. GULF OF ALASKA

Total chromium contents of particulate sediment (μg/ℓ co-existing water; particulate sediment defined by 0.45 μ membrane filter)
Discoverer October 8-17, 1975

Stations	Depth (m)	Cr (μg/ℓ)*
101	3	n.d.
	85	n.d.
119	200	n.d.
124	3	Tr
133	3	n.d.
	70	n.d.
137	95	n.d.
145	3	n.d.
148	100	n.d.
160	3	n.d.
	135	n.d.
164		n.d.

* n.d. - not detectable above background
Tr - 0.04-0.10 μg/ℓ above background

TABLE XII

N.E. GULF OF ALASKA
Silas Bent 31 August - 17 September 1975
T. A. Gosink, Analyst

Chromium contents of sediment extracts (mg/kg).

Station No.	Depth (m)	Cr (mg/kg)
1	-	1.5
3	-	1.9
4	-	0.5
6	-	1.2
7	-	3.4
25	-	2.0
27	-	0.2
28	-	0.9
31	-	4.5
32	-	0.9
39	-	0.2
42	-	1.5
43	-	ND
48	-	1.5
50	-	2.1
51	-	0.8

ND = not detected above blank level

TABLE XIII

LOWER COOK INLET

Moana Wave March 31 - April 15, 1976
T. A. Gosink, Analyst

Chromium contents of sediment extracts (mg/kg).

Station No.	Depth (m)	Cr (mg/kg)
4	-	2.0
10	-	2.5
11	-	3.2
12	-	2.3
18	-	2.4
19	-	1.9
25	-	1.9
26	-	2.7
30	-	1.7

TABLE XIV

N. W. GULF OF ALASKA

Discoverer Leg IV 8-16 October, 1975

T. A. Gosink, Analyst

Selenium, chromium and aluminium contents of surface sediment extracts (μg/g).

Station	Se	Cr	Al
101	-	ND	227
105	ND	ND	518
119	ND	ND	599
121	ND	ND	369
124 (1 cm)	0.17	0.6	117
(25 cm)	0.20	1.3	189
133	0.02	1.8	103
137	ND	ND	18
160	0.02	2.1	55

ND = not detected above blank level

APPENDIX II

HEAVY METAL GEOCHEMISTRY OF THE BEAUFORT SEA SHELF SEDIMENTS

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As of this report writing, a few tentative conclusions can be made on the relative quantities of various metals that can be readily mobilized from sediments of the Beaufort Sea. Considering the acid-reduction technique that has been used to leach out the non-lithogenous fraction, and the data in Table LXIX it seems that the order indicating the quantitative mobility of the various metals would be Fe >> Mn >> Zn > Cu > V > Ni. As a corollary, it is suggested that in case of a significant decrease in the sediment pH and/or the oxidation-reduction potential of the present depositional basin, far more of soluble Fe than any of the other five metals will be mobilized out of the solid sediments into the overlying waters. However, subject to the above conditions the possible order of the percentages of the non-lithogenous fraction of each of the metals which would be readily mobilized in solution, in context to its corresponding total metal contents, would appear to be Mn > Zn > Fe = Cu > Ni = V. The data in Table LXIX also suggest that almost one half of the total Mn content and between 70% to 80% of the Zn, Fe and Cu are tied up *via* ionic bonding in crystal lattice of the mineral grains. Likewise, more than 90% of the Ni and V would appear to be lattice-held.

In attempting to understand the geochemical partitioning patterns of the various heavy metals, the distributional relationships were determined between the lithogenous (i.e., lattice-held) and non-lithogenous metal fractions, gross grain size grades, carbonate and organic carbon contents, and clay mineral assemblages of the 31 sediments analyzed. The relationships thus obtained have been expressed in terms of a correlation coefficient matrix in Table LXX. For the latter analysis, the basic heavy metal data shown in Table LV were considered, while rest of the raw geological-geochemical data on the sediments were extracted from previous studies (Naidu and Hood, 1970; Barnes, 1974; Naidu and Mowatt, 1974; Naidu, 1976).

TABLE LXIX

AVERAGES OF 31 ANALYSES* OF THE TOTAL AND NON-LITHOGENOUS (OR THE FRACTION THAT IS RELATIVELY MORE "READILY MOBILIZED") CONTENTS OF Fe, Mn, Cu, Zn, Ni, AND V IN THE CONTINENTAL SHELF SEDIMENTS OF THE BEAUFORT SEA

Metal	Total (μg/g)	Non-lithogenous fraction (μg/g)	% Non-lithogenous fraction of total
Fe	22000	4658	21
Mn	394	200	51
Cu	30	6	20
Zn	90	27	30
Ni	42	3	7
V	98	8.3	9

* Averages for vanadium are based on 26 rather than 31 samples

The presence of a positive correlation between all metals, except Mn, and organic carbon (Table LXX) seems to construe that organic matter in Beaufort Sea sediments are quantitatively an important 'host' material for most of the metals. However, the type of chemical bonding linking Fe and Cu (and possibly to a smaller extent of Ni) to organic matter seems quite strong; perhaps in the nature of complex metal-organic ligand formation. The possibility of any great amounts of Fe and Cu to have been fixed in organic matter by relatively simple and weaker bonding, characterized by adsorption/ion exchange phenomenon, would seem less attractive to accept. This conclusion is substantiated by the lack of any significant correlation between Fe and Cu in the acid leachates and the organic carbon contents (Table LXX), and existence on the other hand of a strong covariance between the non-lithogenous Fe and Cu with organic carbon (Table LXX). In the shelf area of the Beaufort Sea one can reasonably assume that humate will be the predominant organic group. It is contended that if any large amounts of Fe and Cu were linked up with this humate by ion exchange (i.e., metal exchanged for H^+ in the humate structure) then the two metals would have been readily extracted out in the acid leachates (i.e., H^+ of the acid replacing Fe^{++} and Cu^{++} in the humates). As mentioned earlier there is no evidence to support the latter view. Perhaps, further detailed analysis of metals on various groups of organic compounds, along the lines suggested by Brown *et al.* (1972), would yield more conclusive evidence on the types of metal-organic complexation in the Beaufort Sea sediments.

The strong covariances of the clay grade of sediments with all the non-lithogenous metal fractions and the organic carbon (Table LXX) are quite understandable. Generally quiet, low-energy sedimentary regimes promote larger deposition of clay-sized particles. In addition to other

TABLE LXX

CORRELATION COEFFICIENTS FOR CHEMICAL, TEXTURAL AND CLAY MINERAL COMPOSITIONS OF CONTINENTAL SHELF SEDIMENTS, BEAUFORT SEA, ALASKA*

	LFe	NLFe	LMn	NLMn	LCu	NLCu	LZn	NLZn	LNi	NLNi	TV	Gr	Sd	St	Cl	OC	CO_3	Sm	IL	Ka	Ch
LFe	1.0000																				
NLFe		1.0000																			
LMn			1.0000																		
NLMn		0.4294		1.0000																	
LCu	0.5285	0.4152			1.0000																
NLCu		0.4999		0.5234		1.0000															
LZn							1.0000														
NLZn	0.4644	0.7801			0.5855	0.4883	-0.3628	1.0000													
LNi	0.5317	0.5903		0.4411	0.6746	0.4438		0.5825	1.0000												
NLNi	0.4234	0.6622		0.3883	0.4884	0.7122		0.7974	0.6287	1.0000											
TV	0.8103	0.4535		0.4020	0.6148	0.6123		0.6401	0.7328	0.6354	1.0000										
Gr			0.5530	0.5048								1.0000									
Sd	-0.4971	-0.7414		-0.4649	-0.6412	-0.5592		-0.7595	-0.8006	-0.6584	-0.6879		1.0000								
St		0.5133			0.4304			0.4163	0.4623	0.3842			-0.7364	1.0000							
Cl	0.5652	0.6387		0.4195	0.5974	0.6245		0.7619	0.7187	0.6[illegible]21	0.8167		-0.8442	0.3784	1.0000						
OC	0.4657				0.4662			0.4791	0.5241	0.4491	0.4461		-0.5964	0.5520		1.0000					
CO_3	-0.4911	-0.3704		-0.4382	-0.4481	-0.5469	0.4654	-0.6341	-0.4850	-0.6057	-0.6796		0.5918		-0.6870	-0.4653	1.0000				
Sm	0.4394					0.3688					0.5722	-0.3850			0.5101	0.3683	-0.5292	1.0000			
Il						0.4616													1.0000		
Ka																				1.0000	
Ch					-0.4135															0.8380	1.0000

*Only figures that are significant at 95% or above confidence level (r=0.355), using two-tail test, are cited in the table.

The prefix 'L' to the heavy metals connotes the lithogenous (lattice-held) amount of the metals, whereas the prefix 'NL' to the metals connotes nonlithogenous (or "readily leachable") amount of the metal Gr, Sd, St, Cl, OC, CO_3, Sm, Il, Ka, and Ch are acronyms for gravel, sand, silt, clay, organic carbon, carbonate, smectite, illite, kaolinite, and chlorite respectively.

The kind help of Dr. Charles Geist in the statistical analysis of the chemical data is thankfully acknowledged. The interpretation of the chemical data by Dr. Naidu was financially supported by the State of Alaska.

favorable physiochemical factors (i.e., pH, Eh, salinity etc.), regions with tranquil depositional condition would also be conducive areas for the copious sedimentation, and thus concentration of the hydrodynamically light precipitates of Fe and Mn and any metals scavenged by them, as well as organic debris, along with clay particles. Most likely, significant portions of the above ferric hydroxide in the incipient precipitated state will be in the form of a positively-charged sol. In this state the Fe would tend to get adsorbed on negatively-charged surfaces of clay minerals. The subject concerning similar association of Fe with clays has been dealt with in greater detail by Carroll (1958).

The close covariance of all metals with clay-sized particles (Table LXX) strongly suggests that significant portions of the metals are by some way tied up in the clay itself. There are several mechanisms which can associate the metals with clays which are generally enriched in layered silicate minerals. Evidently no significant amounts of Mn and Zn are lattice-held in the layered silicate mineral particles, as suggested by the absence of a correlation between lithogenous Mn and Zn and clay grade (Table LXX). In contrast to this it would seem that most of the Cu, Ni and V are incorporated in the layer silicate mineral lattice, as reflected by the presence of large proportions of these metals in the lithogenous fraction of sediments (Table LXX) as well as the strong covariance with the clay grade (Table LXX). The remaining relatively small portions of the Cu, Zn, Ni and V are presumably partitioned between adsorbed/ion exchangeable sites of clays. Such as incorporation may materialize either directly through discrete metal ion adsorption/exchange, or indirectly in the form of adsorption of a complex ion 'parcel' constituted of charged ferric hydroxide sol, and the several heavy metals sequestered in it. Goldberg (1954) has discussed at length the process by which such a scavenging of heavy metals by ferric hydroxide is taken.

With the exception of Fe and Cu no clear cut covariance is observed between any of the four specific clay mineral types and the metals (Table LXX). A notable part of the lattice-held Fe of the Beaufort Sea sediments would seem to be associated with smectite (Table LXX). However, the very detailed work of Anderson and Reynolds (1966) with the Umiat Bentonite - a possible major terrestrial source of the above smective - does not support the above contention, as no appreciable nontronitic phases (Fe-rich smectite) have been identified in the bentonite. This of course does not rule out the presence of any appreciable amounts of nontronite in the rest of the drainage basin for the Beaufort Sea sediments. The significant positive correlation between the non-lithogenous Cu and both smectite and illite and the absence of a likewise correlation of the lithogenous Cu with the above minerals (Table LXX), in some degree contradicts our earlier inferences on the possible nature of illites in the Beaufort Sea sediments (Naidu and Mowatt, 1974, p. 251). As opposed to earlier views present evidences would seem to suggest, strictly based on the variances of the various Cu fractions and clay minerals (Table LXX), that the illite of the Beaufort Sea has been mostly derived from the weathering of dioctahedral rather than trioctahearal micas.

Considering the correlation coefficient matrix (Table LXX), it would seem that no significant amounts of the heavy metals are tied up in the coarser size grades as well as in the carbonate phase of the middle and outer shelf sediments of the Beaufort Sea. Somewhat in contrast to this contention are the observations made by Naidu and Mowatt (1974) that in the inner shelf (including the North Slope continental margin and deltas) of the Alaskan Beaufort Sea, notable amounts of Cu most likely are tied up with carbonates. Perhaps this apparent contradiction can be explained in context of the different origin of carbonates in sediments of the two contiguous but different shelf regimes of the Beaufort Sea. It is to be noted that the carbonates in the inshore region of the Beaufort Sea consist predominantly of calcareous mineral and rock components with relatively very little bioclastics. Unlike in the latter region, the carbonate in the open shelf sediments are constituted largely of autochthonous bioclastics with very subordinate amounts of terrigenous calcareous rocky and minerogenous particles. Most of the sediments for this study (Table LXX) were collected from the latter shelf region. The primary terrigenous source rocks for the calcareous nonbioclastics for the Beaufort Sea inner shelf sediments most likely is in the Brooks Range carbonates. Extensive copper ore mineralization are known to exist in these carbonate rocks of the Brooks Range (e.g., the Bornite-Ruby Creek deposits). In light of these observations, the presence of a significant Cu-carbonate positive correlation in the inner shelf sediments is not surprising.

The strong covariance existing between lithogenous Zn and carbonate apparently is a spurious correlation (Table LXX). Any Zn linked up with carbonate would have been quantitatively extracted out into the acid leachates, and reflected with a positive correlation between non-lithogenous Zn and the carbonate contents. However, the strong negative correlation existing between the latter two (Table LXX) strongly supports the above contention that the geochemistry of Zn is in fact independent of the sediment carbonate phase.

TABLE

Beaufort Sea*

A. S. Naidu, Analyst

Heavy metal contents of sediments (gravel free, dry weight).

Sample No.	Fe %			Mn µg/g			Cu µg/g			Zn µg/g			Ni µg/g			V µg/g		
	Total	NL	%NL	Total	NL	%NL	Total	NL	%NL	Total	NL	%NL	Total	NL	NL%	Total	NL	NL%
BSS-62	4.18	0.25	6	270	88	33	43	5	12	130	25	19	50	3	6	275	9.9	4
BSS-83	3.44	0.43	13	270	88	33	43	7	16	75	33	44	41	3	7	170	16.7	10
BSS-88	3.08	0.48	16	300	220	73	61	8	13	90	40	44	47	6	13	185	10.6	6
GLA71-1	2.18	0.53	24	280	150	54	28	19	68	87	24	28	45	5	11	-	-	-
GLA71-3	2.40	0.48	20	260	200	77	24	3	13	75	30	40	39	2	5	120	10.9	-
GLA71-12	2.80	0.51	18	340	260	77	39	7	18	95	40	42	53	6	11	-	-	-
GLA71-23	2.80	0.73	26	440	275	63	38	6	16	101	32	32	57	4	7	160	9.5	6
GLA71-25	2.55	0.55	22	500	400	80	35	7	20	98	25	26	55	3	5	150	11.1	7
GLA71-27	1.55	0.29	19	1460	550	38	18	7	39	72	21	29	33	2	6	-	-	-
GLA71-44	2.22	0.51	23	590	490	83	25	6	24	77	23	30	45	2	4	120	14.4	12
GLA71-63	2.75	0.91	33	490	360	74	35	12	34	92	40	44	51	6	12	160	-	-
GLA71-71	2.12	0.73	34	370	260	70	60	6	10	85	32	38	49	4	8	120	10.9	9
GLA71-72	2.80	0.78	28	1000	700	70	44	19	43	79	36	58	51	8	16	-	-	-
GLA71-78	3.55	0.80	23	630	420	67	47	12	26	95	44	46	66	6	9	225	16.2	7
GLA71-80a	3.25	0.60	19	590	400	68	38	14	37	100	27	27	62	4	6	190	11.3	6
GLA71-80b	3.25	0.55	17	590	400	68	38	11	29	100	27	27	62	4	6	190	12.1	6
GLA71-80c	3.25	0.58	18	590	400	68	38	11	29	100	31	31	62	4	6	190	11.9	6
PDB74-34a	1.33	0.28	21	230	143	62	16	12	75	95	15	16	33	2	6	60	3.2	6
PDB74-34b	1.33	0.23	17	230	138	60	16	11	69	95	17	18	33	2	6	-	-	-
PDB74-39a	1.03	0.15	15	270	90	33	13	1	8	123	13	11	37	2	5	25	2.8	11
PDB74-39b	1.03	0.13	13	270	80	30	13	1	8	123	15	12	37	3	8	-	-	-
PDB74-41	1.48	0.21	14	350	150	43	28	1	4	104	21	20	44	3	7	25	3.2	13
PDB74-43	1.26	0.05	4	290	120	41	12	1	8	123	8	7	25	Tr	Tr	25	2.2	9
70BS-22	1.65	0.38	23	270	138	51	24	4	17	84	25	30	37	2	5	75	9.8	13
71AJT-5	1.48	0.20	14	240	123	51	13	2	15	60	15	25	24	0	0	25	3.8	15
71AJT-20	1.70	0.43	25	320	180	56	26	5	19	100	31	31	43	3	7	75	10.2	14
71AER-15	1.85	0.29	16	310	200	65	24	1	4	91	19	21	43	3	7	75	2.5	3
72AJT-5	1.48	0.33	22	240	120	50	13	2	15	60	27	45	24	2	8	25	6.4	26
72AJT-6	1.43	0.16	11	270	150	56	10	1	10	60	19	32	22	2	9	25	4.9	20
72AJT-8	-	-	-	-	-	-	32	4	13	115	29	25	51	4	8	75	10.2	14
72AER-129a	2.40	1.03	43	310	250	81	30	8	27	108	40	37	45	3	7	100	13.9	14
72AER-129b	2.40	1.23	51	310	245	79	30	6	20	108	46	43	45	4	9	-	-	-
72AER-134	1.20	0.28	23	250	128	51	39	4	10	115	21	18	52	2	4	100	7.2	7
72AER-137	0.98	0.18	18	150	55	37	10	1	10	38	15	40	19	0	0	25	3.2	13
72AER-166	2.58	0.38	15	240	150	63	22	3	14	58	27	47	40	3	8	50	6.6	13
73AER-168	2.68	0.33	12	270	155	57	28	2	7	108	21	19	43	2	5	50	4.6	9

*Archived samples, see 1975-1976 Annual Report for locations.

NL = non-lithogenous fraction.

APPENDIX III

ABSTRACTS OF RECENT PAPERS

CLAY MINERALS IN RECENT SEDIMENTS OF THE CONTINENTAL SHELF, CENTRAL AND WEST GULF OF ALASKA*

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ABSTRACT

Preliminary analysis of bottom-sediment samples by X-ray diffraction has resulted in the recognition of differences between the clay mineral (< 2 μ equivalent spherical diameter layer silicates) assemblages from each of these areas.

Central Gulf of Alaska suites are characterized by predominant illitic (40 to 50%) and chloritic (40 to 50%) components, with a subordinate (generally < 10%) expandable component, and only occasional traces of kaolinite. While the western Gulf of Alaska sediments are not too dissimilar in aspect, there does seem to be somewhat more (∿ 10%) expandable mineral in this region, together with a slightly greater (50 to 60%) proportion of illite, and correspondingly less (30 to 40%) chlorite. These slight but discernible geographic differences would seem most likely to be attributable to the differing lithology of the proximal landmasses, (i.e., predominantly metamorphic terrane of the Chugach Mountains vs. the Alaska Peninsula, where volcanic materials are more abundant).

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* Alaska Science Conference, 1976.

COMPOSITION, SOURCE AND DISPERSAL PATTERN OF CLAY MINERALS IN SOUTHEAST BERING SEA, ALASKA*

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ABSTRACT

X-ray diffraction analysis of the less than 2 μm and 1 μm e.s.d. fraction of 30 surficial sediments, showed that the clay mineral assemblages are comprised of 20-40% glycol expandable components, together with 20-50% of illite, 30-40% of chlorite, and less than 10% of kaolinite and mixed-layered phases. Relatively higher concentrations are observed in the less than 1 μm size. Analytical results of the glycol-solvated clays, subsequent to treatments with separate IN solutions of KCl and $MgCl_2$, imply that the original expandable components are most likely degraded illites, rather than smectites and/or degraded chlorites. Step-wise thermal treatments suggest the presence of a number of mixed-layered phases with vermiculitic components.

Compared to the clay mineral assemblage in the Bristol Bay, relatively smaller concentrations of the expandable component are discernible in the Kuskokwim Bay. This difference seems most readily attributable to the differences in the nature of terrigenous source materials for the two bays, and the absence of large-scale lateral dispersion of fine grain particles in southeast Bering Sea.

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* G. S. A., Seattle, 1977.

X-ray diffraction analyses of the above clays, subsequent to K^+ and Mg^{++} saturation, suggest that significant portions of the expandable mineral components are degraded illites.

Additional work is in progress, endeavoring to characterize the clay mineral components more thoroughly, in hopes of increasing our understanding of the sedimentologic, mineralogic, and geochemical relationships in these portions of the continental shelf of Alaska.

CHARACTERISTICS AND DISPERSAL PATTERN OF CLAY MINERALS IN THE NORTH BERING SEA*

by

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ABSTRACT

X-ray diffraction analysis for clay mineral composition was performed on the <2 μm e.s.d. of 80 sediment samples from the North Bering Sea. Illite is invariably the predominant clay mineral (33 to 51%), with subordinate amounts of a glycol-expandable mineral (10 to 40%), chlorite (18 to 32%) and kaolinite (6 to 18%), and traces of mixed-layered phases. Almost all of the glycol-expandable component appears to be degraded (depotassicated) illite.

A few regional differences in the clay mineral assemblages has been identified. Significantly higher expandable component (31 to 40%) is observed in the area south of the St. Lawrence Island. The region extending off the Yukon River mouth up to the eastern margin of the Chirikov Basin, western half of the Norton Sound and the Shapanberg Strait has significantly higher kaolinite/chlorite ratios. These mineral variations are primarily attributable to local influence of terrigenous source.

Clay minerals distribution patterns in the north Bering and Chukchi Seas substantiate the observation of previous investigators, that the central Chukchi Sea is the major depositional site of the Yukon River clays.

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* G. S. A., Seattle, 1977.

MERCURY SPECIATION IN SEAWATER AND SEDIMENTS FROM THE NORTHEAST GULF OF ALASKA AND THE CHUKCHI-BEAUFORT SEAS*

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ABSTRACT

The total mercury content of surface and bottom seawater and sediments from the northeast Gulf of Alaska ranged between 2-33 ng/l for seawater and 10.8-67.1 ng/g dry weight of sediment. The range of concentrations for the Chukchi-Beaufort Seas was 8-32 ng/l for seawater and 10.0-106.6 ng/g of dry sediment. These values are comparable to levels found elsewhere in the Alaskan coastal environment. No significant amount of organic mercury could be detected in the seawater samples. The amount of elemental and readily reducible mercury in the sediments was less than 2% of the total for all samples. Mercury (reducible and organic) released from the sediments to seawater with mixing ranged between non-detectable and 54.2% of the total mercury. The physical characteristics of the sediments are discussed as a possible explanation for this wide range of values.

UPTAKE OF CADMIUM BY MARINE HETEROTROPHIC BACTERIA AND TRANSFER TO A DEPOSIT FEEDING CLAM

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ABSTRACT

A major portion of the marine renewable resources of Alaska is dependent upon clams. Apart from being themselves exploitable, clams appear to be a major food source for the commercial crabs (and also for important marine mammal species). Such trophic relationships provide relatively direct links from the sediments, which are the major repository for potentially pollutant chemicals, to man. The uptake of one highly toxic metal, cadmium, by a marine heterotrophic bacterial population was found to exceed a concentration factor of 10^3. When cadmium-enriched bacteria were used as the sole food for the deposit-feeding clam *Macoma baltica* (common in Alaskan intertidal environments), the clams also showed enrichment of the metal over controls. The transfer efficiency in this aquaria ingestion experiment was close to one and depuration appeared to be relatively rapid. The significance of these data to the fisheries and potential future pollution in Alaskan waters is discussed.

HEAVY METAL CONTENTS OF BERING SEA SEALS

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ABSTRACT

Cadmium, nickel, copper and zinc contents have been determined for muscle, liver and kidney samples from four species of seal taken in the Bering Sea in spring and early summer (largely within a 300-400 mile radius, and south, of St. Matthew Island). Some interesting patterns emerge and cadmium concentrations, in particular, are relatively high in the organs analyzed. However, in spite of expected preferential feeding habits, the individual species show no clear differential uptake characteristics, neither is there an obvious correlation with age or sex except possibly for muscle contents, but there were far too few samples available to permit a rigorous statistical analysis. These heavy metal data are of interest, firstly because the food chains involved are relatively short and involve those to local human consumption, and secondly because heavy metal contents in the Bering Sea system appear to be generally very low. A detailed survey of soluble copper contents over much the same area, for example, has given values which are just now being generally accepted as representative of deep open ocean waters, and the few benthic biota species analyzed to date (e.g., tanner crab) show concentrations as low or lower than those from (unpolluted) Gulf of Alaska shelf regions.

APPENDIX IV

SAMPLE LOG BY LEASE AREA

SAMPLE LOG BY LEASE AREA

A. NORTHEASTERN GULF OF ALASKA

Sample Type	Elements	# Coll.	# Anal.	# Rejected	# In Progress
Water	Cu	135	122	13	0
	Cd	182	122	13	47
	Pb	135	122	13	0
	Zn	90	80	10	0
	Ni	49	26	23	0
	Ag	20	18	2	0
	Hg (inorganic)	37	37	0	0
	Hg (total)	37	34	3	0
	V	22	22	0	0
	DOC/POC	46	46	0	0
	Nutrients (depths)	163	163	0	0
	STD (depth/ stations)	186/20	186/20	0	0
Individual Samples (Water Analysis)		182			
Biota					
Crab tissue	Cd, Cu, Ni, Zn	18	15	3*	0
	Hg	10	10	0	0
Neptunea	Cd, Cu, Ni, Zn	10	4	6*	0
Turbot	Cd, Cu, Ni, Zn	10	0	10*	0
Pollock	Cd, Cu, Ni, Zn	10	0	10*	0
Rock Sole	Cd, Cu, Ni, Zn	8	0	8*	0
Molopodia	Cd, Cu, Ni, Zn	5	0	5*	0
Biota	Cu, Cd, Ni, Zn	6	0	4	2
Plankton	Cu, Cd, Ni, Zn	6	0	4	2
Individual Samples		67			
Interstitial water					
	Cd	14	0	0	14
Suspended Sediment					
	Mn, V	41	40	0	1
	Al	41	40	0	1
Sediment size analysis		22	19	3	0

*These samples were lost due to power failure in 1976

B. NORTHWESTERN GULF OF ALASKA

Sample Type	Elements	# Coll.	# Anal.	# Rejected	# In Progress
Water	Cd, Pb, Cu, Zn	40	40	0	0
	Se	18	18	0	0
	Cr	8	7	1	0
	V	26	25	1	0
	Ba, As	26	22	4	0
Individual Samples		40			
Biota					
Mytilus	Cd, Cu, Ni, Zn	19	19	0	0
Fucus	Cd, Cu, Ni, Zn	23	23	0	0
Individual Samples		42			
Sediment					
	Mn, V	27	27	0	0
	As, Ba, Co, Cr, Fe (%), Sb	22	22	0	0
	Al, Ca	27	27	0	0
Individual Samples		27			
Suspended Sediment	Mn, V, Al	45	45	0	0
	Cr	12	12	0	0
Individual Samples		45			
Sediment Size Analysis		9	9	0	0
Water	Cd, Pb, Cu, Zn	40	40	0	0
	Se	18	18	0	0
	Cr	8	7	1	0
	V	26	25	1	0
	Ba, As	26	22	4	0
Individual Samples		40			
Biota					
Mytilus	Cd, Cu, Ni, Zn	19	19	0	0
Fucus	Cd, Cu, Ni, Zn	23	23	0	0

C. LOWER COOK INLET

Sample Type	Elements	# Coll.	# Anal.	# Rejected	# In Progress
Biota					
Crab tissue	Cu, Cd, Ni, Zn	33	33	0	0
Macoma	Cu, Cd, Ni, Zn	6	6	0	0
Neptunea	Cu, Cd, Ni, Zn	5	5	0	0
Sole	Cu, Cd, Ni, Zn	4	4	0	0
Mytilus	Cu, Cd, Ni, Zn	8	8	0	0
Fucus	Cu, Cd, Ni, Zn	10	6	0	4
Individual Samples		66			
Sediment	Cu, Cd, Ni, Zn, Mn, Fe	25	9	0	16
	Cr	9	9	0	0
Individual Samples		25			

D. SOUTH BERING SEA

Sample Type	Elements	# Coll.	# Anal.	# Rejected	# In Progress
Water	Cu	206	176	30	0
	Cd	83	55	28	0
	Ni	58	55	3	0
	Pb	206	176	30	0
	Zn (free)	33	29	4	0
	Cr	25	25	0	0
	Ba	20	14	6	0
	As	20	14	6	0
	V	10	10	0	0
Individual Samples		206			

Biota					
Crab tissue	Cd, Cu, Ni, Zn	15	15	0	0
	As, Br, K, Na	15	6	9	0
Pollock	Cd, Cu, Ni, Zn	15	0	15	0
	As, Br, K, Na	15	14	1	0
Rock sole	Cd, Cu, Ni, Zn	15	0	15	0
	As, Br, K, Na	15	9	6	0
Neptunea	Cd, Cu, Ni, Zn	5	5	0	0
	As, Br, K, Na	5	5	0	0
Neptunea gut	Cd, Cu, Ni, Zn	5	5	0	0

Biota					
Plankton	Cu, Cd, Ni, Zn	3	0	3	0
Seal tissue*					
liver	Cu, Cd, Ni, Zn	27	27	0	0
kidney	Cu, Cd, Ni, Zn	27	27	0	0
muscle	Cu, Cd, Ni, Zn	27	27	0	0

*additional seal tissue is available from ADF&G

Misc. biota	Se	12	12	0	0
Mytilus	Cu, Cd, Ni, Zn	6	6	0	0
Fucus	Cu, Cd, Ni, Zn	5	5	0	0
Individual Samples		157			

SOUTH BERING SEA (cont'd)

Sample Type	Elements	# Coll.	# Anal.	# Rejected	# In Progress
Sediment					
	Cu, Cd, Ni, Zn	25	25	0	0
	Cr	20	20	0	0
	Se	12	12	0	0
	Al	41	36	5	0
	Mn, V	29	24	5	0
	Ba	29	29	0	0
	As	29	29	0	0
	Ca	29	24	5	0
Individual Samples		25			
Suspended Sediment					
	Cr	18	18	0	0
	Al	24	24	0	0
	Mn, V	24	24	0	0
Individual Samples		24			
Sediment Size Analysis		62	62	0	0

E. NORTON SOUND/CHUKCHI SEA

Sample Type	Elements	# Coll.	# Anal.	# Rejected	# In Progress
Water		61	0	0	61
Sediment	Cu, Cd, Ni, Zn, Mn, Fe	33	33	0	0
Sediment Size Analysis		65	64	1	0

F. BEAUFORT SEA

Sample Type	Elements	# Coll.	# Anal.	# Rejected	# In Progress
Water	Cd	26	0	0	26
	Pb	26	0	0	26
	Cu	26	0	0	26
	Cr (total)	26	24	2	0
	Cr (filtrate)	26	20	6	0
	Se (total)	26	26	0	0
	Se (filtrate)	26	23	3	0
Individual Samples		26			
Sediment	Cu	9	0	0	9
	Cd	9	0	0	9
	Ni	9	0	0	9
	Zn	9	0	0	9
	Se	9	9	0	0
	Cr	9	6	3	0
Individual Samples		9			
Archived Sediment	Cr	-	46	-	-
Individual Samples		46			

Note: This luting does not include samples from the Yakutat and Resurrection Bay specific study sites.

SAMPLE LOG FOR Cr/Se BY LEASE AREA
(Subcontract to Dr. T. A. Gosink)

A. BEAUFORT SEA

Sample Type	Element	# Coll.	# Anal.	# Rejected	# Archived
Water	Cr	52	44	8	0
	Se	52	49	3	0
Biota	Cr	1	1	0	0
	Se	1	1	0	0
Sediment	Cr	55	52	3	0
	Se	9	9	0	0

B. BERING SEA

Sample Type	Element	# Coll.	# Anal.	# Rejected	# Archived
Water	Cr	62	48	14	0
	Se	18	0	18	0
Biota	Cr	1	1	0	0
	Se	18	14	4	0
Sediment	Cr	20	20	0	18
	Se	12	12	0	0

C. GULF OF ALASKA

Sample Type	Element	# Coll.	# Anal.	# Rejected	# Archived
Water	Cr	49	43	6	0
	Se	18	18	0	0
Biota	Cr	0	0	0	0
	Se	0	0	0	0
Sediment	Cr	36	34	2	11
	Se	11	9	2	0

APPENDIX V

INDEX TO DATA IN PREVIOUS REPORTS

INDEX TO DATA IN PREVIOUS REPORTS

Format	Description	Year	Report	Page
	A. GULF OF ALASKA			
Fig.	N.E. Intertidal Localities	1977	Annual	15
Fig.	N.E. Intertidal Localities	1977	Annual	21
Table	N.E. Intertidal Localities	1977	Annual	16
Fig.	E. Gulf Stations	1977	Annual	14
Fig.	W. Gulf Stations	1977	Annual	20
Table	W. Gulf Intertidal Localities	1977-78	2	24
Table	Kodiak Intertidal Localities	1977-78	2	24
	Water			
Table	R/V *Acona* #200	1975	Annual	48-49
	R/V *Acona* #207 u.f.	1975	Annual	51
	Oceanographer u.f.	1975	Annual	50
	Townsend Cromwell	1976	Annual	76
	N.W. Gulf *Discoverer*	1976	Annual	79
	N.W. Gulf Se and Cr	1976	Annual	81
	Discoverer 1975	1977	Annual	56
	N.W. Gulf *Discoverer*	1977	Annual	58
	Discoverer Hg	1977	Annual	63-64
	Discoverer V	1977	Annual	67-68
	Soluble Summary	1977	Annual	132
	Biota			
Table	Salmon	1975	Annual	46
	Crab Hg	1976	Annual	84
	N.E. Gulf Crab	1976	Annual	85
		1977	Annual	162
	N.E. Gulf *Neptunea*	1976	Annual	86
		1977	Annual	162
	N.W. Gulf Cr	1976	Annual	89
	N.E. Gulf Hg	1976	Annual	
	N.E. Gulf Commercial Crab	1977	Annual	45
	N.E. Gulf *Mytilus* Summary	1977	Annual	154
	N.W. Gulf *Fucus* and *Mytilus* Summary	1977-78	1	13-14
	Kodiak *Fucus* and *Mytilus* Summary	1977-78	1	13-14
	N.E. Gulf *Fucus* Summary	1977-78	2	26
	Sediment			
	Suspended Ba and As	1977-78	2	30
	N.E. Gulf Size Fractionation	1978	Annual	99
	N.W. Gulf Size Fractionation	1978	Annual	100
	N.E. Gulf Clay Mineralogy	1978	Annual	101
	N.W. Gulf Clay Mineralogy	1978	Annual	102
	N.E. Gulf *Silas Bent* Cr	1977	Annual	81
	N.W. Gulf *Discoverer* Cr, Se, Al	1977	Annual	83

	Hg Summary	1977-78	1	16
	N.E. and N.W. Gulf Clay Mineralogy Summary	1977-78	1	23-25
	N.E. Gulf Sediment Extract Summary	1977-78	2	45

B. S. BERING SEA

Water

Fig.	Station Grid	1977	Annual	23
Table	*Discoverer* 1975 u.f.	1976	Annual	77-78
	Discoverer 1975 Cr	1976	Annual	89
	Discoverer 1975 V	1977	Annual	69
	Volna Cu and Pb	1977-78	3	55+
	Volna Station Localities	1977-78	3	11
Fig.	*Volna* Station Localities	1977-78	3	12

Biota

Table	Intertidal Localities	1977-78	2	25
	Fucus and *Mytilus*	1977-78	1	13-14
	Tanner Crab	1977	Annual	70
	Neptunes	1977	Annual	71
	Se	1977	Annual	75
	Rocksole and *Neptunea* As	1977-78	2	27
	Pallock and Crab As	1977-78	2	28
	Mammals - Species Data	1977-78	2	4-5
Fig.	Mammals - Species Data	1977-78	2	6
Table	Analyses	1977-78	3	59-62

Sediment

	Suspended Ba and As	1977-78	2	32
	Cr, Se, Al	1977	Annual	84-88
	Clay Mineralogy	1977	Annual	129
	Clay Mineralogy	1977-78	1	22
	Cr	1976	Annual	88
	Clay Mineralogy	1976	Annual	103
	Size Fractionation Data	1977-78	3	25-26
Fig.	% Clay	1977-78	3	27
	% Mud	1977-78	3	28
Table	Summary of Extractions	1977-78	3	24-30

C. BEAUFORT SEA

Water

Fig.	*Glacier* Operations	1977	Annual	29
Table	Cr, Se	1977	Annual	65

Sediment

	Cr Archived Samples	1977	Annual	86-88
	Cr, Se *Glacier*	1977	Annual	89
	Non-lith % Archived	1977	Annual	128

D. NORTON SOUND

Table	*Discoverer* 1976 Operations	1977	Annual	27
Fig.	*Discoverer* 1976 Operations	1977-78	2	11
	Sediment			
Table	Size Fractionation Data	1977-78	2	17
Fig.	% Mud	1977-78	2	19
Table	% Mud and Heavy Metals	1977-78	2	21
	Correlations	1977-78	2	23

E. CHUKCHI SEA

	Sediment			
Table	*Discoverer* 1976 Operations	1977	Annual	28
Fig.	*Discoverer* 1976 Operations	1977-78	2	13
Table	Size Fractionation Data	1977-78	2	18
	% Mud and Heavy Metals	1977-78	2	22
	Correlations	1977-78	2	23

F. YAKUTAT BAY

Fig.	Stations	1977	Annual	19
	Stations	1977-78	2	7
Table	Hydro Data	1977-78	2	33+
	Water - V and Mn	1977-78	3	22
Fig.	Water V	1977-78	3	23
	Water Mn	1977-78	3	24
Table	Nutrients	1977-78	3	32+

G. RESURRECTION BAY

	Acona #254 Operations	1977-78	3	4
	Acona #254 Stations	1977-78	3	9

APPENDIX VI

YAKUTAT BAY HYDROGRAPHIC NUTRIENT DATA

```
AC   CRUISE 234 CONSECUTIVE STATION NO.  40,   YAK003    13/ 9/76
-------------------------------                              1.0 HOURS GMT

  LATITUDE = 59  52.5N   LONGITUDE = 139  40.0W   SONIC DEPTH =  256 M

  1-DIGIT WEATHER CODE IS (X2) AND INDICATES CONTINUOUS LAYER
  CLOUD TYPE --- (6) ---STRATOCUMULUS        ,
  CLOUD AMOUNT --- (8) ---8/8 TOTAL     ,
  VISIBILITY --- (7) ---10-20 KM
----------------------------------------------------------------------------
I          DIRECTION           SPEED                                        I
I WIND      25 -  34 DEGR    14 KNOTS                                       I
----------------------------------------------------------------------------
I          DIRECTION          HEIGHT        PERIOD                          I
I SEA       25 -  34 DEGR    0.2 M.            SECS                         I
I SWELL        -     DEGR        M.            SECS                         I
----------------------------------------------------------------------------
I TEMPERATURES -DRY =     9.4 DEGR C.   BAROMETRIC PR. =1002.1 MB        I
I              -WET =         DEGR C.   TRANSPARENCY    =          M        I
----------------------------------------------------------------------------

                                  OBSERVED

 TIME    DEP     TEMP     SAL     SIG-T      OXY    PO4     NH3    NO2     NO3     NO    SIO3    PH    T ALK
  1.1      0    9.86A   27.261   20.99      7.82    .20     .7      .      1.6   712.6    6      .      .
  1.1     10    6.87A   28.282   22.20      6.72    .80     .6      .     11.8   706.2   22      .      .
  1.1     20    7.00C   29.006   22.75      6.55    .80     .6      .     12.2   694.6   22      .      .
  1.1     30    9.08A   29.840   23.12      6.29    .70     .7      .      9.0   642.6   20      .      .
  1.1     50   10.93A   30.708   23.49      5.96    .90     .9      .      3.8   566.3   16      .      .
  1.1     75    9.42B   31.180   24.11      5.84   1.00     .7      .     11.1   621.3   22      .      .
  1.1    100    8.72B   31.344   24.34      5.79   1.40     .5      .     12.9   633.0   24      .      .
  1.1    125    6.03A   31.545   24.86      6.18    .90     .7      .     14.7   684.1   31      .      .
  1.1    150    5.51B   31.545   24.92      6.33    .90     .7      .     17.5   722.6   32      .      .
  1.1    175    5.21B   31.553   24.96      6.35   1.00     .7      .     19.4   741.5   32      .      .
  1.1    200T   5.04B   31.563   24.99      6.42    .80     .2      .     20.3   755.9   35      .      .
  1.1    245    4.75A   31.579   25.03      6.45   1.00     .2      .     21.6   770.3   35      .      .

                                  STANDARD

         DEP     TEMP     SAL     SIG-T      OXY          SP VOL      DEL D
           0     9.86   27.261   20.99      7.82         680.12       .000
          10     6.87   28.282   22.20      6.72         564.53       .062
          20     7.00   29.006   22.75      6.55         511.77       .116
          30     9.08   29.840   23.12      6.29         476.89       .165
          50    10.93   30.708   23.49      5.96         441.38       .257
          75     9.42   31.180   24.11      5.84         382.85       .360
         100     8.72   31.344   24.35      5.79         360.66       .453
         150     5.51   31.545   24.92      6.33         305.21       .620
         200     5.04   31.563   24.99      6.42         299.16       .771
         250     4.72   31.581   25.04      6.45         294.82       .919
```

```
AC   CRUISE 234 CONSECUTIVE STATION NO.  41.   YAK005     13/ 9/76
-----------------------------                                2.6 HOURS GMT

  LATITUDE = 59  44.0N   LONGITUDE = 139  40.5W   SONIC DEPTH =  179 M

  1-DIGIT WEATHER CODE IS (X2) AND INDICATES CONTINUOUS LAYER
  CLOUD TYPE --- (0) ---CIRRUS                   .
  CLOUD AMOUNT --- (8) ---8/8 TOTAL      .
  VISIBILITY --- (8) ---20-50 KM
-----------------------------------------------------------------
I            DIRECTION         SPEED                             I
I WIND        95 - 104 DEGR    10 KNOTS                          I
-----------------------------------------------------------------
I            DIRECTION        HEIGHT      PERIOD                 I
I SEA          0 -    0 DEGR   0.7 M.        SECS                I
I SWELL          -      DEGR       M.        SECS                I
-----------------------------------------------------------------
I TEMPERATURES -DRY =   11.1 DEGR C.   BAROMETRIC PR. =1001.6 MB  I
I              -WET =        DEGR C.   TRANSPARENCY   =        M  I
-----------------------------------------------------------------

                                 OBSERVED

 TIME    DEP     TEMP     SAL     SIG-T     OXY    PO4    NH3    NO2    NO3    NO    SIO3   PH    T ALK
  2.6      0   10.77B   27.816   21.28     7.96    .20    .2     .       .1   711.6    4     .       .
  2.6     10   10.49B     .        .       6.92    .30    .4     .      1.2   628.6    8     .       .
  2.6     20    9.99A   29.885   23.01     6.27    .30    .7     .      6.1   614.7   16     .       .
  2.6     30   10.49B   30.700   23.56     6.06    .30    .4     .      1.6   555.4   13     .       .
  2.6     50   10.01B   31.160   24.00     5.83    .60    .5     .     10.1   611.4   18     .       .
  2.6     75    8.46D   31.518   24.52     5.74    .60    .4     .      7.8   582.7   23     .       .
  2.6    100    6.64B   31.532   24.78     5.79    .80    .6     .     18.7   685.2   28     .       .
  2.6    125    5.41A   31.615   24.99     5.86   1.70    .5     .     17.9   684.3   37     .       .
  2.6    150    4.73A   31.685   25.12     5.88    .70    .5     .     19.7   702.3   35     .       .
  2.6    170    4.46A   31.713   25.17     5.80   1.60    .4     .     23.7   731.1   43     .       .

                                 STANDARD

         DEP     TEMP     SAL     SIG-T     OXY       SP VOL     DEL D
           0    10.77   27.816   21.28     7.96      652.64      .000
          10    10.49   29.070   22.30     6.92      555.17      .060
          20     9.99   29.885   23.01     6.27      486.98      .112
          30    10.49   30.700   23.56     6.06      434.49      .159
          50    10.01   31.160   24.00     5.83      393.06      .241
          75     8.46   31.518   24.52     5.74      343.68      .333
         100     6.64   31.532   24.78     5.79      318.89      .416
         150     4.73   31.685   25.12     5.88      286.44      .567
```

```
AC   CRUISE 234 CONSECUTIVE STATION NO.  42,   YAK007     13/ 9/76
-----------------------------------------                 3.6 HOURS GMT

  LATITUDE = 59  39.5N   LONGITUDE = 139  46.0W   SONIC DEPTH =  170 M

  1-DIGIT WEATHER CODE IS (X2) AND INDICATES CONTINUOUS LAYER
  CLOUD TYPE --- (0) ---CIRRUS              ,
  CLOUD AMOUNT --- (8) ---8/8 TOTAL    ,
  VISIBILITY --- (8) ---20-50 KM
-------------------------------------------------------------------------
I          DIRECTION          SPEED                                     I
I WIND      95 - 104 DEGR      5 KNOTS                                  I
-------------------------------------------------------------------------
I          DIRECTION        HEIGHT      PERIOD                          I
I SEA      205 - 214 DEGR   0.5 M.         SECS                         I
I SWELL          -   DEGR       M.         SECS                         I
-------------------------------------------------------------------------
I TEMPERATURES -DRY =  11.1 DEGR C.   BAROMETRIC PR. =1001.3 MB    I
I              -WET =       DEGR C.   TRANSPARENCY   =        M    I
-------------------------------------------------------------------------

                                         OBSERVED

 TIME    DEP     TEMP     SAL    SIG-T    OXY    PO4    NH3    NO2    NO3    NO    SIO3    PH    T ALK
  3.6      0   10.14A  27.529   21.16    7.68   .20     .4     .       .4  689.3     9     .      .
  3.6     10   10.83A  29.671   22.71    6.35   .50     .6     .      4.5  607.4    14     .      .
  3.6     20   10.13A  30.193   23.23    6.17   .70     .6     .      7.7  620.2    16     .      .
  3.6     30   10.37A  30.408   23.36    6.11   .60     .8     .      3.1  573.4    16     .      .
  3.6     50   11.41A  31.123   23.73    5.99   .70     .4     .      3.7  568.1    13     .      .
  3.6     75    9.55C  31.651   24.46    5.78   .70     .4     .     11.4  618.6    20     .      .
  3.6    100    8.41D  31.595   24.59    5.77  1.00     .5     .     15.0  650.1    25     .      .
  3.6    125    8.10A  31.651   24.68    5.75   .60     .5     .     10.9  611.5    20     .      .
  3.6    150    7.98A  31.686   24.72    5.62   .70     .5     .     17.5  659.3    31     .      .
  3.6    160    7.94A  31.684   24.72    5.64   .80     .5     .     16.9  655.6    31     .      .

                                         STANDARD

         DEP     TEMP     SAL    SIG-T    OXY      SP VOL    DEL D
           0    10.14  27.529   21.16    7.68     664.31     .000
          10    10.83  29.671   22.71    6.35     515.98     .059
          20    10.13  30.193   23.23    6.17     466.27     .108
          30    10.37  30.408   23.36    6.11     454.22     .154
          50    11.41  31.123   23.73    5.99     418.78     .241
          75     9.55  31.651   24.46    5.78     349.89     .337
         100     8.41  31.595   24.59    5.77     337.56     .423
         150     7.98  31.686   24.72    5.62     325.43     .589
```

```
AC   CRUISE 234 CONSECUTIVE STATION NO.  39.   YAK009     12/ 9/76
---------------------------------------------               22.7 HOURS GMT

 LATITUDE = 59  40.0N   LONGITUDE = 139  59.5W   SONIC DEPTH =  157 M

 1-DIGIT WEATHER CODE IS (X2) AND INDICATES CONTINUOUS LAYER
 CLOUD TYPE --- (6) ---STRATOCUMULUS       .
 CLOUD AMOUNT --- (8) ---8/8 TOTAL    ,
 VISIBILITY --- (8) ---20-50 KM
--------------------------------------------------------------------------
I             DIRECTION          SPEED                                   I
I WIND       135 - 144 DEGR     12 KNOTS                                 I
--------------------------------------------------------------------------
I             DIRECTION        HEIGHT       PERIOD                       I
I SEA        135 - 144 DEGR   1.0 M.           SECS                      I
I SWELL           -    DEGR       M.           SECS                      I
--------------------------------------------------------------------------
I TEMPERATURES -DRY =   12.2 DEGR C.   BAROMETRIC PR. =1003.5 MB         I
I              -WET =        DEGR C.   TRANSPARENCY   =         M        I
--------------------------------------------------------------------------

                                     OBSERVED

  TIME    DEP     TEMP     SAL     SIG-T     OXY   PO4    NH3    NO2    NO3     NO   SIO3    PH    T ALK
  22.7      0   11.10A  27.416   20.91     6.96   .40     .5     .     1.1   631.3   14     .       .
  22.7     10   12.21B  29.046   21.98     6.37   .50     .9     .      .1   569.6   12     .       .
  22.7     20   12.21A  29.589   22.40     5.71   .40    1.4     .     1.5   523.3   13     .       .
  22.7     30   12.13A  30.077   22.79     6.21  1.20     .9     .     1.9   571.5   11     .       .
  22.7     50   11.44A  30.598   23.32     6.05   .60     .9     .     4.5   580.6   14     .       .
  22.7     75    8.90C  31.475   24.42     5.72   .80     .5     .    14.4   640.3   25     .       .
  22.7    100    7.86C  31.628   24.69     5.71  1.50     .4     .    15.9   652.9   29     .       .
  22.7    125    7.54A  31.677   24.77     5.66   .80     .6     .    18.7   673.6   32     .       .
  22.7    145    7.30A  31.712   24.83     5.58  1.60     .5     .    18.9   668.3   33     .       .

                                     STANDARD

          DEP     TEMP     SAL     SIG-T     OXY        SP VOL     DEL D
            0    11.10  27.416   20.91     6.96        687.62      .000
           10    12.21  29.046   21.98     6.37        585.51      .064
           20    12.21  29.589   22.40     5.71        545.52      .120
           30    12.13  30.077   22.79     6.21        508.22      .173
           50    11.44  30.598   23.32     6.05        458.09      .270
           75     8.90  31.475   24.42     5.72        353.21      .371
          100     7.86  31.628   24.69     5.71        327.47      .456
          150     7.24  31.721   24.85     5.56        312.90      .616
```

```
AC   CRUISE 234 CONSECUTIVE STATION NO.  38,   YAK012    12/ 9/76
---------------------------                                20.7 HOURS GMT

  LATITUDE = 59  27.2N   LONGITUDE = 140  12.9W   SONIC DEPTH =  223 M

  1-DIGIT WEATHER CODE IS (X2) AND INDICATES CONTINUOUS LAYER
  CLOUD TYPE --- (6) ---STRATOCUMULUS      ,
  CLOUD AMOUNT --- (8) ---8/8 TOTAL    ,
  VISIBILITY --- (8) ---20-50 KM
------------------------------------------------------------------------
I          DIRECTION          SPEED                                    I
I WIND      85 -  94 DEGR    20 KNOTS                                  I
------------------------------------------------------------------------
I          DIRECTION        HEIGHT       PERIOD                        I
I SEA       85 -  94 DEGR   2.0 M.          SECS                       I
I SWELL        -     DEGR       M.          SECS                       I
------------------------------------------------------------------------
I TEMPERATURES -DRY =  12.7 DEGR C.   BAROMETRIC PR. =1003.4 MB        I
I              -WET =       DEGR C.   TRANSPARENCY   =       M         I
------------------------------------------------------------------------

                                          OBSERVED

 TIME     DEP     TEMP      SAL     SIG-T     OXY    PO4     NH3    NO2    NO3    NO    SIO3    PH    T ALK
 20.7       0   12.18B   31.248    23.69     6.28    .50    1.1      .      .6   566.1   11      .       .
 20.7      10   12.11C   31.401    23.82     6.26    .60     .5      .      .6   564.3   11      .       .
 20.7      20   12.06B   31.706    24.06     6.27    .40    1.0      .     2.2   579.6   10      .       .
 20.7      30   11.98A   31.747    24.11     6.40    .60     .6      .      .6   576.8   10      .       .
 20.7      50    9.25H   31.824    24.64     5.58    .90     .5      .    10.2   590.0   21      .       .
 20.7      75    6.93B   31.991    25.10     5.11   1.40     .5      .    21.2   647.0   35      .       .
 20.7     100    6.58A   32.096    25.23     5.48   1.30     .3      .    18.2   653.1   35      .       .
 20.7     125    6.13A   32.333    25.47     5.56   2.00     .2      .    20.3   679.1   35      .       .
 20.7     150    5.57B   32.803    25.91     5.06   2.10     .4      .    23.7   665.1   41      .       .
 20.7     175    5.41B   33.436    26.43     3.24   1.10     .4      .    27.9   540.4   48      .       .
 20.7     200T   5.42A   33.621    26.57     2.82   2.10     .8      .    31.0   530.8   60      .       .
 20.7     215    5.41A   33.738    26.67     2.50   2.90     .3      .    33.8   527.4   62      .       .

                                          STANDARD

          DEP     TEMP      SAL     SIG-T     OXY          SP VOL     DEL D
            0    12.18   31.248    23.69     6.28         422.13     .000
           10    12.11   31.401    23.82     6.26         409.77     .042
           20    12.06   31.706    24.06     6.27         386.56     .081
           30    11.98   31.747    24.11     6.40         382.30     .120
           50     9.25   31.824    24.64     5.58         332.13     .191
           75     6.93   31.991    25.10     5.11         287.95     .269
          100     6.58   32.096    25.23     5.48         276.01     .339
          150     5.57   32.803    25.91     5.06         211.69     .461
          200     5.42   33.621    26.57     2.82         149.34     .551
```

```
AC   CRUISE 234 CONSECUTIVE STATION NO.  43,    ICY005     14/ 9/76
---------------------------                                  15.5 HOURS GMT

  LATITUDE = 59  56.0N   LONGITUDE = 141  32.5W   SONIC DEPTH =   65 M

  1-DIGIT WEATHER CODE IS (X2) AND INDICATES CONTINUOUS LAYER
  CLOUD TYPE --- (7) ---STRATUS              ,
  CLOUD AMOUNT --- (8) ---8/8 TOTAL    ,
  VISIBILITY --- (7) ---10-20 KM
-----------------------------------------------------------------
I          DIRECTION        SPEED                               I
I WIND      55 -  64 DEGR   28 KNOTS                            I
-----------------------------------------------------------------
I          DIRECTION       HEIGHT     PERIOD                    I
I SEA        0 -    0 DEGR  3.0 M.       SECS                   I
I SWELL        -      DEGR      M.       SECS                   I
-----------------------------------------------------------------
I TEMPERATURES -DRY =    7.2 DEGR C.   BAROMETRIC PR. = 998.0 MB  I
I              -WET =        DEGR C.   TRANSPARENCY   =       M  I
-----------------------------------------------------------------

                                         OBSERVED

 TIME     DEP      TEMP     SAL     SIG-T     OXY    PO4     NH3    NO2    NO3    NO    SIO3    PH    T ALK
 15.5       0      9.83A  27.651   21.30     6.49    .       .      .      .                   .       .
 15.5      10     11.25C  28.878   22.02     6.56    .       .      .      .                   .       .
 15.5      20     11.62B  29.617   22.53     6.37    .       .      .      .                   .       .
 15.5      30     11.843  30.039   22.81     6.30    .       .      .      .                   .       .
 15.5      50     12.07A  30.871   23.42     6.30    .       .      .      .                   .       .

                                         STANDARD

          DEP      TEMP     SAL     SIG-T     OXY        SP VOL     DEL D
            0      9.83   27.651   21.30     6.49       650.60      .000
           10     11.25   28.878   22.02     6.56       581.65      .062
           20     11.62   29.617   22.53     6.37       533.24      .117
           30     11.84   30.039   22.81     6.30       505.96      .169
           50     12.07   30.871   23.42     6.30       448.89      .265
```

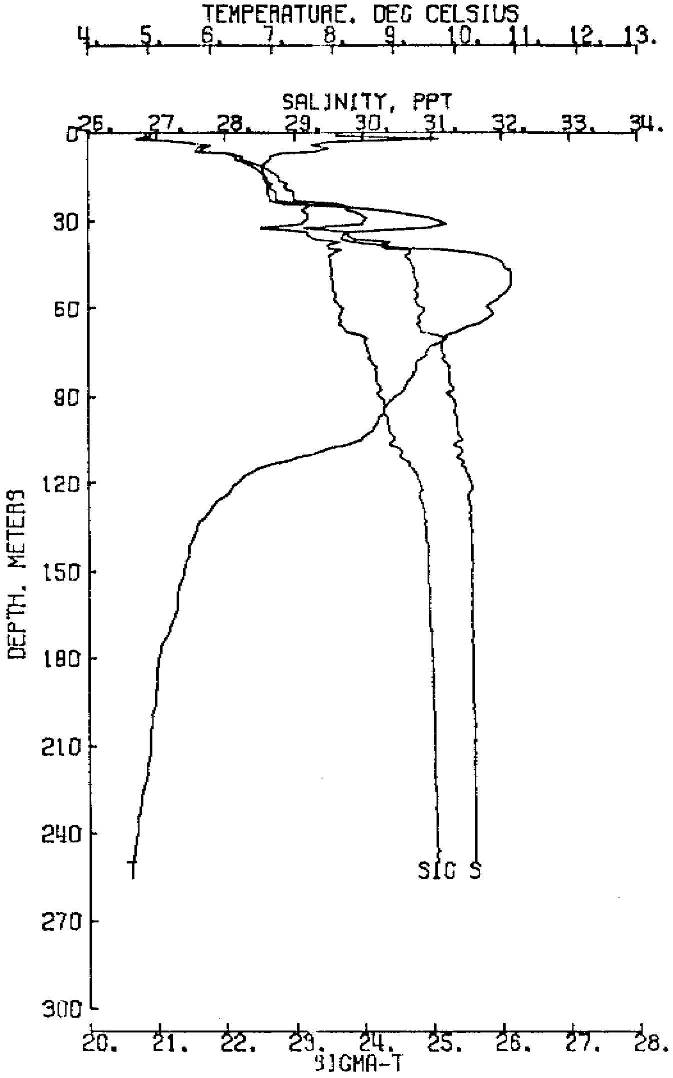
```
AC   CRUISE 234 CONSECUTIVE STATION NO.  40.   YAK003    13/ 9/76
---------------------------                          1.0 HOURS GMT

 LATITUDE = 59  52.5N   LONGITUDE = 139  40.0W   SONIC DEPTH =  256 M


 1-DIGIT WEATHER CODE IS (X2) AND INDICATES CONTINUOUS LAYER
 CLOUD TYPE --- (6) ---STRATOCUMULUS      .
 CLOUD AMOUNT --- (8) ---8/8 TOTAL    .
 VISIBILITY --- (7) ---10-20 KM
-----------------------------------------------------------------
I          DIRECTION        SPEED                               I
I WIND      25 -  34 DEGR   14 KNOTS                            I
-----------------------------------------------------------------
I          DIRECTION       HEIGHT     PERIOD                    I
I SEA       25 -  34 DEGR  0.2 M.        SECS                   I
I SWELL        -     DEGR      M.        SECS                   I
-----------------------------------------------------------------
I TEMPERATURES -DRY =    9.4 DEGR C.   BAROMETRIC PR. =1002.1 MB  I
I              -WET =        DEGR C.   TRANSPARENCY    =       M  I
-----------------------------------------------------------------



       DEPTH     TEMPERATURE    SALINITY      SIGMA-T      DELTA-D
       METERS       DEG C         PPT                       DYN M
         0.          8.07        26.843        20.92       0.
         1.0         8.07        26.843        20.92       0.007
         5.0         7.94        27.665        21.58       0.033
        10.0         6.89        28.400        22.29       0.062
        15.0         6.88        28.777        22.58       0.089
        20.0         6.93        28.981        22.74       0.116
        25.0         8.21        29.769        23.19       0.140
        30.0         9.75        30.014        23.15       0.164
        35.0         8.16        29.780        23.20       0.189
        40.0         9.74        30.696        23.68       0.211
        45.0        10.79        30.719        23.53       0.233
        50.0        10.91        30.773        23.55       0.255
        75.0         9.52        31.142        24.06       0.359
       100.0         8.70        31.352        24.35       0.452
       150.0         5.55        31.561        24.93       0.613
       200.0         5.02        31.585        25.01       0.764
```



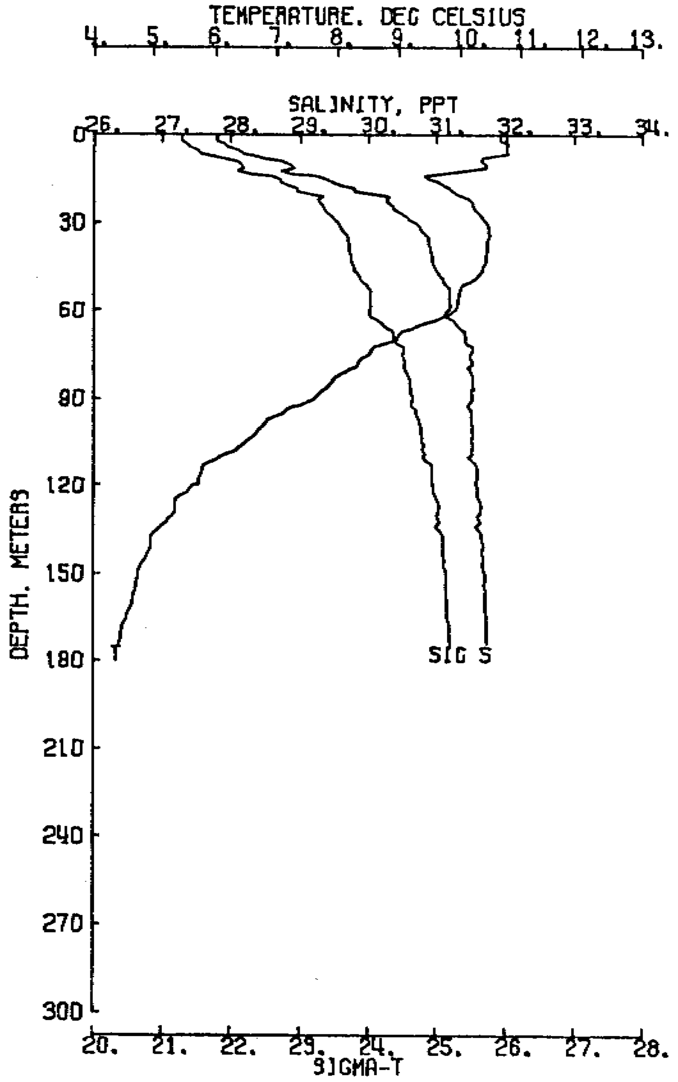
CRUISE 234 STATION 40

```
AC   CRUISE 234 CONSECUTIVE STATION NO.  41.   YAK005     13/ 9/76
---------------------------                                 2.6 HOURS GMT

  LATITUDE = 59  44.0N   LONGITUDE = 139  40.5W   SONIC DEPTH =  179 M

  1-DIGIT WEATHER CODE IS (X2) AND INDICATES CONTINUOUS LAYER
  CLOUD TYPE --- (0) ---CIRRUS                .
  CLOUD AMOUNT --- (8) ---8/8 TOTAL   .
  VISIBILITY --- (8) ---20-50 KM
-----------------------------------------------------------------------
I          DIRECTION        SPEED                                     I
I WIND      95 - 104 DEGR   10 KNOTS                                  I
-----------------------------------------------------------------------
I          DIRECTION       HEIGHT      PERIOD                         I
I SEA        0 -    0 DEGR 0.7 M.         SECS                        I
I SWELL      -      DEGR      M.          SECS                        I
-----------------------------------------------------------------------
I TEMPERATURES -DRY =  11.1 DEGR C.   BAROMETRIC PR. =1001.6 MB  I
I              -WET =       DEGR C.   TRANSPARENCY   =        M  I
-----------------------------------------------------------------------


        DEPTH      TEMPERATURE    SALINITY      SIGMA-T      DELTA-D
        METERS       DEG C          PPT                        DYN M
          0.         10.65         27.799        21.28        0.
          1.0        10.65         27.799        21.28        0.007
          5.0        10.76         28.108        21.51        0.032
         10.0        10.43         28.883        22.16        0.063
         15.0         9.49         29.392        22.71        0.090
         20.0         9.93         29.995        23.11        0.115
         25.0        10.25         30.378        23.35        0.138
         30.0        10.45         30.702        23.57        0.161
         35.0        10.48         30.871        23.70        0.182
         40.0        10.44         30.911        23.74        0.203
         45.0        10.38         30.972        23.79        0.224
         50.0        10.17         31.091        23.92        0.244
         75.0         8.50         31.487        24.49        0.338
        100.0         6.74         31.509        24.75        0.422
        150.0         4.73         31.700        25.13        0.572
```



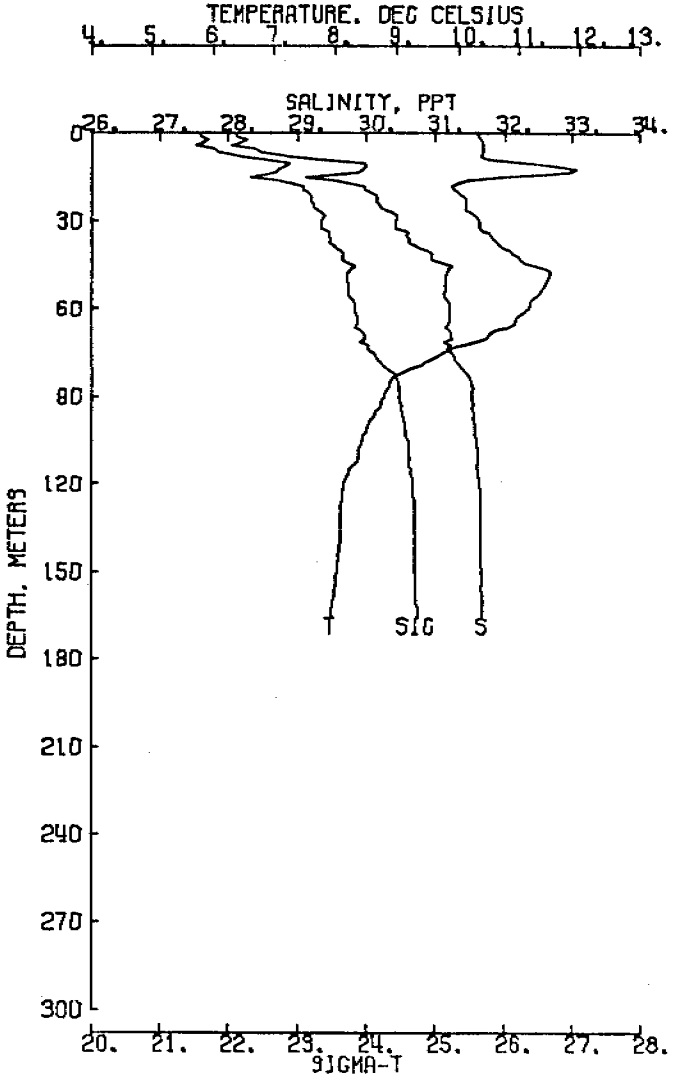
CRUISE 234 STATION 41

```
AC   CRUISE 234 CONSECUTIVE STATION NO.  42.   YAK007     13/ 9/76
---------------------------                              3.6 HOURS GMT

  LATITUDE = 59  39.5N   LONGITUDE = 139  46.0W   SONIC DEPTH =  170 M

  1-DIGIT WEATHER CODE IS (X2) AND INDICATES CONTINUOUS LAYER
  CLOUD TYPE --- (0) ---CIRRUS                  .
  CLOUD AMOUNT --- (8) ---9/8 TOTAL    .
  VISIBILITY --- (8) ---20-50 KM
----------------------------------------------------------------------
I            DIRECTION         SPEED                                 I
I WIND        95 - 104 DEGR     5 KNOTS                              I
----------------------------------------------------------------------
I            DIRECTION        HEIGHT      PERIOD                     I
I SEA        205 - 214 DEGR  0.5 M.          SECS                    I
I SWELL          -      DEGR      M.          SECS                   I
----------------------------------------------------------------------
I TEMPERATURES -DRY =  11.1 DEGR C.   BAROMETRIC PR. =1001.3 MB  I
I              -WET =       DEGR C.   TRANSPARENCY    =        M  I
----------------------------------------------------------------------
```

DEPTH METERS	TEMPERATURE DEG C	SALINITY PPT	SIGMA-T	DELTA-D DYN M
0.	10.33	28.113	21.58	0.
1.0	10.33	28.113	21.58	0.006
5.0	10.40	28.385	21.78	0.031
10.0	11.12	29.988	22.90	0.059
15.0	10.68	29.136	22.32	0.085
20.0	9.98	30.055	23.15	0.110
25.0	10.11	30.222	23.25	0.134
30.0	10.34	30.420	23.37	0.156
35.0	10.54	30.584	23.46	0.179
40.0	10.84	30.855	23.62	0.201
45.0	11.29	31.241	23.85	0.222
50.0	11.46	31.130	23.73	0.243
75.0	9.72	31.252	24.12	0.344
100.0	8.52	31.575	24.56	0.433
150.0	8.03	31.675	24.70	0.599



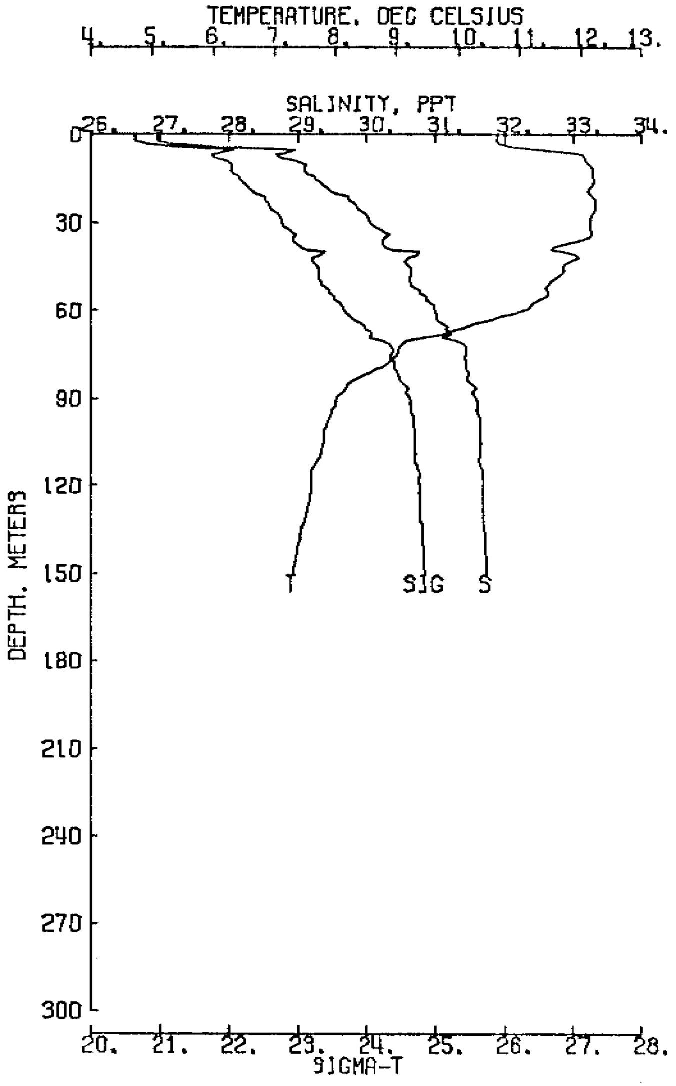
CRUISE 234 STATION 42

```
AC   CRUISE 234 CONSECUTIVE STATION NO.  39.    YAK009     12/ 9/76
--------------------------                                  22.7 HOURS GMT

  LATITUDE = 59  40.0N    LONGITUDE = 139  59.5W    SONIC DEPTH =  157 M


  1-DIGIT WEATHER CODE IS (X2) AND INDICATES CONTINUOUS LAYER
  CLOUD TYPE --- (6) ---STRATOCUMULUS      ,
  CLOUD AMOUNT --- (8) ---8/8 TOTAL    ,
  VISIBILITY --- (8) ---20-50 KM
------------------------------------------------------------------
I          DIRECTION          SPEED                              I
I WIND     135 - 144 DEGR    12 KNOTS                            I
------------------------------------------------------------------
I          DIRECTION         HEIGHT       PERIOD                 I
I SEA      135 - 144 DEGR   1.0 M.          SECS                 I
I SWELL        -     DEGR       M.          SECS                 I
------------------------------------------------------------------
I TEMPERATURES -DRY =  12.2 DEGR C.   BAROMETRIC PR. =1003.5 MB  I
I              -WET =       DEGR C.   TRANSPARENCY    =       M  I
------------------------------------------------------------------
```

DEPTH METERS	TEMPERATURE DEG C	SALINITY PPT	SIGMA-T	DELTA-D DYN M
0.	10.62	26.951	20.63	0.
1.0	10.62	26.951	20.63	0.007
5.0	11.34	28.963	22.07	0.034
10.0	12.15	29.119	22.05	0.064
15.0	12.21	29.264	22.15	0.093
20.0	12.11	29.557	22.39	0.121
25.0	12.24	29.887	22.62	0.148
30.0	12.15	30.080	22.79	0.173
35.0	12.13	30.272	22.94	0.198
40.0	11.71	30.769	23.40	0.222
45.0	11.71	30.649	23.31	0.245
50.0	11.50	30.659	23.36	0.268
75.0	9.01	31.446	24.38	0.370
100.0	7.82	31.640	24.71	0.455
150.0	7.30	31.740	24.86	0.615



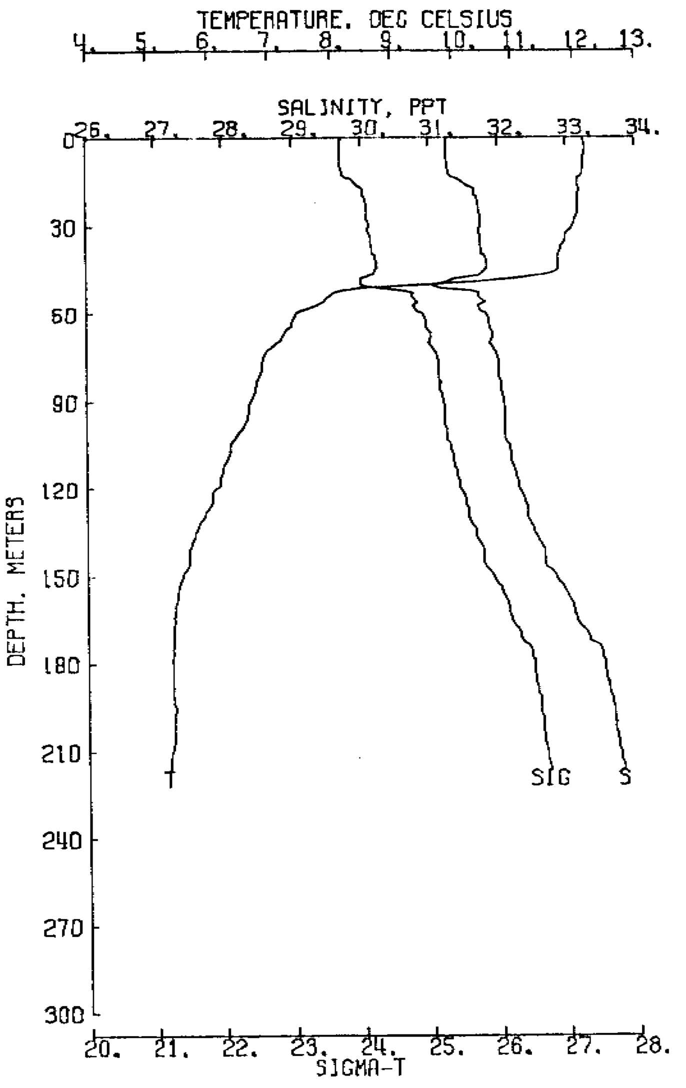
CRUISE 234 STATION 39

```
AC   CRUISE 234 CONSECUTIVE STATION NO.  38.   YAK012     12/ 9/76
---------------------------                                20.7 HOURS GMT

  LATITUDE = 59  27.2N   LONGITUDE = 140  12.9W   SONIC DEPTH =  223 M

  1-DIGIT WEATHER CODE IS (X2) AND INDICATES CONTINUOUS LAYER
  CLOUD TYPE --- (6) ---STRATOCUMULUS      .
  CLOUD AMOUNT --- (8) ---8/8 TOTAL    .
  VISIBILITY --- (8) ---20-50 KM
---------------------------------------------------------------------
I           DIRECTION          SPEED                                I
I WIND       85 -  94 DEGR   20 KNOTS                               I
---------------------------------------------------------------------
I           DIRECTION         HEIGHT       PERIOD                   I
I SEA        85 -  94 DEGR   2.0 M.          SECS                   I
I SWELL           -     DEGR       M.        SECS                   I
---------------------------------------------------------------------
I TEMPERATURES -DRY =  12.7 DEGR C.   BAROMETRIC PR. =1003.4 MB    I
I              -WET =       DEGR C.   TRANSPARENCY   =         M    I
---------------------------------------------------------------------
```

DEPTH METERS	TEMPERATURE DEG C	SALINITY PPT	SIGMA-T	DELTA-D DYN M
0.	12.18	31.257	23.69	0.
1.0	12.18	31.257	23.69	0.004
5.0	12.18	31.257	23.69	0.021
10.0	12.15	31.271	23.71	0.042
15.0	12.05	31.510	23.91	0.063
20.0	12.07	31.702	24.06	0.082
25.0	12.06	31.745	24.09	0.102
30.0	11.98	31.747	24.11	0.121
35.0	11.84	31.761	24.15	0.140
40.0	11.72	31.806	24.20	0.159
45.0	11.72	31.796	24.20	0.178
50.0	9.45	31.050	24.00	0.197
75.0	6.89	31.995	25.11	0.274
100.0	6.55	32.105	25.24	0.345
150.0	5.56	32.818	25.92	0.468
200.0	5.42	33.662	26.61	0.554



CRUISE 234 STATION 38

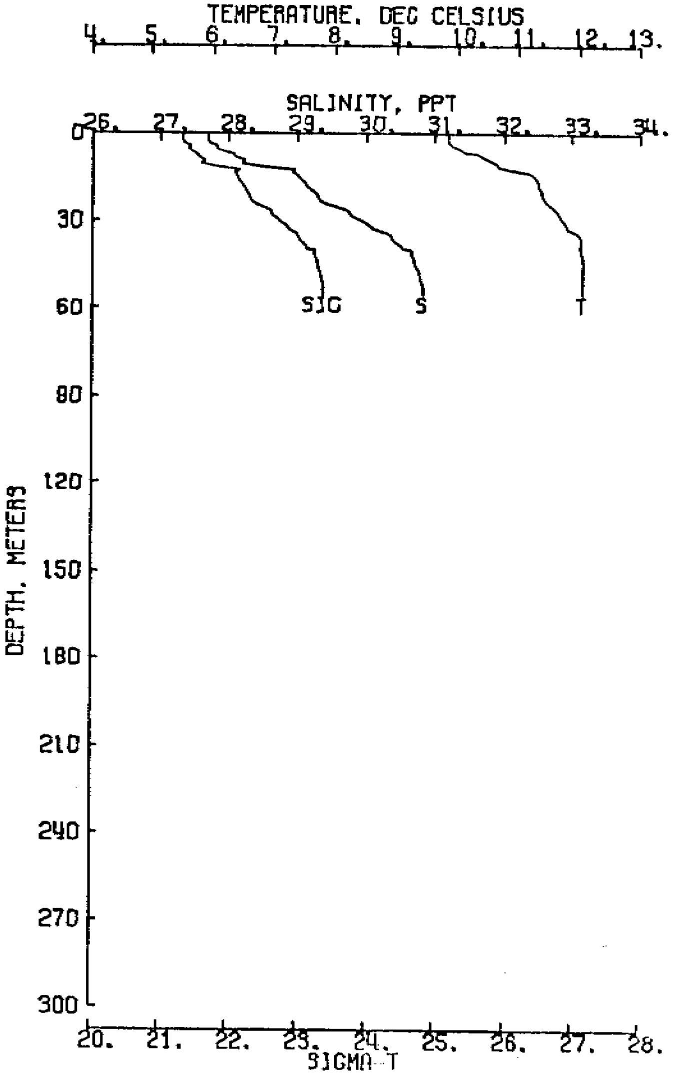
```
AC   CRUISE 234 CONSECUTIVE STATION NO.  43.   1CY005      14/ 9/76
--------------------------                                   15.5 HOURS GMT

  LATITUDE = 59  56.0N   LONGITUDE = 141  32.5W   SONIC DEPTH =   65 M


  1-DIGIT WEATHER CODE IS (X2) AND INDICATES CONTINUOUS LAYER
  CLOUD TYPE --- (7) ---STRATUS
  CLOUD AMOUNT --- (8) ---8/8 TOTAL
  VISIBILITY --- (7) ---10-20 KM
---------------------------------------------------------------
I          DIRECTION         SPEED                             I
I WIND      55 -  64 DEGR   28 KNOTS                           I
---------------------------------------------------------------
I          DIRECTION        HEIGHT      PERIOD                 I
I SEA        0 -    0 DEGR  3.0 M.         SECS                I
I SWELL        -      DEGR     M.          SECS                I
---------------------------------------------------------------
I TEMPERATURES -DRY =    7.2 DEGR C.   BAROMETRIC PR. = 998.0 MB  I
I              -WET =        DEGR C.   TRANSPARENCY   =       M   I
---------------------------------------------------------------



    DEPTH      TEMPERATURE    SALINITY      SIGMA-T       DELTA-D
    METERS        DEG C         PPT                        DYN M
      0.           9.83        27.689        21.33         0.
      1.0          9.83        27.689        21.33         0.006
      5.0         10.04        27.844        21.42         0.032
     10.0         10.64        28.198        21.60         0.064
     15.0         11.27        29.028        22.13         0.093
     20.0         11.38        29.234        22.27         0.121
     25.0         11.56        29.597        22.52         0.149
     30.0         11.74        29.956        22.77         0.175
     35.0         12.01        30.340        23.02         0.200
     40.0         12.04        30.654        23.25         0.223
     45.0         12.05        30.717        23.30         0.247
     50.0         12.05        30.784        23.35         0.270
```



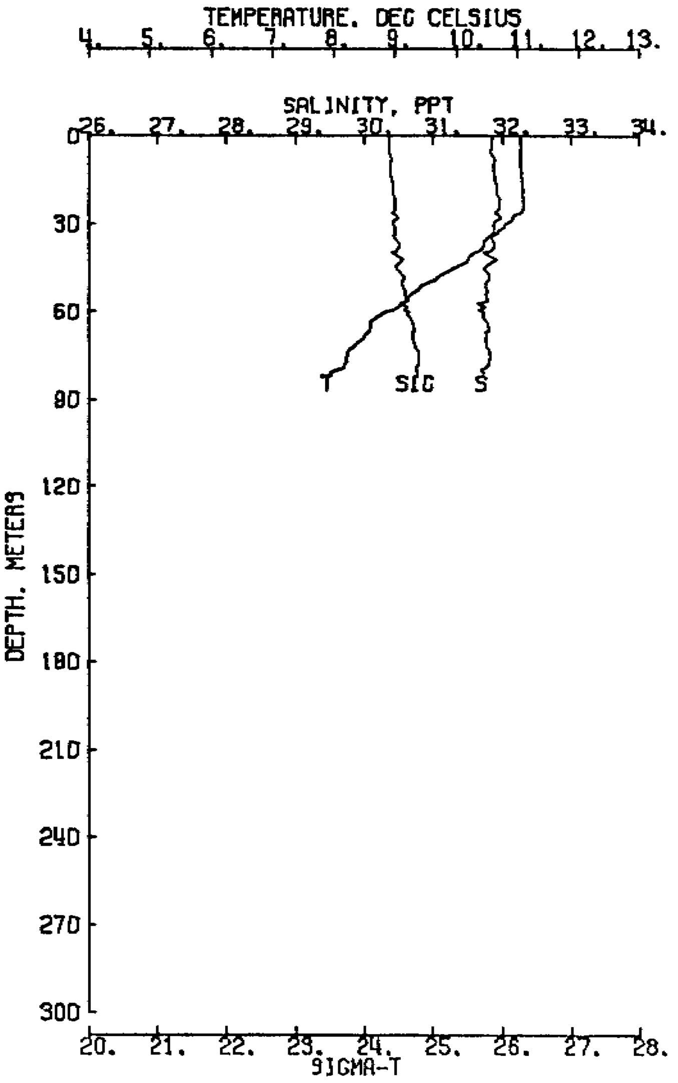
CRUISE 234 STATION 43

```
AC   CRUISE 234 CONSECUTIVE STATION NO.  44.   ICY010     14/ 9/76
--------------------------                                 17.8 HOURS GMT

  LATITUDE = 59  45.0N   LONGITUDE = 141  44.0W   SONIC DEPTH =   90 M

  1-DIGIT WEATHER CODE IS (X2) AND INDICATES CONTINUOUS LAYER
  CLOUD TYPE --- (6) ---STRATOCUMULUS
  CLOUD AMOUNT --- (7) ---7/8
  VISIBILITY --- (6) ---4-10 KM
--------------------------------------------------------------
I         DIRECTION        SPEED                             I
I WIND    895 - 544 DEGR   35 KNOTS                          I
--------------------------------------------------------------
I         DIRECTION       HEIGHT     PERIOD                  I
I SEA      85 -  94 DEGR      M.         SECS                I
I SWELL        -    DEGR      M.         SECS                I
--------------------------------------------------------------
I TEMPERATURES -DRY =   9.4 DEGR C.   BAROMETRIC PR. = 997.3 MB  I
I              -WET =       DEGR C.   TRANSPARENCY   =       M   I
--------------------------------------------------------------


        DEPTH    TEMPERATURE   SALINITY     SIGMA-T      DELTA-D
        METERS      DEG C        PPT                      DYN M
          0.        11.06       31.853       24.36        0.
          1.0       11.06       31.853       24.36        0.004
          5.0       11.06       31.831       24.34        0.018
         10.0       11.06       31.874       24.38        0.036
         15.0       11.07       31.900       24.39        0.054
         20.0       11.09       31.925       24.41        0.071
         25.0       11.09       31.953       24.43        0.089
         30.0       10.80       31.879       24.42        0.106
         35.0       10.50       31.848       24.45        0.124
         40.0       10.29       31.738       24.40        0.141
         45.0        9.92       31.743       24.47        0.159
         50.0        9.53       31.759       24.54        0.176
         75.0        8.21       31.818       24.79        0.258
```



CRUISE 234 STATION 44

```
AC   CRUISE 240 CONSECUTIVE STATION NO.   2.   YAK003      9/ 4/77
-------------------------------                               9.7 HOURS GMT

  LATITUDE = 59  52.5N   LONGITUDE = 139  40.0W   SONIC DEPTH =  260 M

  1-DIGIT WEATHER CODE IS (X1) AND INDICATES PARTLY CLOUDY
  CLOUD TYPE --- ( ) ---NOT RECORDED          .
  CLOUD AMOUNT --- ( ) ---NOT RECORDED,
  VISIBILITY --- ( ) ---NOT RECORDED
------------------------------------------------------------------------
I             DIRECTION           SPEED                                I
I WIND         15 -  24 DEGR        KNOTS                              I
------------------------------------------------------------------------
I             DIRECTION          HEIGHT        PERIOD                  I
I SEA           0 -    0 DEGR        M.            SECS                I
I SWELL           -      DEGR        M.            SECS                I
------------------------------------------------------------------------
I TEMPERATURES -DRY =    5.0 DEGR C.   BAROMETRIC PR. =1005.0 MB   I
I              -WET =        DEGR C.   TRANSPARENCY   =         M   I
------------------------------------------------------------------------

                                 OBSERVED

 TIME    DEP    TEMP    SAL    SIG-T    OXY   PO4   NH3   NO2   NO3    NO   SIO3   PH   T ALK
  9.7      0   5.72B  30.290  23.91   7.95  1.48  00.9  0.25  12.7  824.1   27    .      .
  9.7     10   5.57A  30.432  24.04   8.04  1.95  00.5  0.30  14.8  851.0   31    .      .
  9.7     20   5.52B  30.611  24.19   7.74  2.00  00.4  0.29  14.9  825.1   29    .      .
  9.7     30   5.47A  30.886  24.41   7.49  2.20  00.3  0.28  17.0  821.7   32    .      .
  9.7     50   5.60A  31.029  24.51   7.60  2.16  00.5  0.32  24.1  895.4   51    .      .
  9.7     75   5.65B  31.086  24.55   7.29  2.39  00.2  0.28  17.8  811.1   32    .      .
  9.7    100   5.69A  31.147  24.59   7.28  2.16  00.5  0.28  16.5  798.5   31    .      .
  9.7    150   5.76A  31.239  24.66   7.40  2.36  00.3  0.30  17.2  815.5   30    .      .
  9.7    200T  5.78A  31.282  24.69   7.46  2.41  00.5  0.32  18.3  830.7   32    .      .
  9.7    250T  5.81A  31.332  24.72    .    2.40  00.1  0.36  16.9          34    .      .
                                 STANDARD

         DEP    TEMP    SAL    SIG-T    OXY      SP VOL    DEL D
           0    5.72  30.290  23.91   7.95     400.80     .000
          10    5.57  30.432  24.04   8.04     388.57     .039
          20    5.52  30.611  24.19   7.74     374.63     .078
          30    5.47  30.886  24.41   7.49     353.47     .114
          50    5.60  31.029  24.51   7.60     344.23     .184
          75    5.65  31.086  24.55   7.29     340.64     .269
         100    5.69  31.147  24.59   7.28     336.67     .354
         150    5.76  31.239  24.65   7.40     330.93     .521
         200    5.78  31.282  24.69   7.46     328.35     .686
         250    5.81  31.332  24.72    .       325.41     .849
```

```
AC   CRUISE 240 CONSECUTIVE STATION NO.    3,   YAK005        9/ 4/77
---------------------------                                  12.3 HOURS GMT

  LATITUDE = 59  44.5N   LONGITUDE = 139  40.5W   SONIC DEPTH =  182 M

  1-DIGIT WEATHER CODE IS (X1) AND INDICATES PARTLY CLOUDY
  CLOUD TYPE --- ( ) ---NOT RECORDED          .
  CLOUD AMOUNT --- ( ) ---NOT RECORDED.
  VISIBILITY --- ( ) ---NOT RECORDED
---------------------------------------------------------------------
I          DIRECTION          SPEED                                 I
I WIND      15 -  24 DEGR     5 KNOTS                               I
---------------------------------------------------------------------
I          DIRECTION        HEIGHT      PERIOD                      I
I SEA        0 -   0 DEGR      M.         SECS                      I
I SWELL        -     DEGR      M.         SECS                      I
---------------------------------------------------------------------
I TEMPERATURES -DRY =    5.0 DEGR C.   BAROMETRIC PR. =1003.2 MB    I
I              -WET =        DEGR C.   TRANSPARENCY   =       M     I
---------------------------------------------------------------------

                                 OBSERVED

 TIME   DEP    TEMP    SAL    SIG-T   OXY   PO4   NH3   NO2   NO3    NO   SIO3   PH   T ALK
 12.3     0   5.74B  30.488  24.06   7.74  2.11  00.3  0.29  14.6  822.4   32    .     .
 12.3    10   5.60A  30.612  24.18   7.88  2.20  00.2  0.32  15.5  843.0   33    .     .
 12.3    20   5.60B  30.721  24.26   7.79  2.15  00.6  0.31  14.2  823.3   30    .     .
 12.3    30   5.63A  30.862  24.37   8.30  2.38  00.7  0.37  15.6  881.4   33    .     .
 12.3    50   5.67A  31.187  24.62   7.44  2.41  00.4  0.36  16.2  810.0   33    .     .
 12.3    75   5.75A  31.400  24.78   7.37  2.30  00.5  0.38  15.5  797.5   31    .     .
 12.3   100   5.79A  31.456  24.82   7.32  2.45  00.5  0.38  16.5  802.0   32    .     .
 12.3   150   5.94B  31.520  24.86   7.51  2.51  00.5  0.36  17.0  823.5   33    .     .
 12.3   175T  5.93B  31.525  24.86   7.24  2.54  00.6  0.34  16.9  798.5   33    .     .

                                 STANDARD

        DEP    TEMP    SAL    SIG-T   OXY     SP VOL   DEL D
          0    5.74  30.488  24.06   7.74    386.13    .000
         10    5.60  30.612  24.18   7.88    375.35    .038
         20    5.60  30.721  24.26   7.79    367.21    .075
         30    5.63  30.862  24.37   8.30    356.98    .111
         50    5.67  31.187  24.62   7.44    333.12    .180
         75    5.75  31.400  24.78   7.37    318.19    .262
        100    5.79  31.456  24.82   7.32    314.62    .341
        150    5.94  31.520  24.86   7.51    311.94    .497
```

```
AC   CRUISE 240 CONSECUTIVE STATION NO.    1,   YAK007      9/ 4/77
---------------------------------                                 6.3 HOURS GMT

  LATITUDE = 59  39.5N   LONGITUDE = 139  46.0W   SONIC DEPTH =  172 M

  1-DIGIT WEATHER CODE IS (X1) AND INDICATES PARTLY CLOUDY
  CLOUD TYPE --- ( ) ---NOT RECORDED         ,
  CLOUD AMOUNT --- ( ) ---NOT RECORDED,
  VISIBILITY --- ( ) ---NOT RECORDED
-------------------------------------------------------------------------
I            DIRECTION         SPEED                                    I
I WIND           -       DEGR     KNOTS                                 I
-------------------------------------------------------------------------
I            DIRECTION        HEIGHT      PERIOD                        I
I SEA         0 -    0 DEGR      M.          SECS                       I
I SWELL          -     DEGR      M.          SECS                       I
-------------------------------------------------------------------------
I TEMPERATURES -DRY =    5.0 DEGR C.   BAROMETRIC PR. =1005.2 MB    I
I              -WET =        DEGR C.   TRANSPARENCY   =          M    I
-------------------------------------------------------------------------

                                  OBSERVED

 TIME     DEP      TEMP     SAL     SIG-T     OXY    PO4     NH3    NO2    NO3     NO    SIO3    PH   T ALK
  6.3       0     6.00B   30.199   23.81     7.76   2.02   00.5   0.29   15.6   833.2    35     .      .
  6.3      10     5.96A   30.272   23.87     7.74   2.24   00.5   0.30   16.6   840.4    35     .      .
  6.3      20     5.69A   30.418   24.17     7.70   2.28   00.9   0.36   17.4   844.1    34     .      .
  6.3      30     5.75A   31.051   24.51     7.52   2.25   00.5   0.33   17.1   825.3    33     .      .
  6.3      50     5.75B   31.281   24.69     7.43   2.41   00.7   0.36   17.6   821.8    34     .      .
  6.3      75     5.74A   31.389   24.77     7.32   2.43   00.6   0.37   17.7   812.8    33     .      .
  6.3     100     5.80A   31.452   24.82     7.38   2.51   00.9   0.38   18.3   823.6    34     .      .
  6.3     150     5.88A   31.555   24.89      .     2.31   00.8   0.37   17.7            32     .      .
  6.3     167T    5.89A   31.546   24.88     7.26   2.44   00.7   0.35   17.7   807.5    32     .      .

                                  STANDARD

          DEP      TEMP     SAL     SIG-T     OXY        SP VOL     DEL D
            0     6.00    30.199   23.81     7.76       410.67      .000
           10     5.96    30.272   23.87     7.74       404.79      .041
           20     5.69    30.618   24.17     7.70       375.91      .080
           30     5.75    31.051   24.51     7.52       344.09      .116
           50     5.75    31.281   24.69     7.43       326.95      .183
           75     5.74    31.389   24.78     7.32       318.90      .264
          100     5.80    31.452   24.82     7.38       315.03      .343
          150     5.88    31.555   24.89     7.33       308.63      .499
```

```
AC   CRUISE 24[illegible] CONSECUTIVE STATION NO.   5,   YAK009    10/ 4/77
--------------------------                                   4.8 HOURS GMT

  LATITUDE = 59  40.0N   LONGITUDE = 139  59.5W   SONIC DEPTH =  159 M

  1-DIGIT WEATHER CODE IS (X6) AND INDICATES RAIN
  CLOUD TYPE --- ( ) ---NOT RECORDED        ,
  CLOUD AMOUNT --- ( ) ---NOT RECORDED.
  VISIBILITY --- ( ) ---NOT RECORDED
-------------------------------------------------------------------
I           DIRECTION          SPEED                              I
I WIND      165 - 174 DEGR     10 KNOTS                           I
-------------------------------------------------------------------
I           DIRECTION         HEIGHT       PERIOD                 I
I SEA       165 - 174 DEGR    0.5 M.          SECS                I
I SWELL           -   DEGR        M.          SECS                I
-------------------------------------------------------------------
I TEMPERATURES -DRY =     5.0 DEGR C.   BAROMETRIC PR. = 994.9 MB  I
I              -WET =         DEGR C.   TRANSPARENCY   =       M   I
-------------------------------------------------------------------

                                    OBSERVED

 TIME    DEP     TEMP     SAL     SIG-T     OXY   PO4    NH3   NO2   NO3    NO    SIO3   PH    T ALK
  4.8      0    5.62A   30.584   24.15     7.69  2.18   00.8  0.37  14.7  818.9   31    .       .
  4.8     10    5.65A   30.600   24.16     7.68  2.28   00.8  0.35  15.5  825.2   32    .       .
  4.8     20    5.72A   30.685   24.22     7.65  2.31   00.6  0.38  15.5  822.5   32    .       .
  4.8     30    5.82A   31.090   24.53     7.51  2.39   00.7  0.38  16.3  817.2   32    .       .
  4.8     50    5.87A   31.309   24.70     7.49  2.36   00.4  0.39  16.4  916.3   32    .       .
  4.8     75    5.87A   31.498   24.85     7.39  2.30   00.3  0.41  16.5  807.4   32    .       .
  4.8    100    5.93B   31.598   24.92     7.35  2.42   00.2  0.45  16.5  804.7   32    .       .
  4.8    150T   6.07B   31.685   24.97     7.15  2.29   00.4  0.33  15.4  777.0   29    .       .
                                    STANDARD

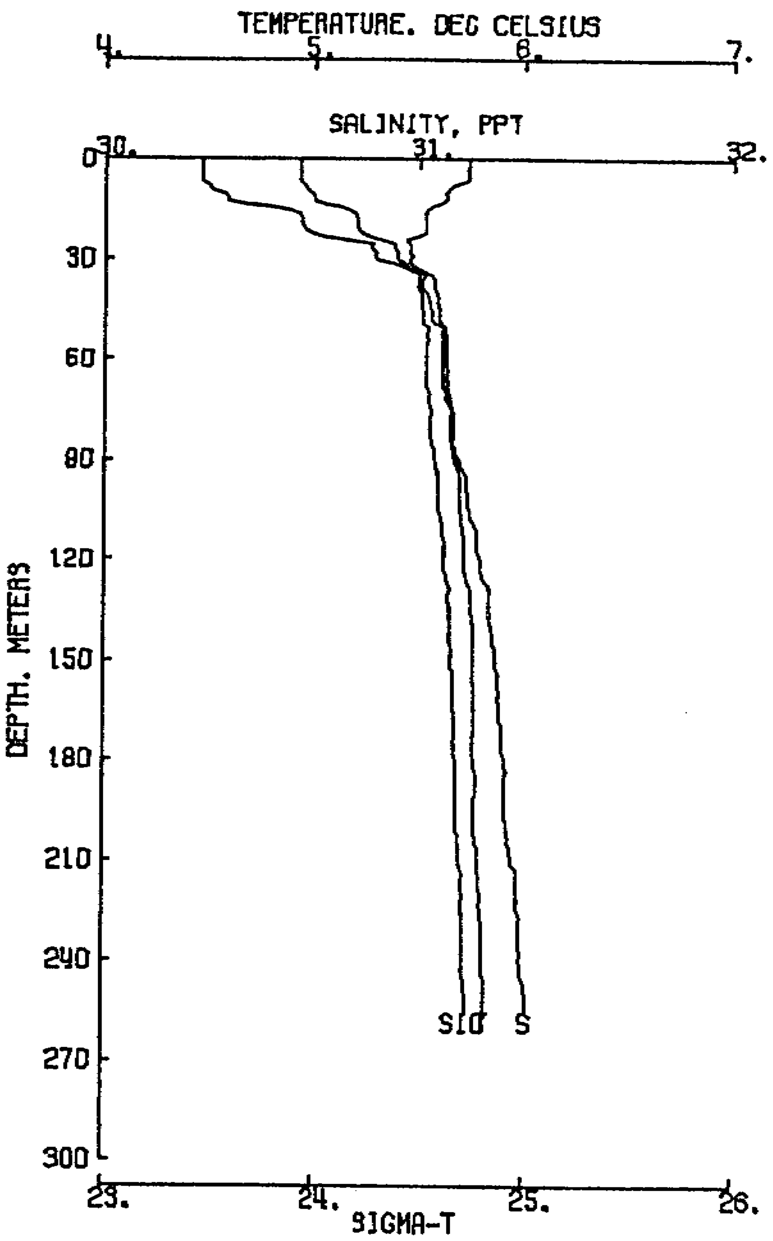
         DEP     TEMP     SAL     SIG-T     OXY       SP VOL     DEL D
           0     5.62   30.584   24.15     7.69      377.63      .000
          10     5.65   30.600   24.16     7.68      376.79      .038
          20     5.72   30.685   24.22     7.65      371.20      .075
          30     5.82   31.090   24.53     7.51      341.93      .111
          50     5.87   31.309   24.70     7.49      326.18      .178
          75     5.87   31.498   24.85     7.38      312.18      .257
         100     5.93   31.598   24.92     7.35      305.56      .335
         150     6.07   31.685   24.97     7.15      301.10      .486
```

```
AC   CRUISE 240 CONSECUTIVE STATION NO.   2.   YAK003      9/ 4/77
--------------------------                                9.7 HOURS GMT

  LATITUDE = 59  52.5N   LONGITUDE = 139  40.0W   SONIC DEPTH =  260 M

  1-DIGIT WEATHER CODE IS (X1) AND INDICATES PARTLY CLOUDY
  CLOUD TYPE --- ( ) ---NOT RECORDED          .
  CLOUD AMOUNT --- ( ) ---NOT RECORDED.
  VISIBILITY --- ( ) ---NOT RECORDED
-----------------------------------------------------------------------
I           DIRECTION           SPEED                                 I
I WIND       15 -  24 DEGR        KNOTS                               I
-----------------------------------------------------------------------
I           DIRECTION          HEIGHT     PERIOD                      I
I SEA         0 -    0 DEGR       M.          SECS                    I
I SWELL         -      DEGR       M.          SECS                    I
-----------------------------------------------------------------------
I TEMPERATURES -DRY =    5.0 DEGR C.   BAROMETRIC PR. =1005.0 MB    I
I              -WET =        DEGR C.   TRANSPARENCY   =        M    I
-----------------------------------------------------------------------


      DEPTH      TEMPERATURE    SALINITY       SIGMA-T       DELTA-D
      METERS        DEG C         PPT                         DYN M
        0.          5.73        30.312         23.93         0.
        1.0         5.73        30.312         23.93         0.004
        5.0         5.73        30.315         23.93         0.020
       10.0         5.62        30.383         23.99         0.040
       15.0         5.54        30.590         24.17         0.059
       20.0         5.53        30.631         24.20         0.078
       25.0         5.45        30.852         24.38         0.096
       30.0         5.45        30.868         24.40         0.114
       35.0         5.56        31.017         24.50         0.132
       40.0         5.58        31.026         24.51         0.149
       45.0         5.60        31.039         24.52         0.166
       50.0         5.61        31.079         24.55         0.183
       60.0         5.63        31.072         24.54         0.217
       70.0         5.64        31.092         24.55         0.252
       75.0         5.66        31.104         24.56         0.269
       80.0         5.66        31.100         24.56         0.286
       90.0         5.67        31.128         24.58         0.320
      100.0         5.69        31.154         24.60         0.353
      125.0         5.72        31.203         24.63         0.437
      150.0         5.76        31.246         24.66         0.520
      175.0         5.77        31.268         24.68         0.603
      200.0         5.77        31.281         24.69         0.685
      250.0         5.82        31.346         24.73         0.849
```



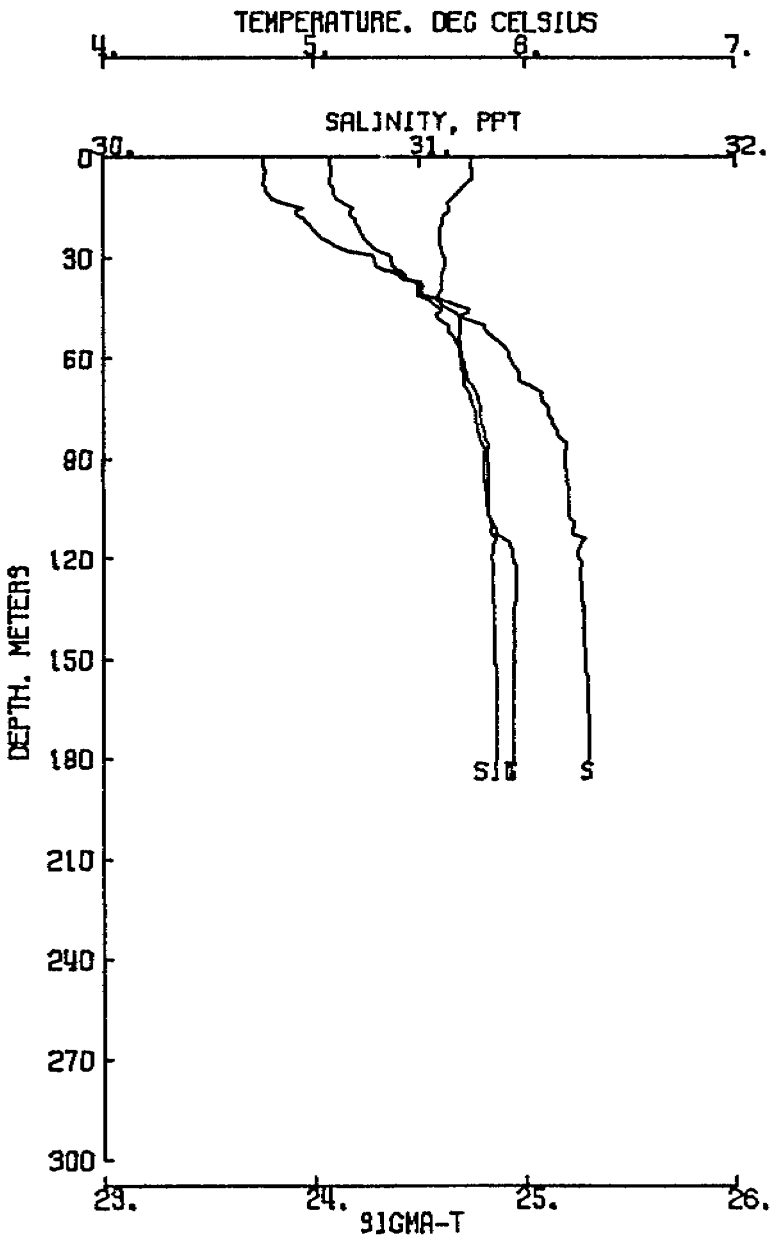
CRUISE 240 STATION 2

```
AC   CRUISE 240 CONSECUTIVE STATION NO.    3,   YAK005         9/ 4/77
--------------------------                                     12.3 HOURS GMT

  LATITUDE = 59  44.5N   LONGITUDE = 139  40.5W   SONIC DEPTH =  182 M


  1-DIGIT WEATHER CODE IS (X1) AND INDICATES PARTLY CLOUDY
  CLOUD TYPE --- ( ) ---NOT RECORDED        .
  CLOUD AMOUNT --- ( ) ---NOT RECORDED.
  VISIBILITY --- ( ) ---NOT RECORDED
----------------------------------------------------------------------
I              DIRECTION          SPEED                              I
I WIND      15 -  24 DEGR     5 KNOTS                                I
----------------------------------------------------------------------
I              DIRECTION        HEIGHT      PERIOD                   I
I SEA        0 -    0 DEGR        M.          SECS                   I
I SWELL         -     DEGR        M.          SECS                   I
----------------------------------------------------------------------
I TEMPERATURES -DRY =     5.0 DEGR C.   BAROMETRIC PR. =1003.2 MB   I
I              -WET =         DEGR C.   TRANSPARENCY   =        M   I
----------------------------------------------------------------------


          DEPTH       TEMPERATURE    SALINITY       SIGMA-T        DELTA-D
          METERS         DEG C          PPT                         DYN M
             0.          5.74         30.504         24.08         0.
             1.0         5.74         30.504         24.08         0.004
             5.0         5.75         30.513         24.08         0.019
            10.0         5.69         30.519         24.09         0.038
            15.0         5.64         30.630         24.19         0.058
            20.0         5.61         30.652         24.21         0.076
            25.0         5.60         30.720         24.26         0.095
            30.0         5.62         30.860         24.37         0.113
            35.0         5.61         30.936         24.43         0.131
            40.0         5.60         31.007         24.49         0.148
            45.0         5.64         31.159         24.61         0.165
            50.0         5.69         31.206         24.64         0.182
            60.0         5.69         31.292         24.70         0.215
            70.0         5.73         31.386         24.77         0.247
            75.0         5.76         31.413         24.79         0.263
            80.0         5.78         31.423         24.80         0.279
            90.0         5.81         31.463         24.83         0.311
           100.0         5.82         31.473         24.83         0.342
           125.0         5.96         31.511         24.85         0.421
           150.0         5.95         31.528         24.86         0.499
           175.0         5.94         31.537         24.87         0.577
```



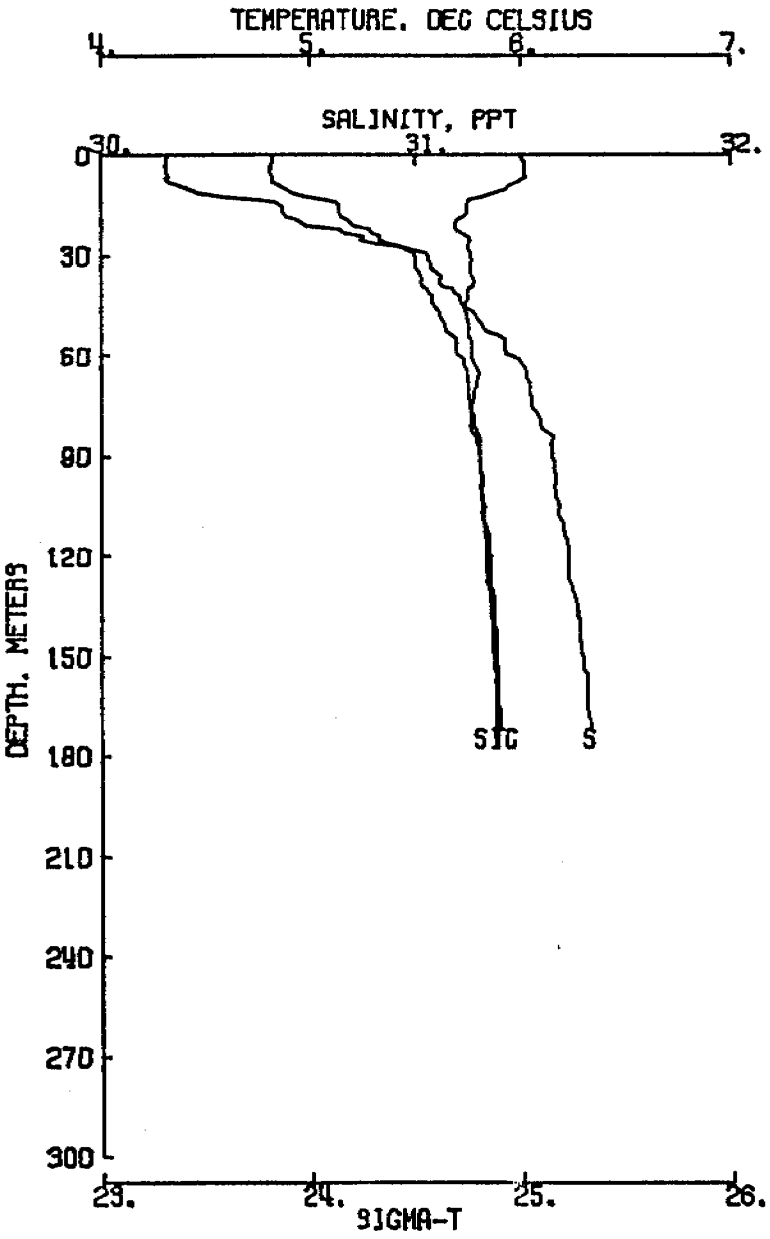
CRUISE 240 STATION 3

```
AC   CRUISE 240 CONSECUTIVE STATION NO.   1.   YAK007       9/ 4/77
---------------------------                                  6.3 HOURS GMT

  LATITUDE = 59  39.5N   LONGITUDE = 139  46.0W   SONIC DEPTH =  172 M


  1-DIGIT WEATHER CODE IS (X1) AND INDICATES PARTLY CLOUDY
  CLOUD TYPE --- ( ) ---NOT RECORDED          .
  CLOUD AMOUNT --- ( ) ---NOT RECORDED,
  VISIBILITY --- ( ) ---NOT RECORDED
---------------------------------------------------------------
I           DIRECTION         SPEED                           I
I WIND          -      DEGR      KNOTS                        I
---------------------------------------------------------------
I           DIRECTION        HEIGHT     PERIOD                I
I SEA         0 -    0 DEGR      M.         SECS              I
I SWELL         -      DEGR      M.         SECS              I
---------------------------------------------------------------
I TEMPERATURES -DRY =    5.0 DEGR C.   BAROMETRIC PR. =1005.2 MB  I
I              -WET =        DEGR C.   TRANSPARENCY   =       M   I
---------------------------------------------------------------


         DEPTH     TEMPERATURE   SALINITY      SIGMA-T      DELTA-D
         METERS      DEG C         PPT                       DYN M
           0.         6.00       30.210        23.82        0.
           1.0        6.00       30.210        23.82        0.004
           5.0        6.02       30.210        23.81        0.021
          10.0        5.92       30.287        23.89        0.041
          15.0        5.74       30.577        24.13        0.061
          20.0        5.69       30.635        24.19        0.079
          25.0        5.76       30.826        24.33        0.098
          30.0        5.76       31.041        24.50        0.115
          35.0        5.76       31.064        24.52        0.133
          40.0        5.75       31.114        24.56        0.150
          45.0        5.74       31.153        24.59        0.167
          50.0        5.75       31.207        24.63        0.183
          60.0        5.76       31.307        24.71        0.216
          70.0        5.79       31.364        24.75        0.249
          75.0        5.77       31.372        24.76        0.265
          80.0        5.76       31.400        24.78        0.281
          90.0        5.80       31.436        24.81        0.312
         100.0        5.82       31.444        24.81        0.344
         125.0        5.85       31.487        24.84        0.423
         150.0        5.89       31.531        24.87        0.501
```



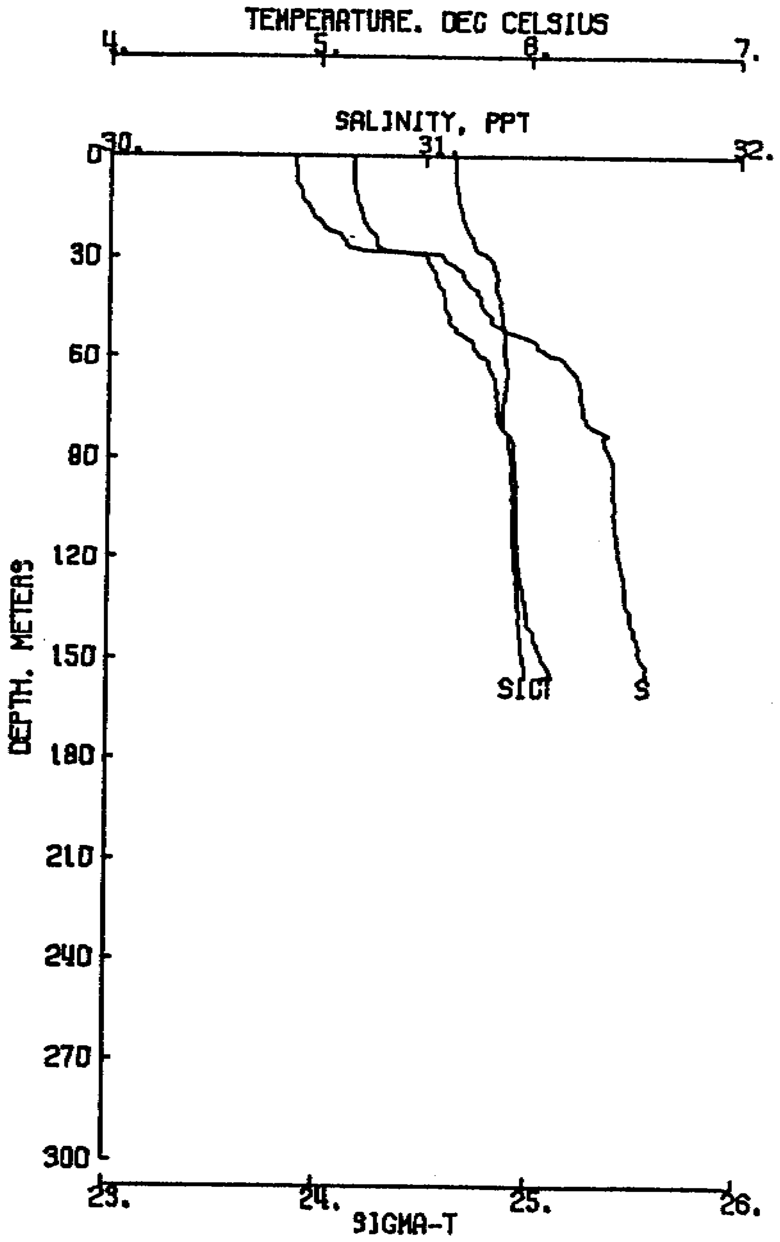
CRUISE 240 STATION 1

```
AC   CRUISE 240 CONSECUTIVE STATION NO.    5.   YAK009     10/ 4/77
---------------------------                                  4.8 HOURS GMT

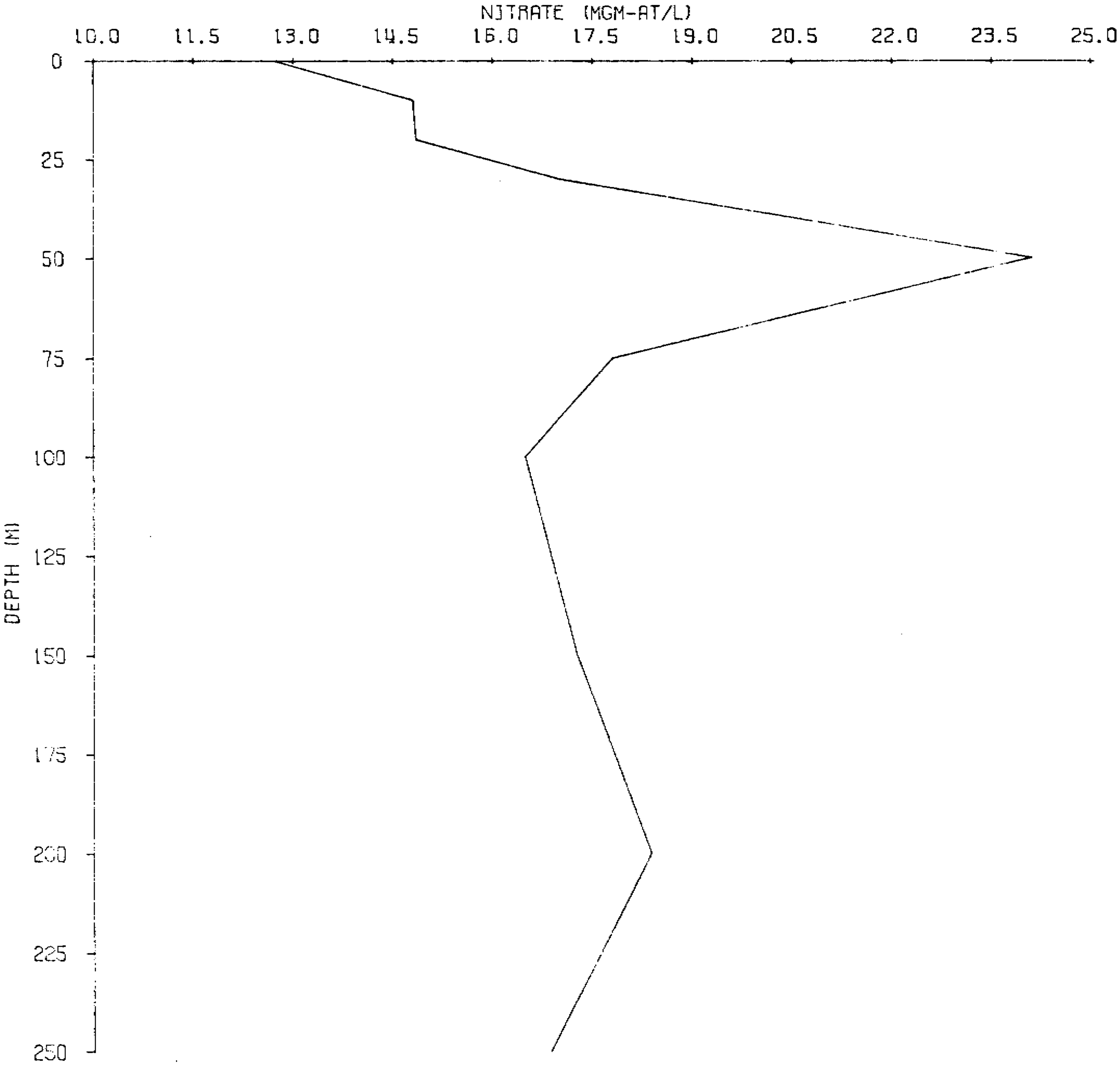
  LATITUDE = 59  40.0N   LONGITUDE = 139  59.5W   SONIC DEPTH =  159 M

  1-DIGIT WEATHER CODE IS (X6) AND INDICATES RAIN
  CLOUD TYPE --- ( ) ---NOT RECORDED        .
  CLOUD AMOUNT --- ( ) ---NOT RECORDED,
  VISIBILITY --- ( ) ---NOT RECORDED
----------------------------------------------------------------------
I             DIRECTION         SPEED
I WIND      165 - 174 DEGR    10 KNOTS                                I
                                                                      I
----------------------------------------------------------------------
I             DIRECTION        HEIGHT      PERIOD                     I
I SEA       165 - 174 DEGR   0.5 M.          SECS                     I
I SWELL          -      DEGR       M.        SECS                     I
----------------------------------------------------------------------
I TEMPERATURES -DRY =     5.0 DEGR C.   BAROMETRIC PR. = 994.9 MB   I
I              -WET =         DEGR C.   TRANSPARENCY    =        M   I
----------------------------------------------------------------------

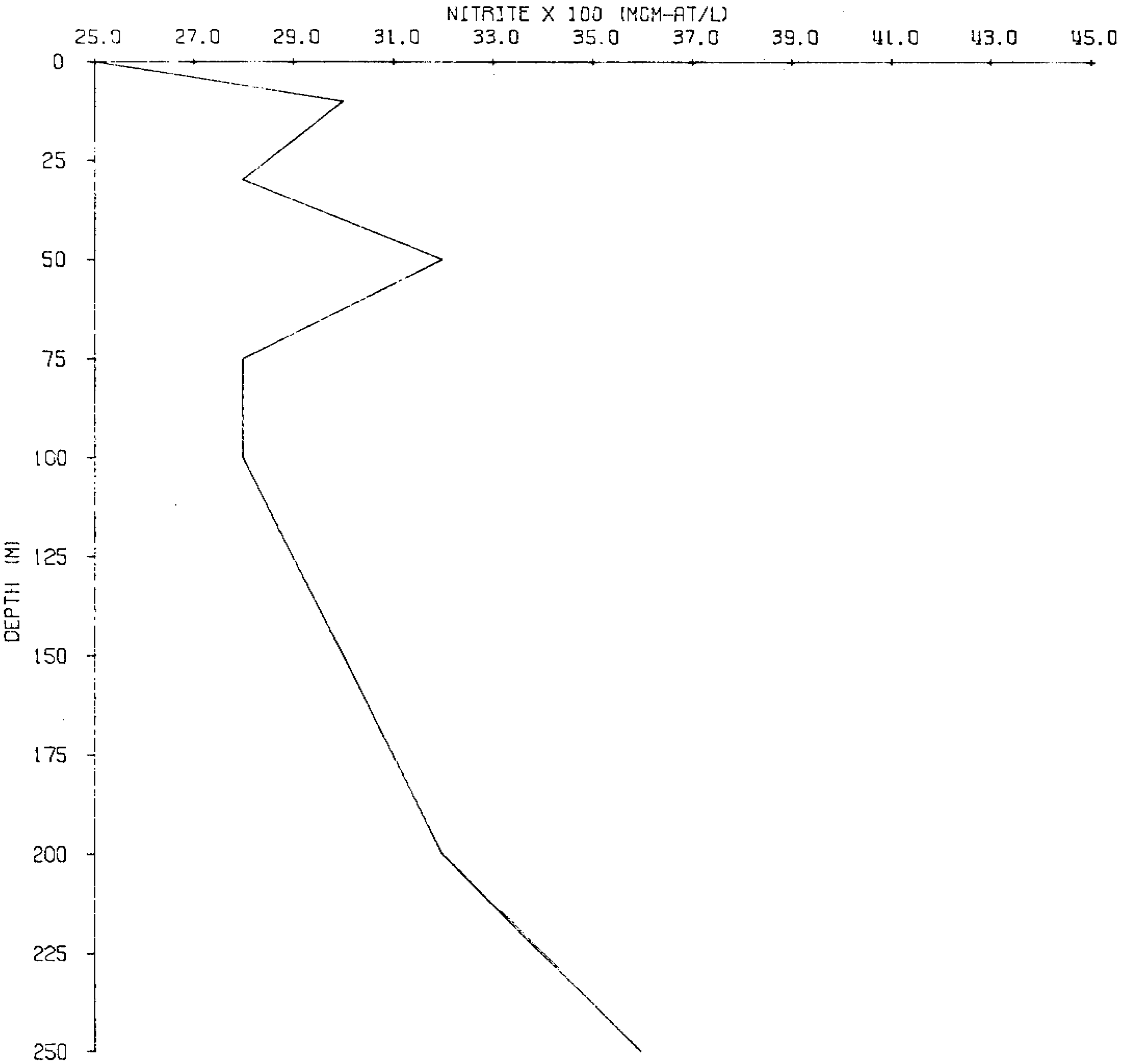

          DEPTH      TEMPERATURE     SALINITY      SIGMA-T      DELTA-D
          METERS        DEG C          PPT                       DYN M
           0.           5.64         30.588        24.16         0.
           1.0          5.64         30.588        24.16         0.004
           5.0          5.64         30.591        24.16         0.019
          10.0          5.65         30.606        24.17         0.038
          15.0          5.67         30.631        24.19         0.057
          20.0          5.69         30.665        24.21         0.075
          25.0          5.73         30.749        24.27         0.094
          30.0          5.81         31.060        24.51         0.112
          35.0          5.94         31.122        24.55         0.129
          40.0          5.84         31.167        24.59         0.146
          45.0          5.86         31.186        24.60         0.163
          50.0          5.88         31.219        24.63         0.179
          60.0          5.89         31.427        24.79         0.212
          70.0          5.89         31.497        24.84         0.243
          75.0          5.87         31.503        24.85         0.259
          80.0          5.87         31.522        24.86         0.275
          90.0          5.93         31.595        24.92         0.305
         100.0          5.94         31.602        24.92         0.336
         125.0          5.96         31.634        24.94         0.412
         150.0          6.07         31.692        24.98         0.488
```



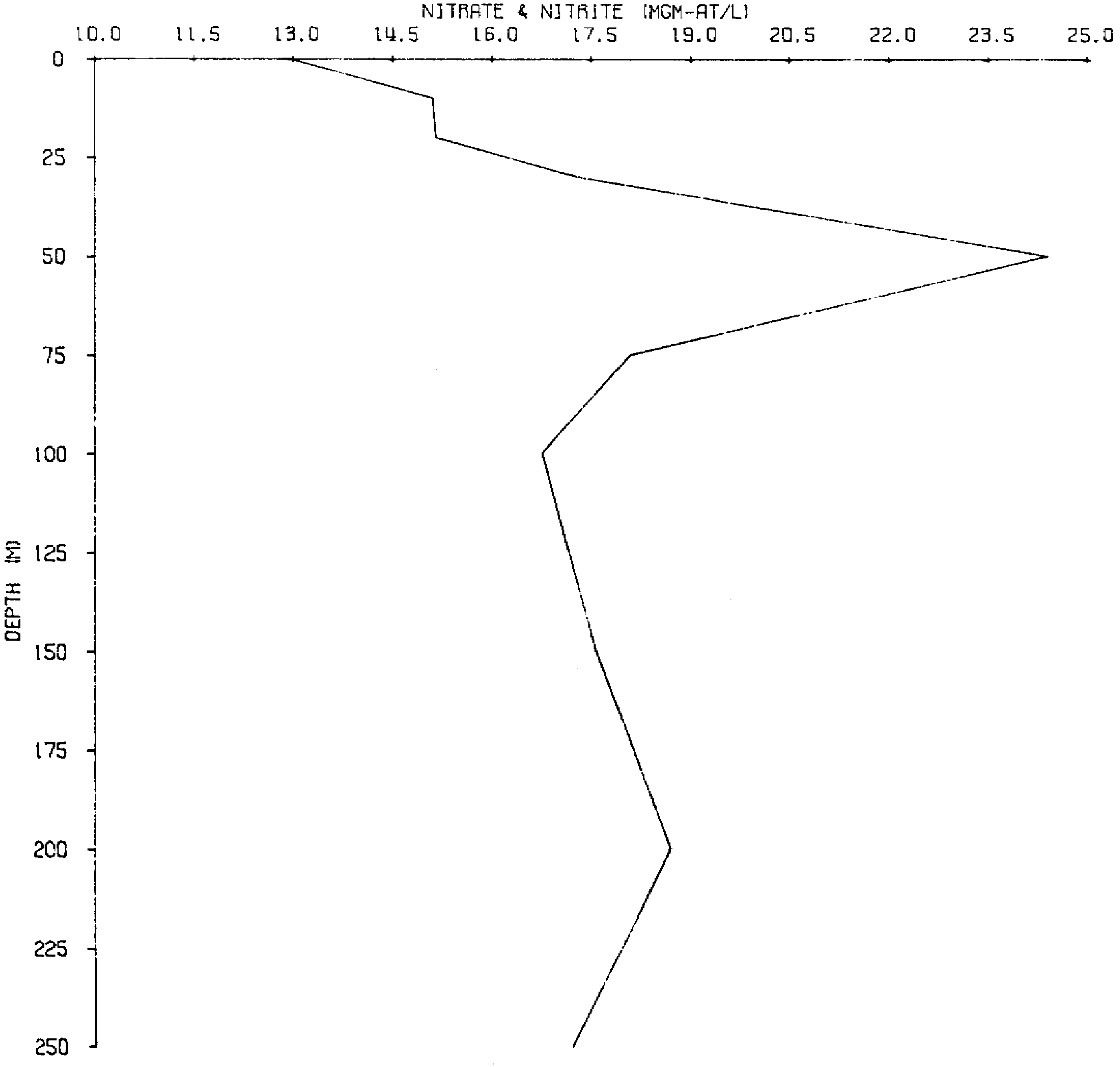
CRUISE 240 STATION 5



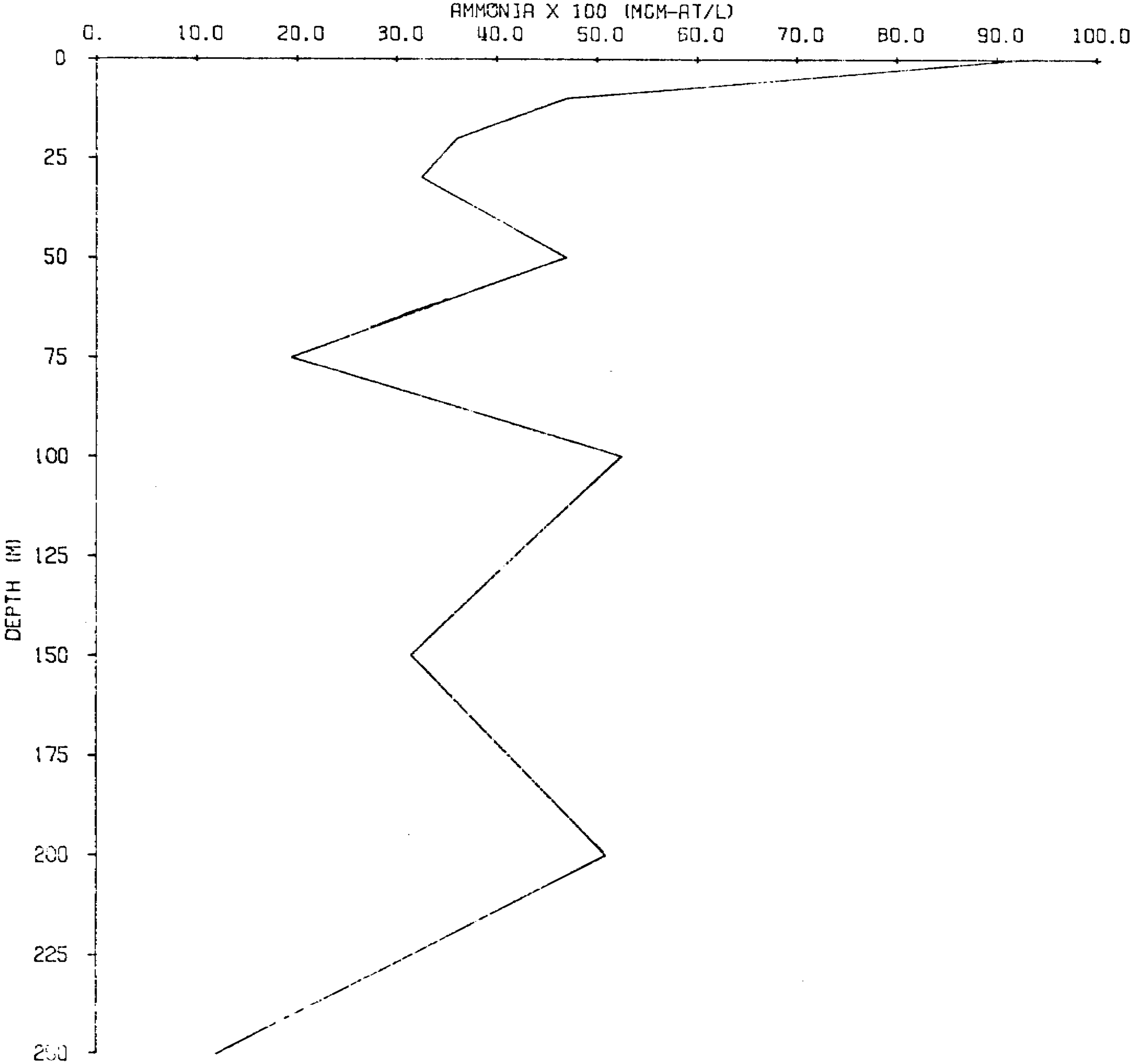
CRUISE 240, YAK 003.



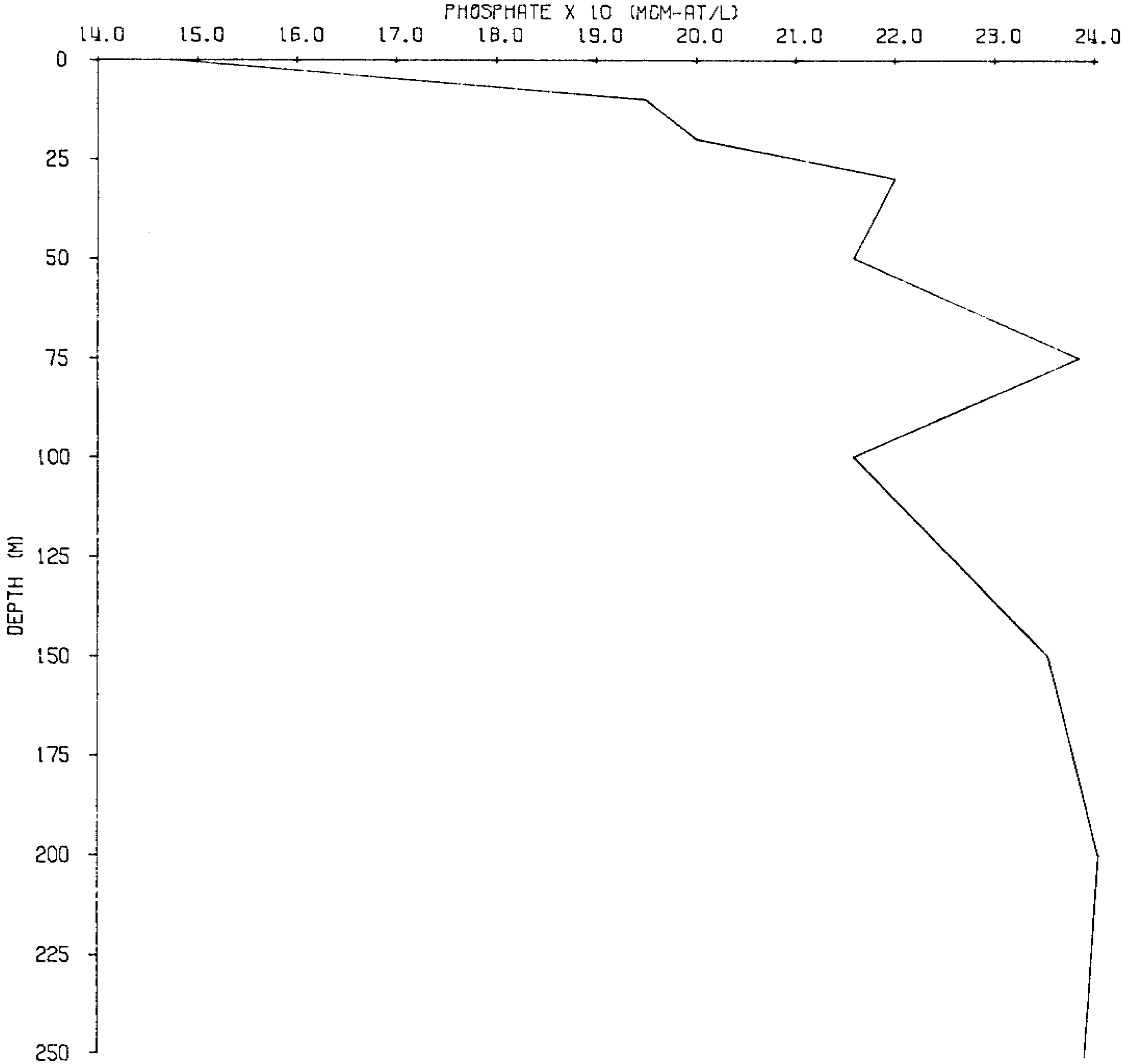
CRUISE 240. TAK 003.



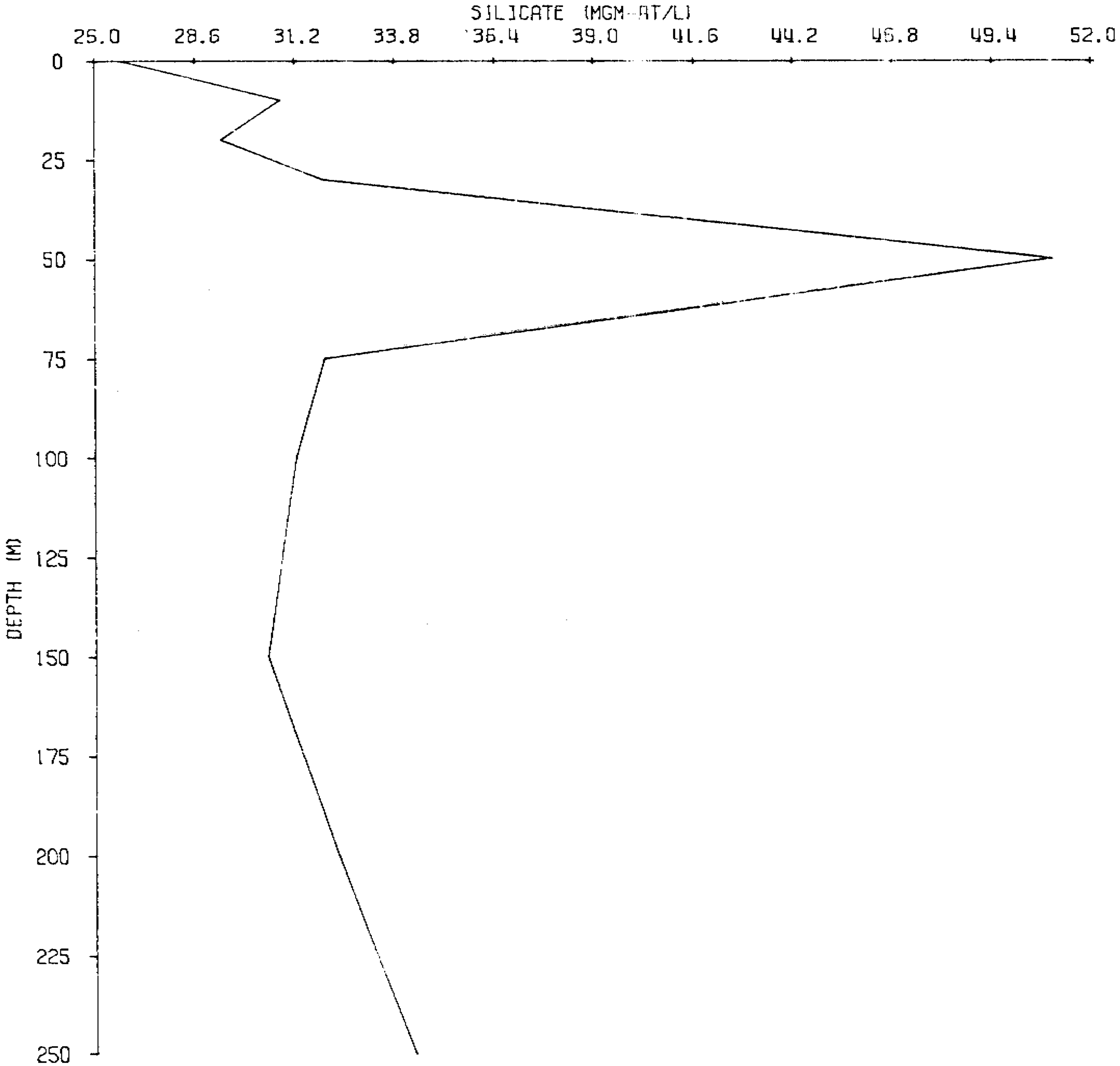
CRUISE 240. YAK 003



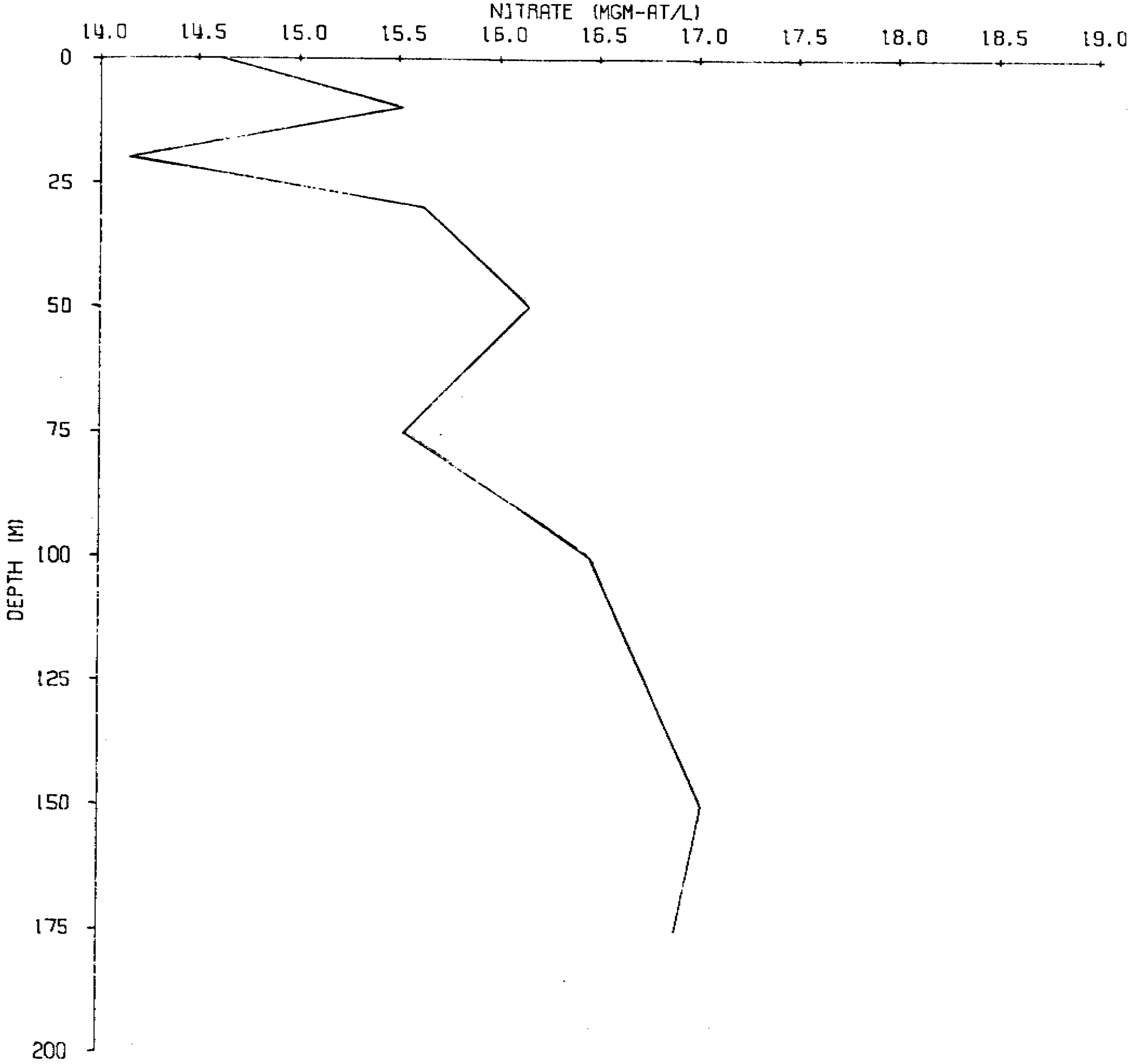
CRUISE 240. YAK 003



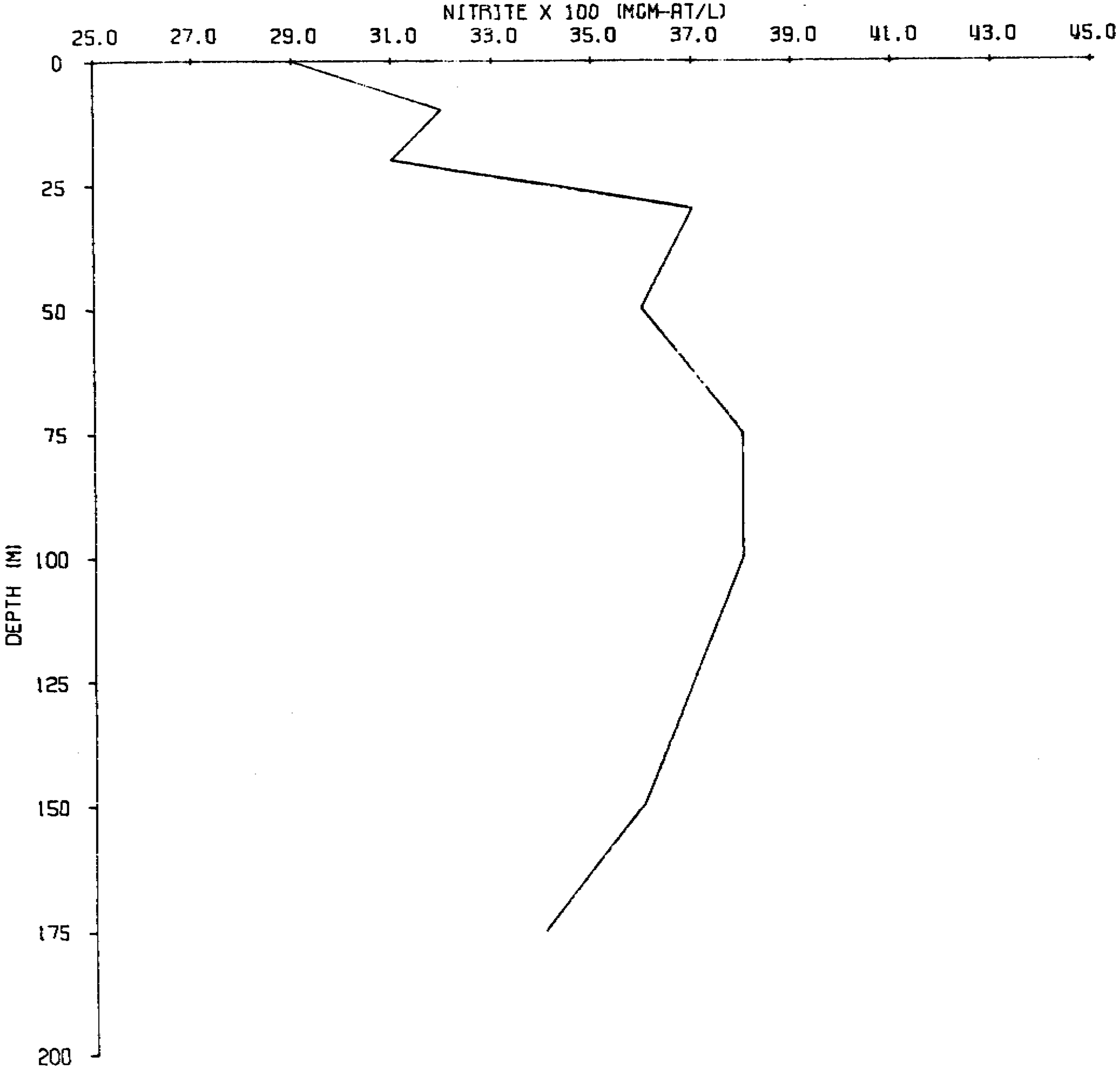
CRUI:E 240, YAK 003



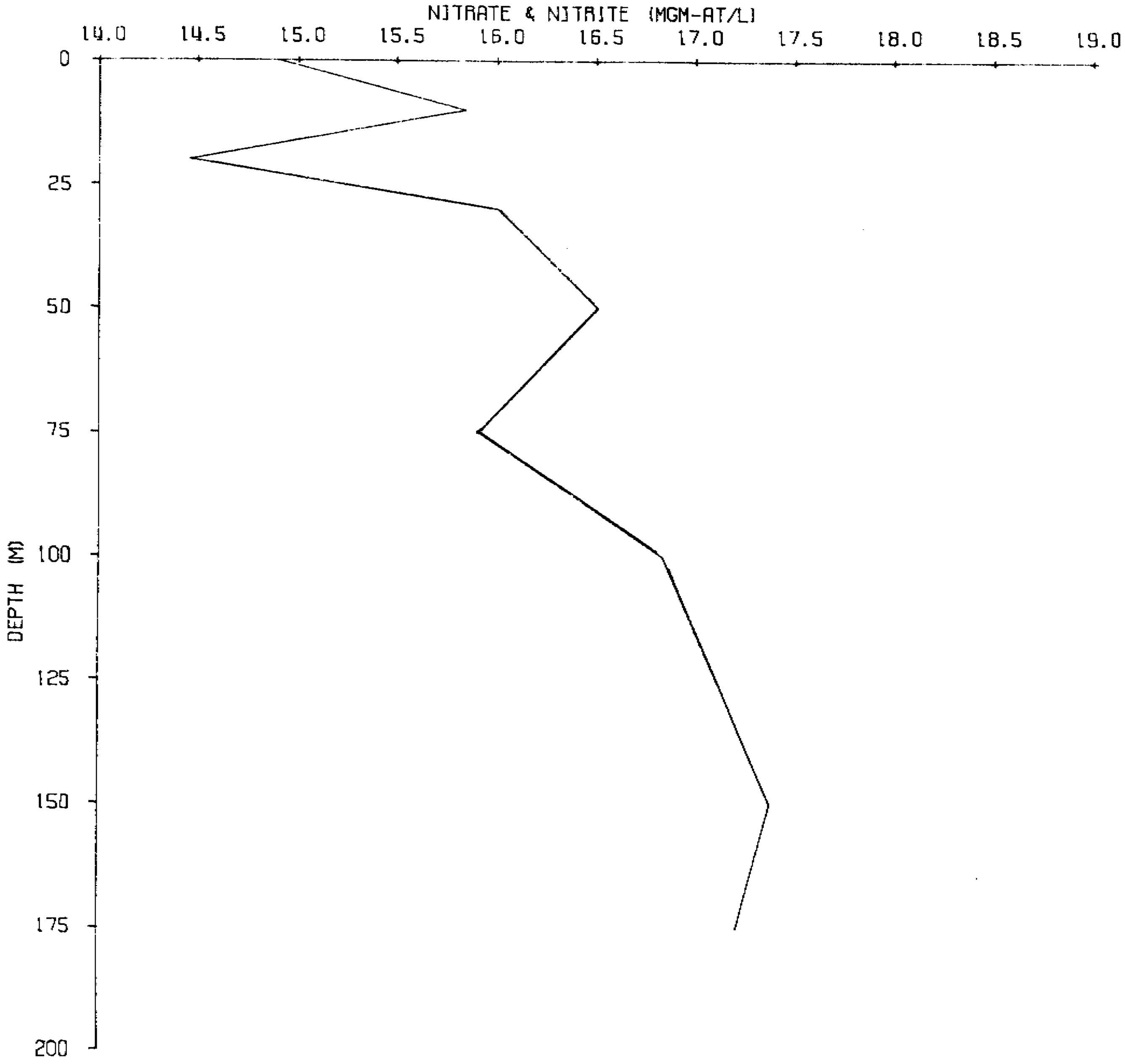
CRUISE 240. YAK 003



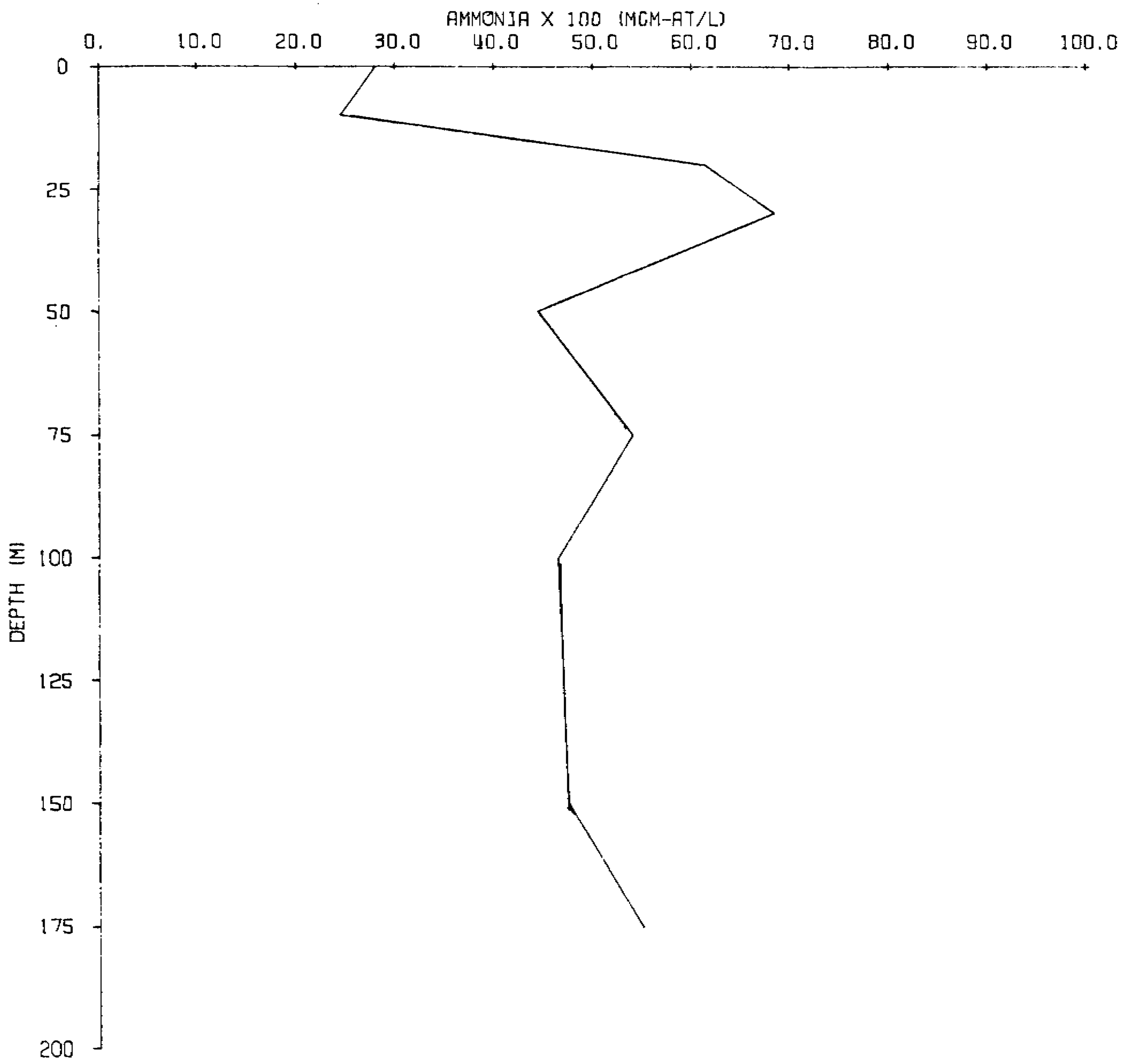
CRUISE 240, YAK 005.



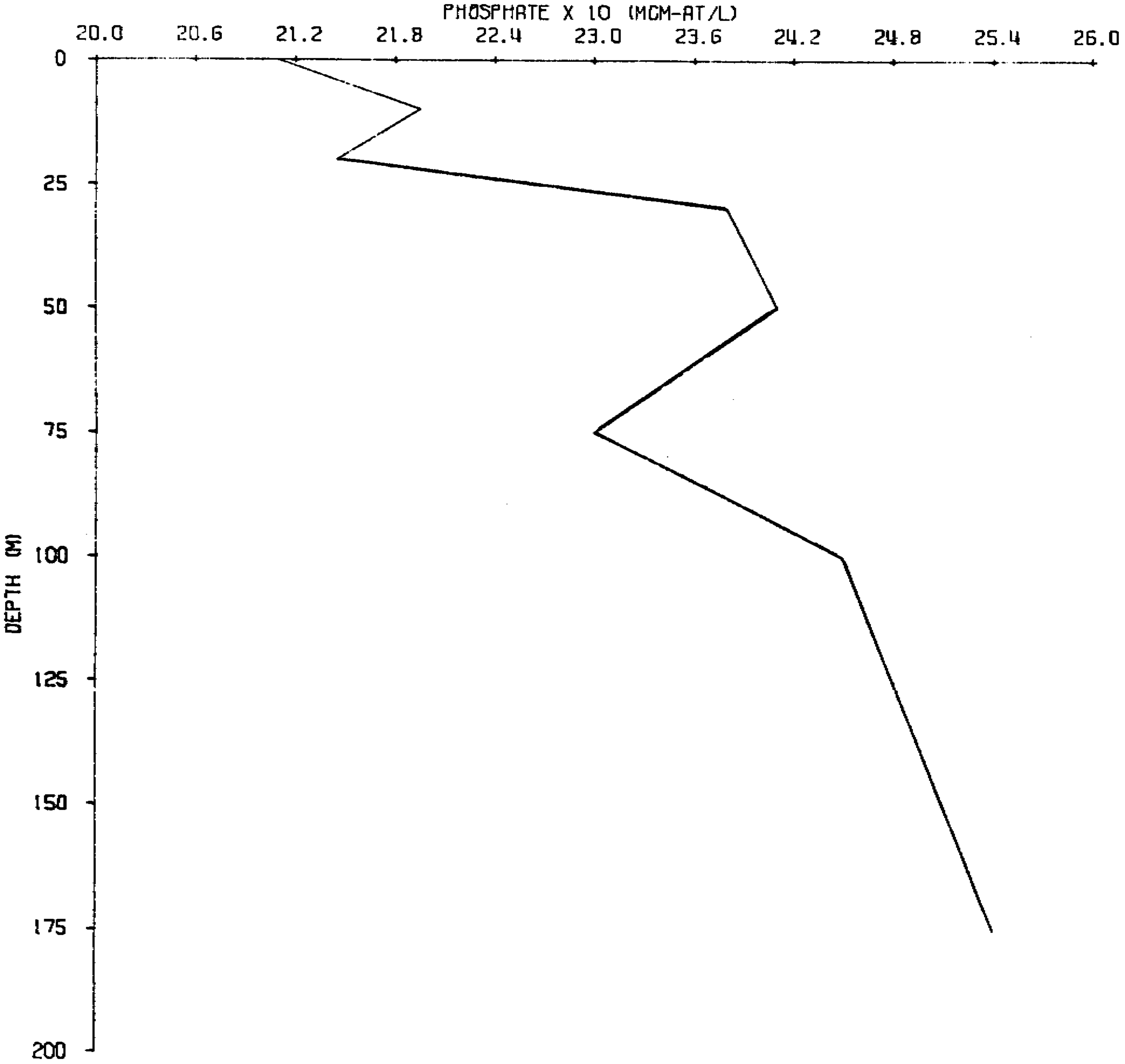
CRUISE 240. TAK 005.



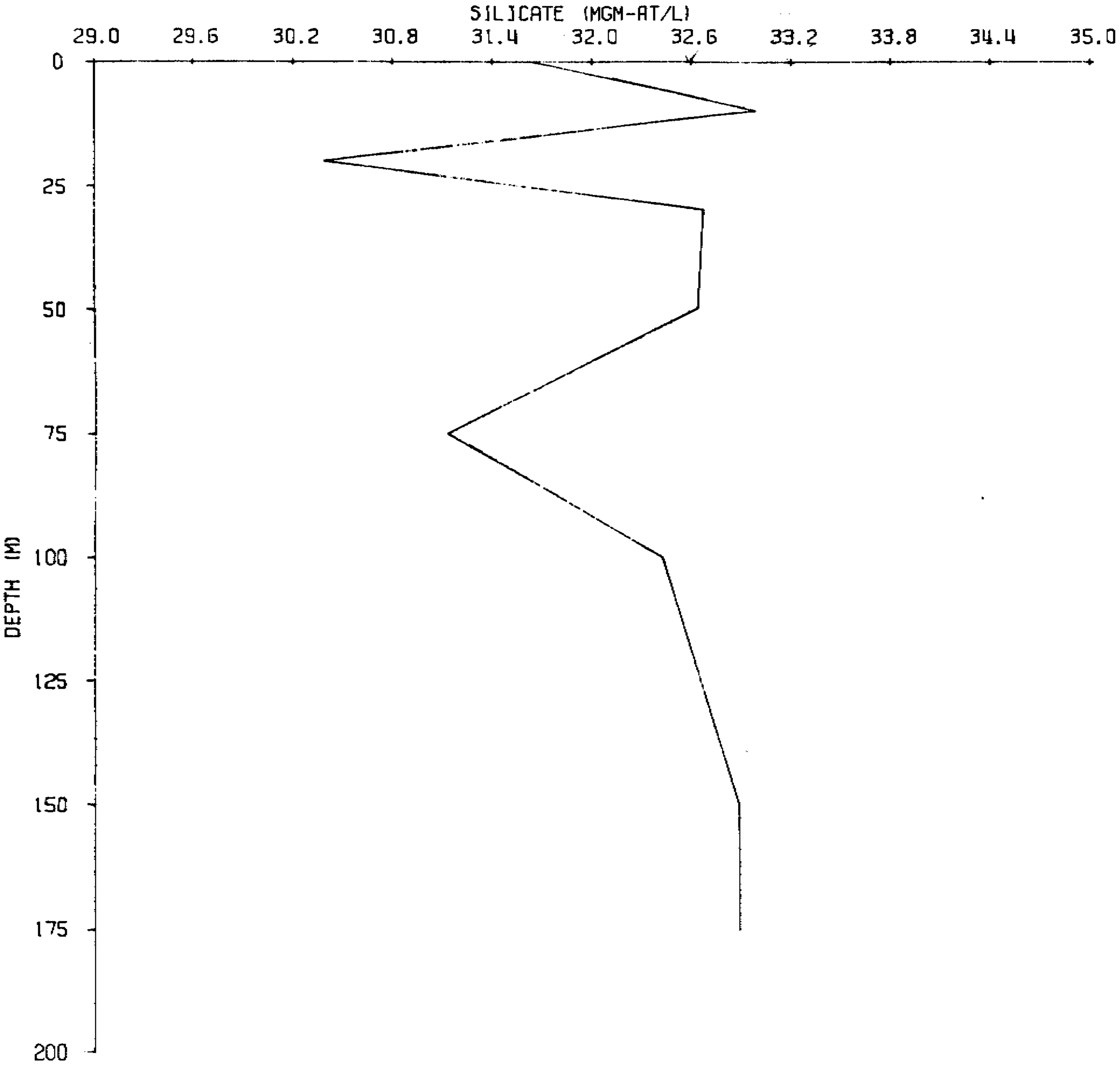
CRUISE 240, YAK 005



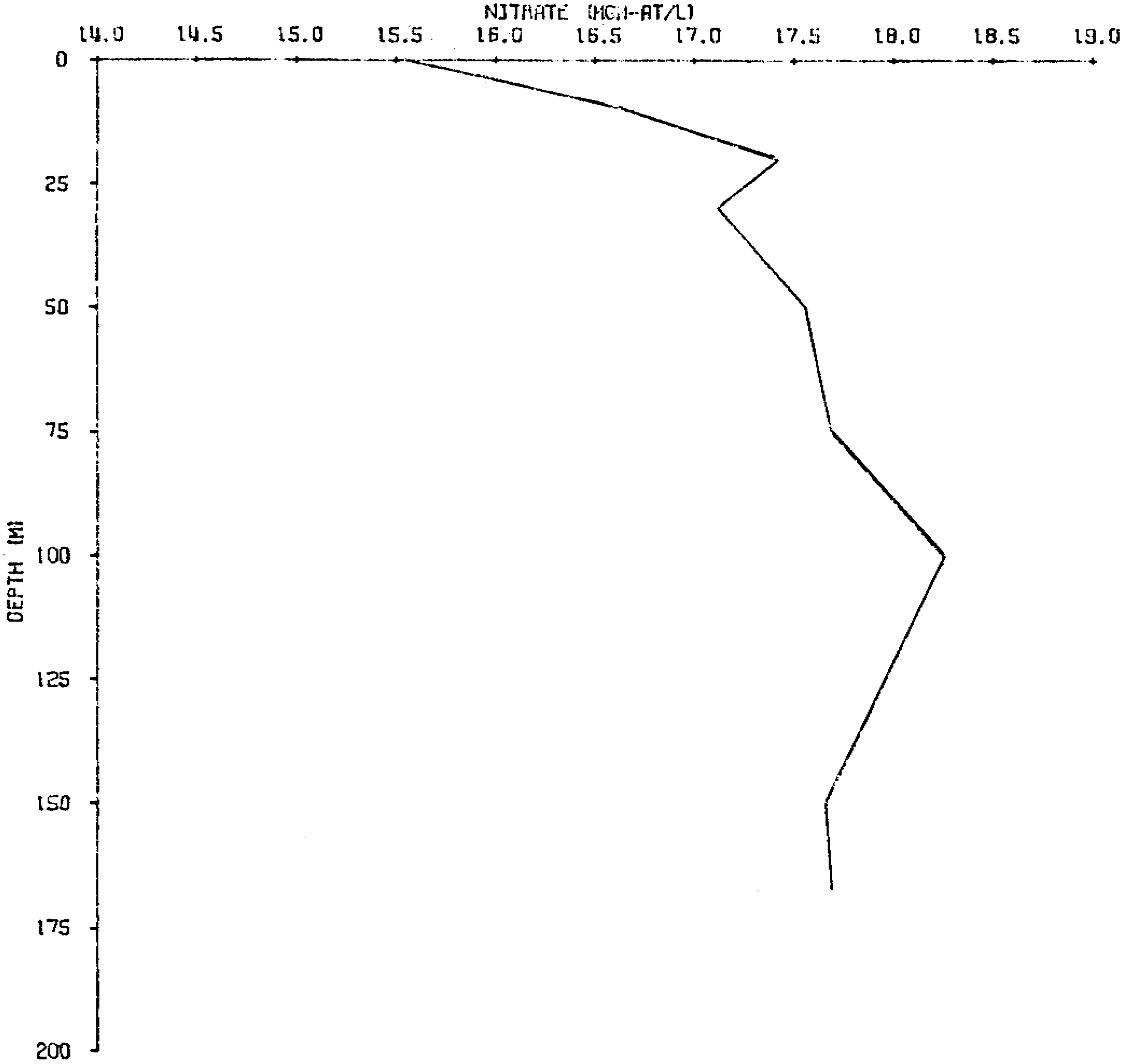
CRUISE 240, YAK 005



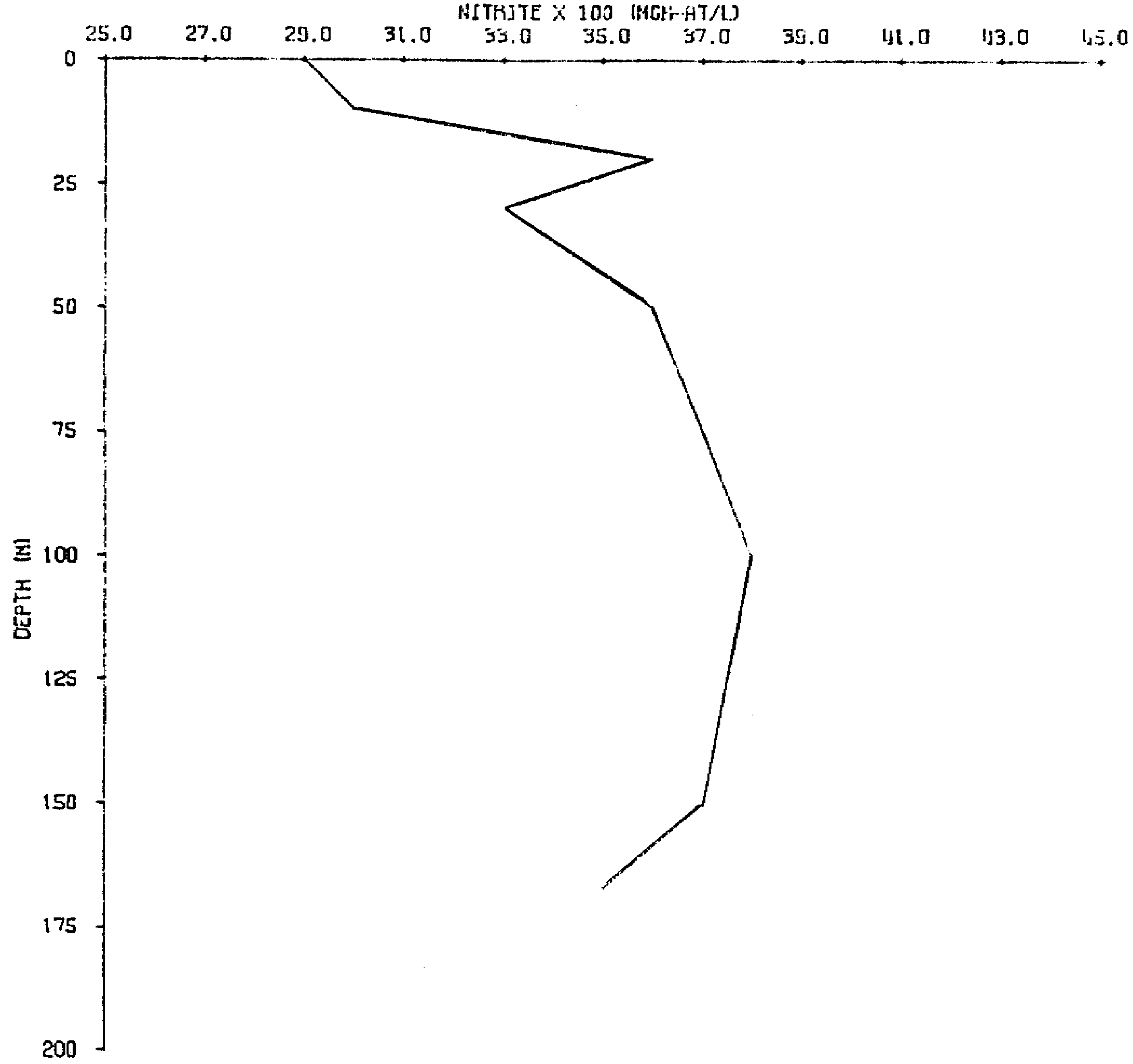
CRUISE 240, TAK 005



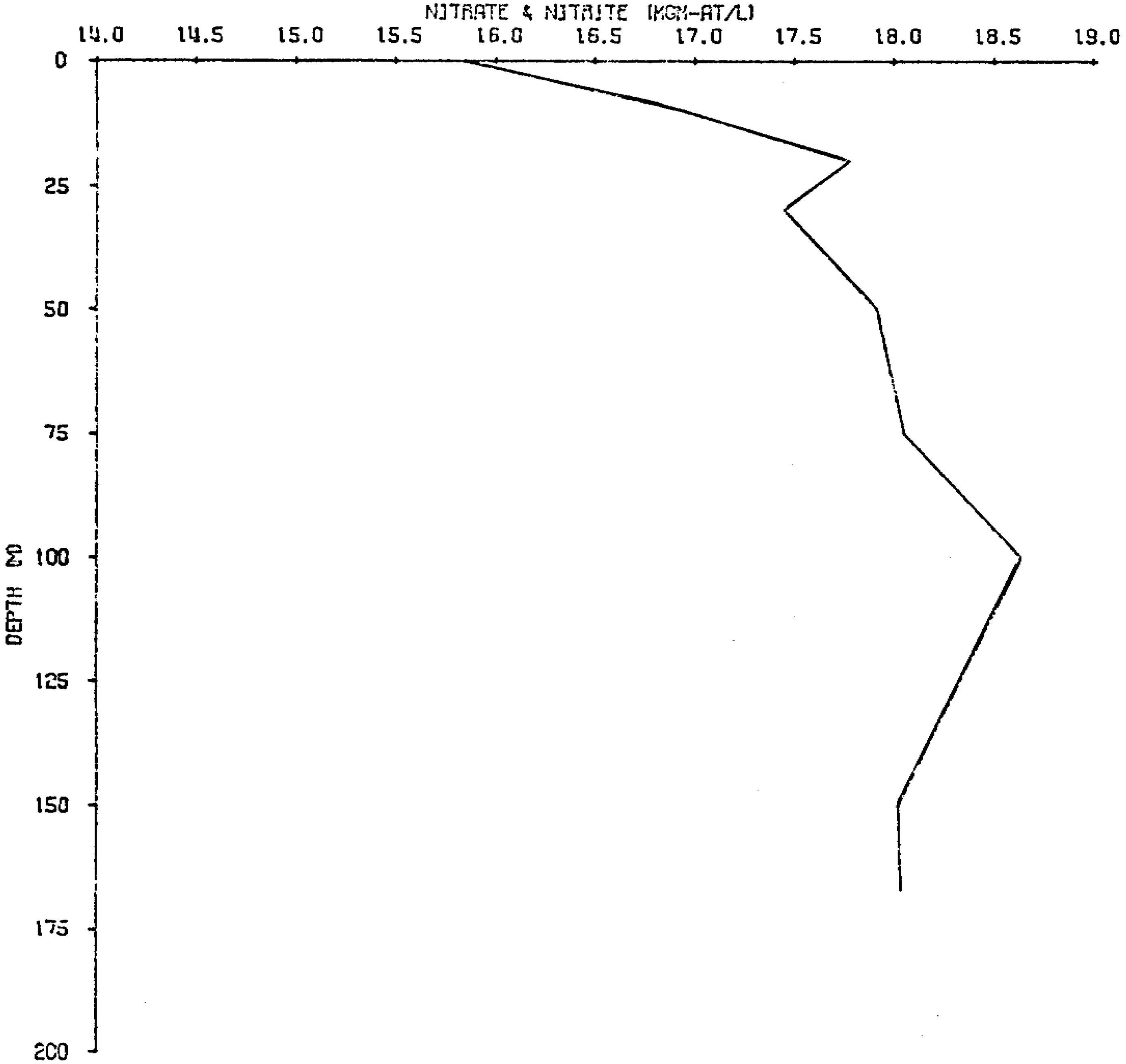
CRUISE 240, TAK 005



CRUISE 240, TAK 007.



CRUISE 240, TAK 007.



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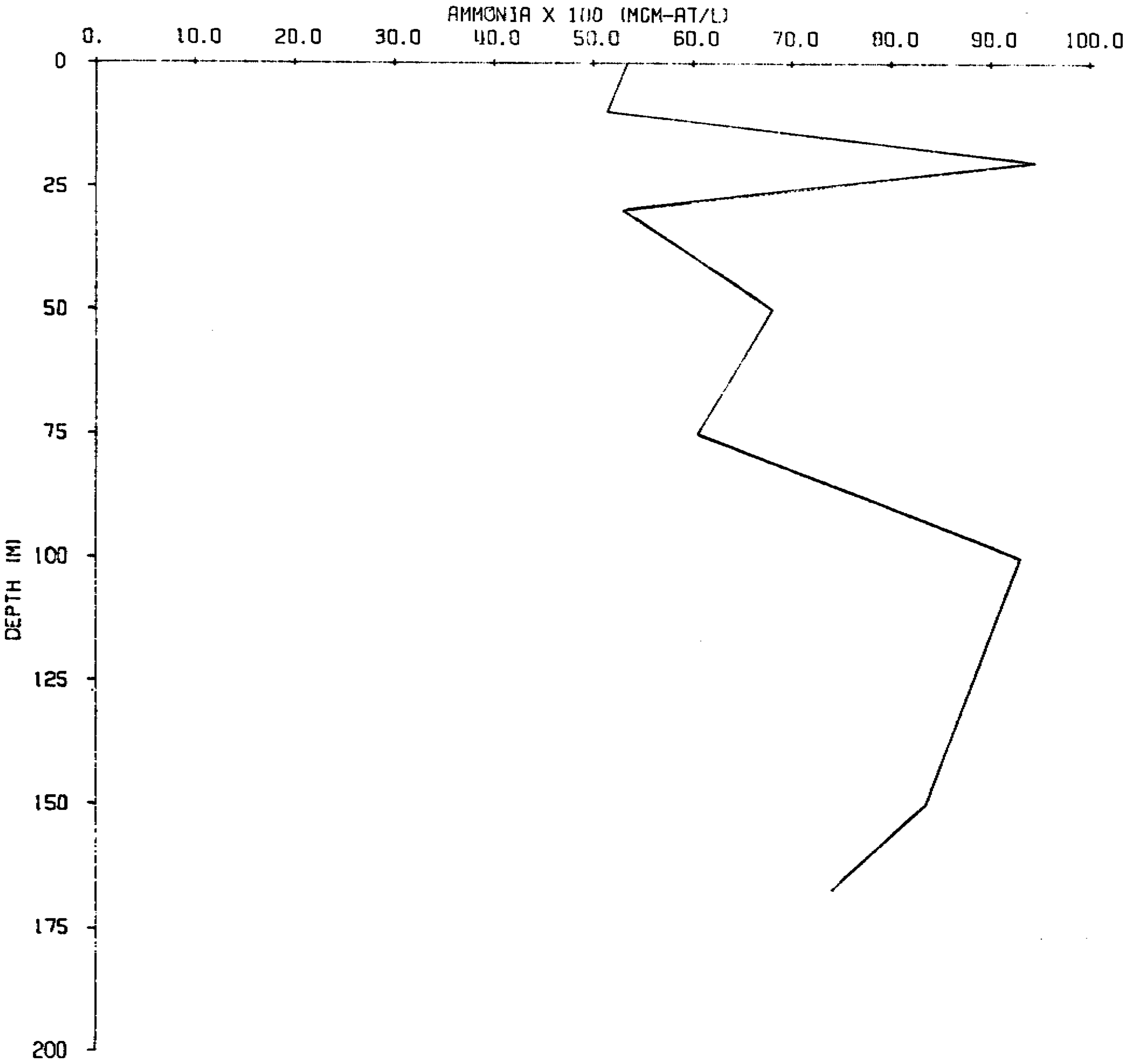

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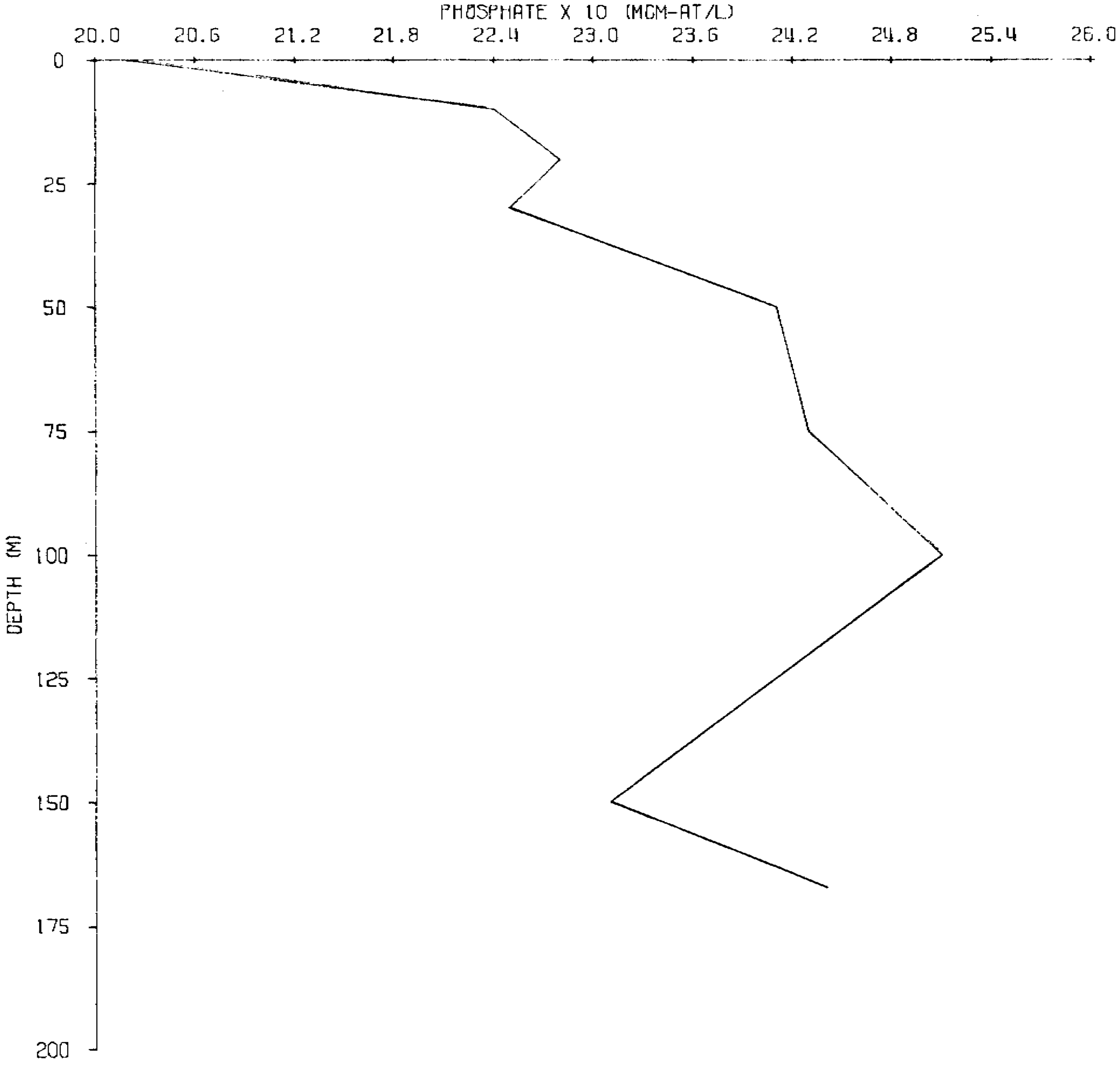

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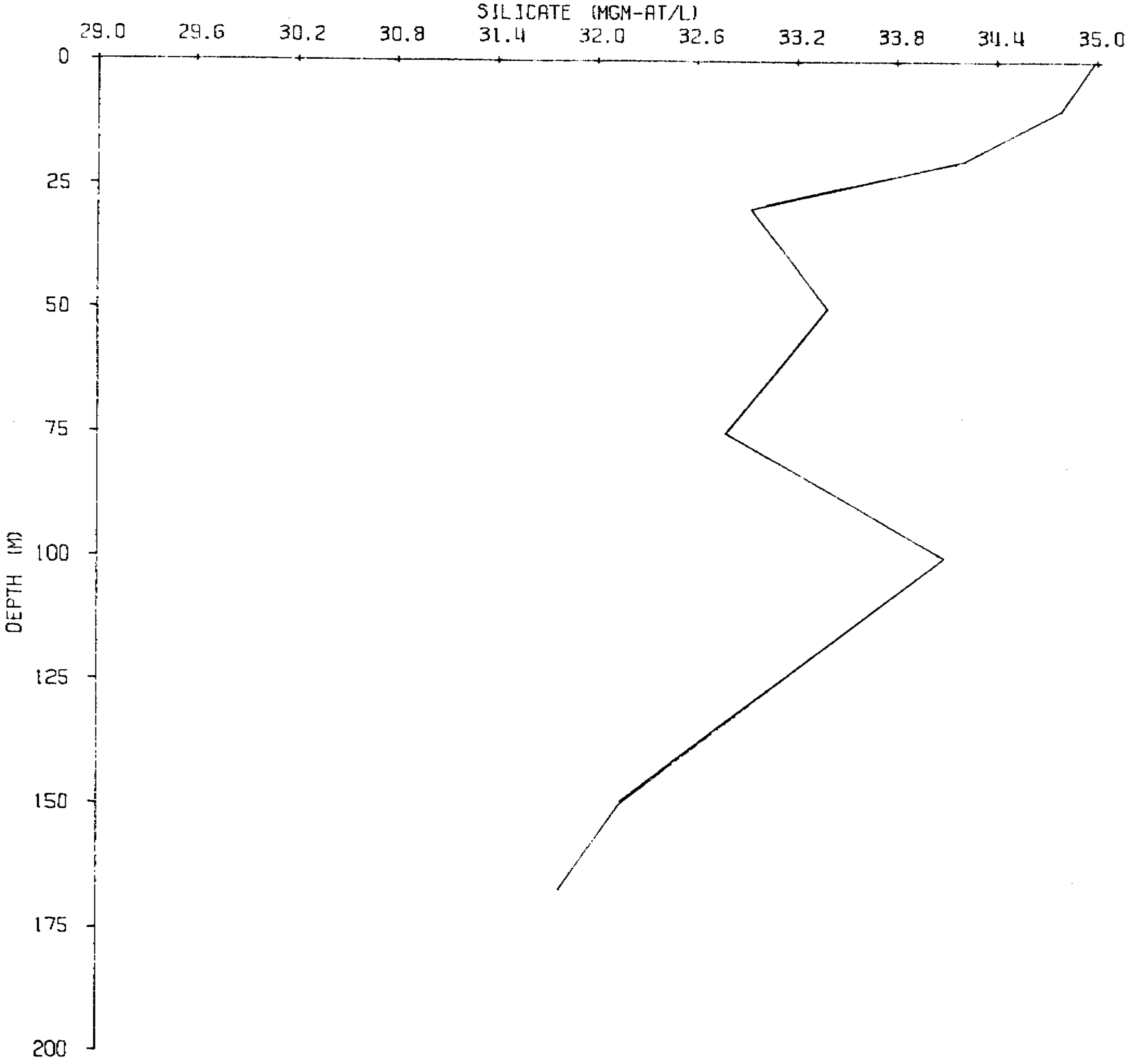
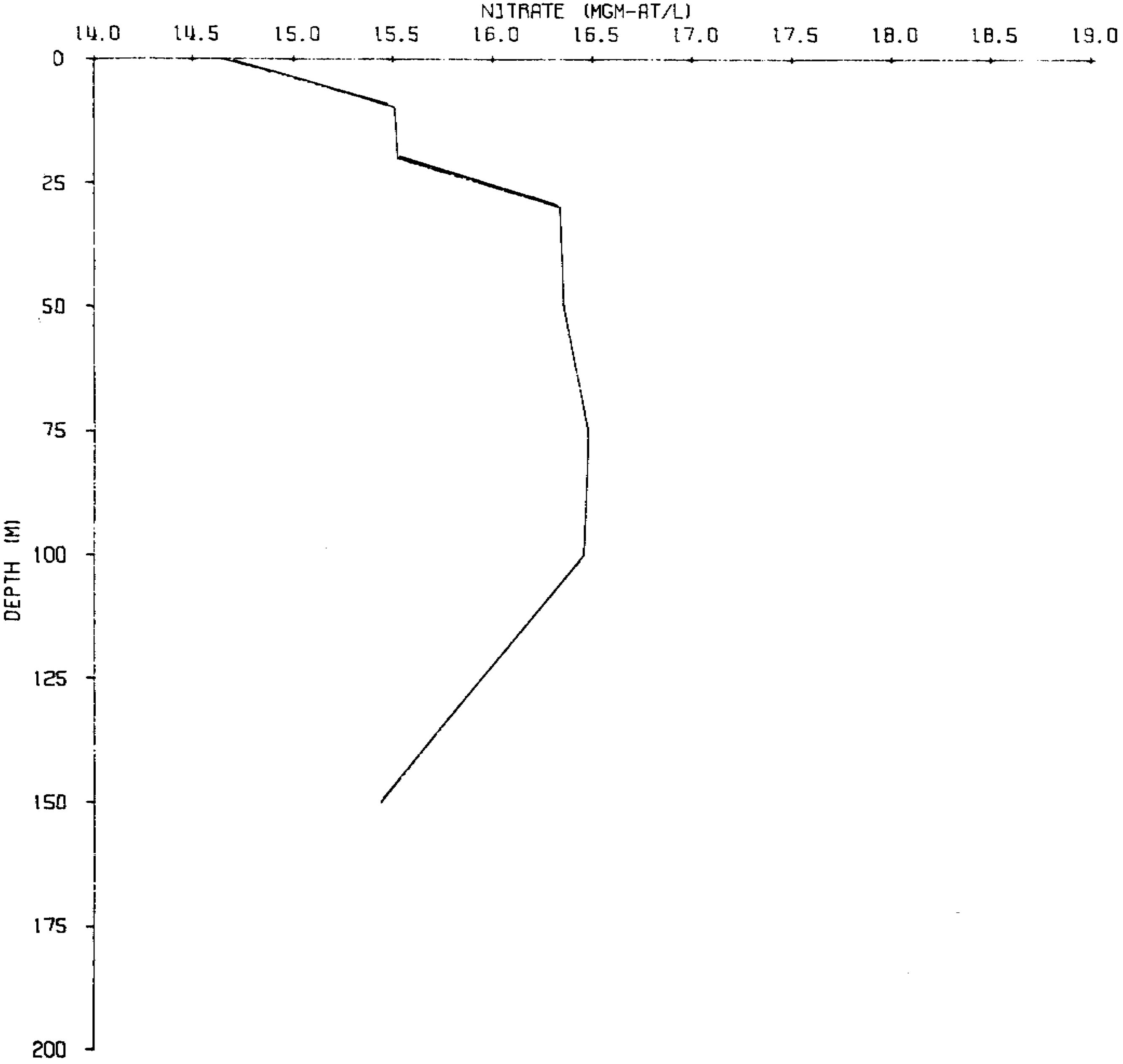
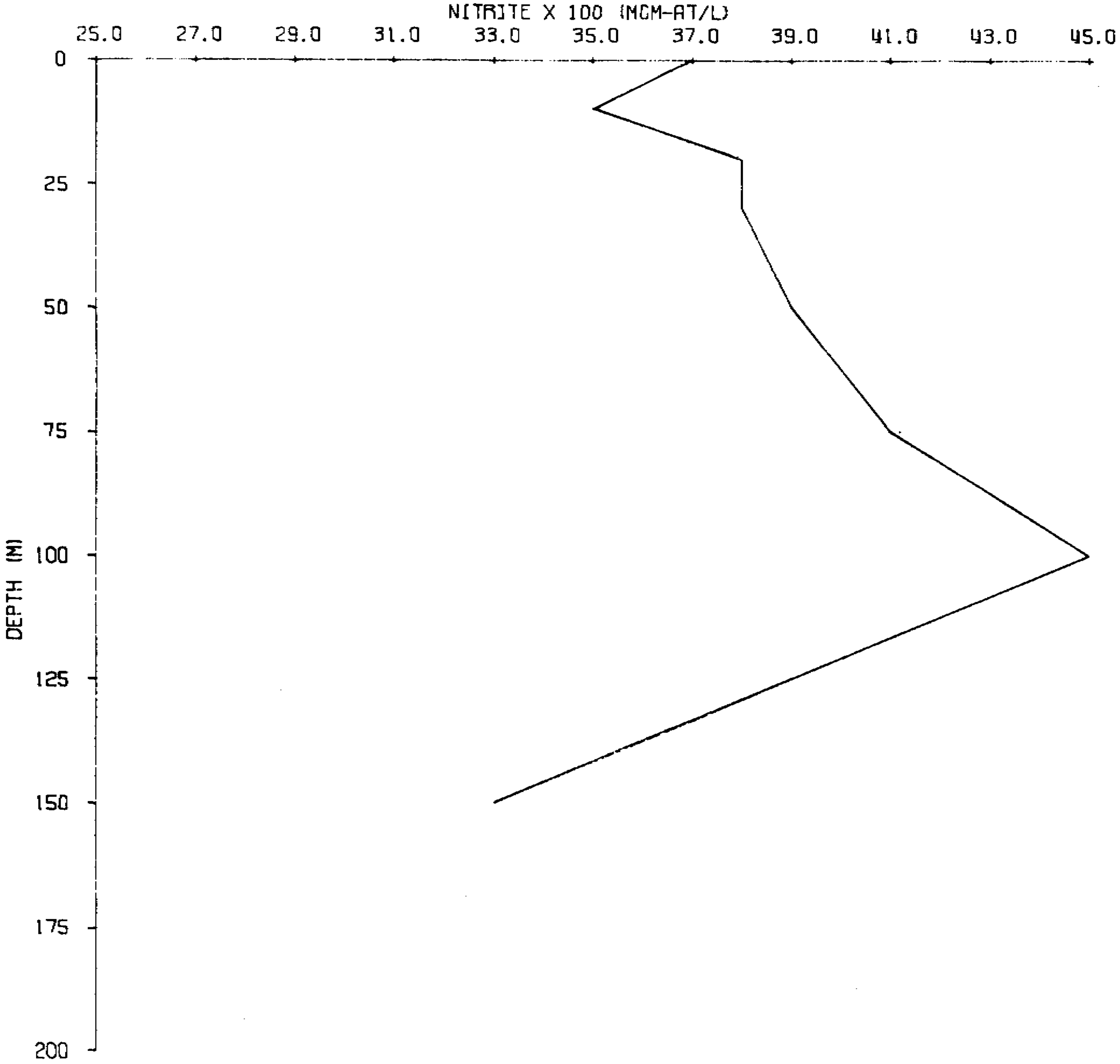


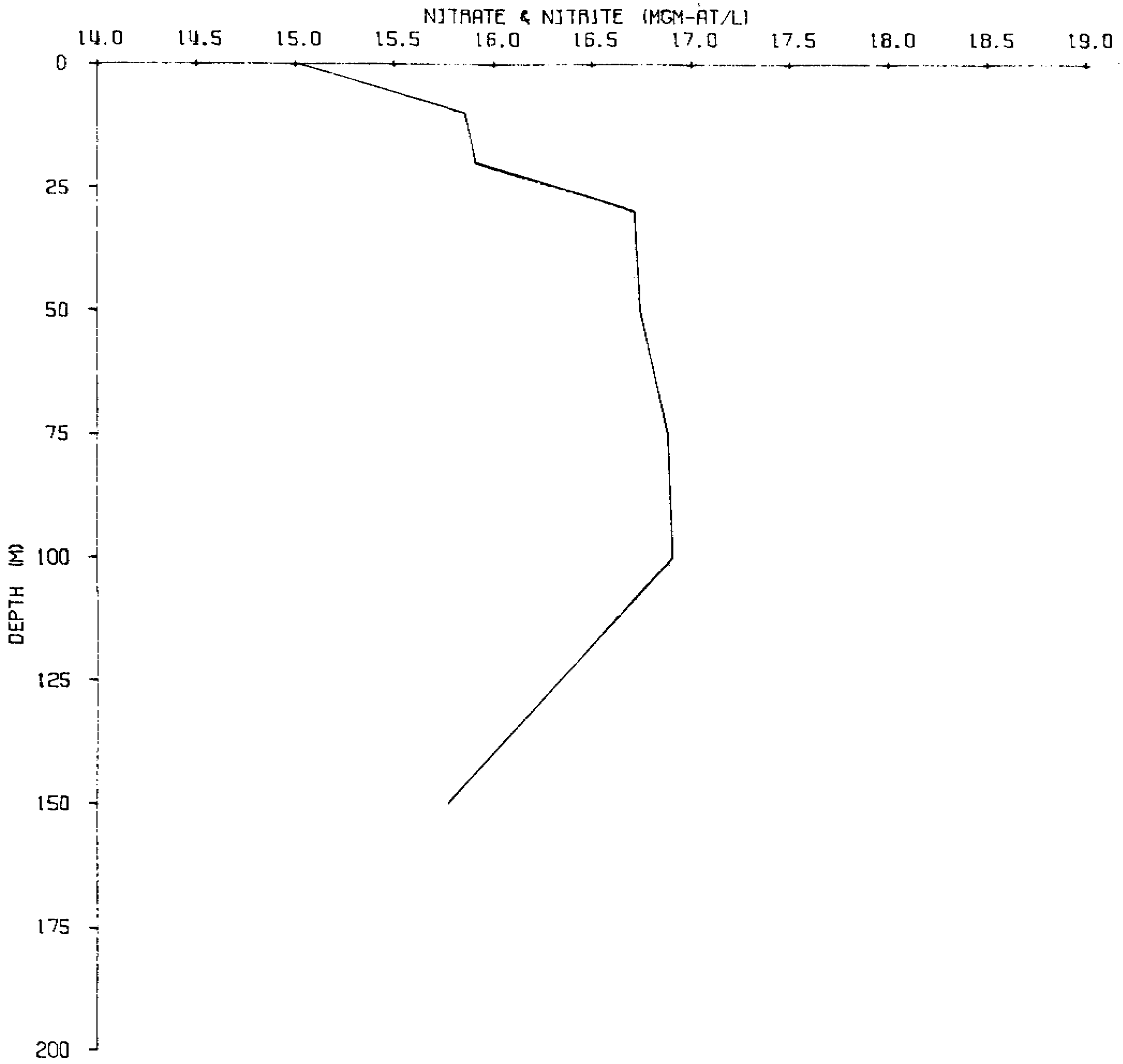
CRUISE 240, YAK 007



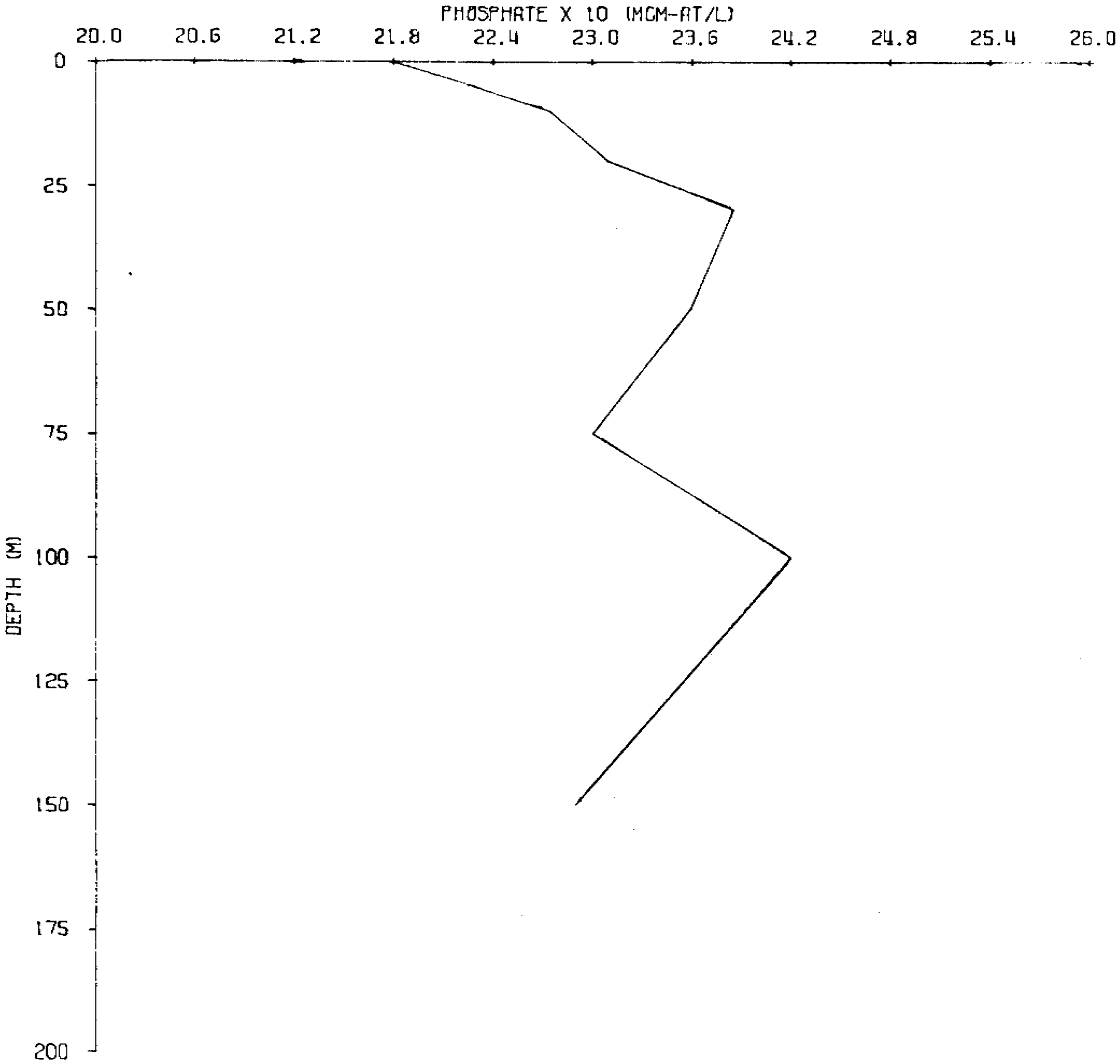
CRUISE 240. YAK 009.



CRUISE 240, TAK 009.



CRUISE 240. YAK 009



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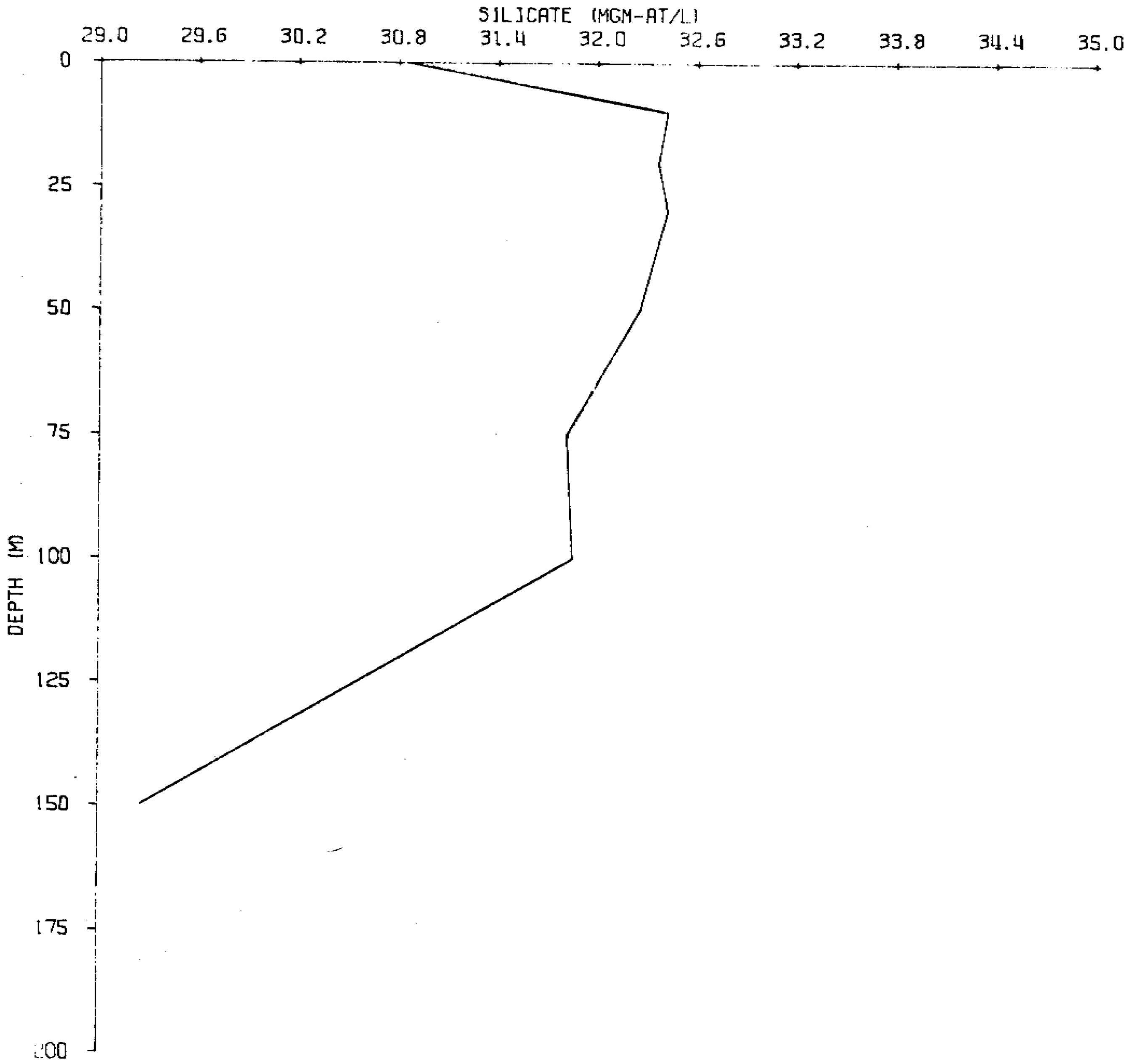

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                                                          6.6 HOURS GMT

  LATITUDE = 59  52.5N   LONGITUDE = 139  40.0W   SONIC DEPTH =  256 M

  1-DIGIT WEATHER CODE IS (X1) AND INDICATES PARTLY CLOUDY
  CLOUD TYPE --- (3) ---ALTOCUMULUS        .
  CLOUD AMOUNT --- (2) ---2/8          .
  VISIBILITY --- (6) ---4-10 KM
-------------------------------------------------------------------------
I            DIRECTION          SPEED                                    I
I WIND        15 -  24 DEGR       KNOTS                                  I
-------------------------------------------------------------------------
I            DIRECTION        HEIGHT       PERIOD                        I
I SEA        215 - 224 DEGR   1.0 M.          SECS                       I
I SWELL          -     DEGR       M.          SECS                       I
-------------------------------------------------------------------------
I TEMPERATURES -DRY =          DEGR C.   BAROMETRIC PR. =1015.4 MB       I
I              -WET =          DEGR C.   TRANSPARENCY   =          M     I
-------------------------------------------------------------------------

                                 OBSERVED

 TIME    DEP     TEMP     SAL     SIG-T     OXY    PO4    NH3    NO2    NO3    NO   SIO3    PH    T ALK
  6.6      0   15.07B  21.600   15.72    7.64   0.00   00.2   0.02   00.4  685.7    5      .       .
  6.6     10    7.88C  29.199   22.79    7.76   0.31   00.3   0.08   00.7  699.1   10      .       .
  6.6     20    7.53B  30.363   23.75    6.44   0.89   00.7   0.17   07.2  639.8   15      .       .
  6.6     30    7.74C  30.578   23.89    6.39   0.98   00.8   0.25   09.2  653.3   17      .       .
  6.6     50    8.51A  31.145   24.22    6.24   1.06   01.0   0.34   09.9  646.2   20      .       .
  6.6     75    8.67B  31.569   24.53    6.16   1.08   01.0   0.38   09.9  639.1   21      .       .
  6.6    100    8.49A  31.680   24.64    6.10   1.13   01.1   0.42   11.6  649.0   23      .       .
  6.6    150    8.27A  31.685   24.68    6.06   0.88   00.8   0.26   07.8  611.2   15      .       .
  6.6    200T   8.07A  31.681   24.70    6.05   1.18   01.0   0.49   12.6  653.5   25      .       .
  6.6    250T   7.05B  31.545   24.74    6.00   1.16   01.4   0.43   12.6  649.1   23      .       .

                                 STANDARD

         DEP     TEMP     SAL     SIG-T     OXY      SP VOL     DEL D
           0    15.07   21.600   15.72    7.64    1188.82      .000
          10     7.88   29.199   22.79    7.76     508.16      .085
          20     7.53   30.363   23.75    6.44     416.69      .131
          30     7.74   30.578   23.89    6.39     403.43      .172
          50     8.51   31.145   24.22    6.24     371.83      .250
          75     8.67   31.569   24.53    6.16     342.88      .339
         100     8.49   31.680   24.64    6.10     332.38      .423
         150     8.27   31.685   24.68    6.06     329.55      .589
         200     8.07   31.681   24.70    6.05     327.72      .753
         250     7.05   31.545   24.74    6.00     324.73      .916
```

```
AC   CRUISE 244 CONSECUTIVE STATION NO.    3.    YAK 05      28/ 7/77
---------------------------                                    8.3 HOURS GMT

  LATITUDE = 59  44.0N   LONGITUDE = 139  40.5W   SONIC DEPTH =  183 M

  1-DIGIT WEATHER CODE IS (  ) AND INDICATES NOT RECORDED
  CLOUD TYPE --- ( ) ---NOT RECORDED           ,
  CLOUD AMOUNT --- ( ) ---NOT RECORDED,
  VISIBILITY --- ( ) ---NOT RECORDED
----------------------------------------------------------------------------
I            DIRECTION          SPEED                                      I
I WIND           -       DEGR      KNOTS                                   I
----------------------------------------------------------------------------
I            DIRECTION        HEIGHT      PERIOD                           I
I SEA        215 - 224 DEGR  0.5 M.          SECS                          I
I SWELL          -     DEGR      M.          SECS                          I
----------------------------------------------------------------------------
I TEMPERATURES -DRY =            DEGR C.   BAROMETRIC PR. =1014.7 MB       I
I              -WET =            DEGR C.   TRANSPARENCY    =       M       I
----------------------------------------------------------------------------

                                          OBSERVED

 TIME     DEP      TEMP     SAL     SIG-T      OXY     PO4     NH3     NO2     NO3      NO     SIO3     PH     T ALK
  8.3      0     13.530  24.039    17.88     8.43    0.03    00.2    0.06    00.4   756.2      5       .        .
  8.3     10     12.010  29.995    22.75     6.65    0.41    00.4    0.09    01.3   605.4     10       .        .
  8.3     20     12.568  31.181    23.56     6.38    0.44    00.6    0.11    01.2   580.4     10       .        .
  8.3     30     11.338  31.531    24.06     6.32    0.58    00.8    0.17    02.5   586.7     12       .        .
  8.3     50      9.778  31.705    24.46     6.25    0.95    01.2    0.30    06.7   618.3     19       .        .
  8.3     75      8.908  31.792    24.68     6.11    1.12    01.3    0.36    09.9   634.6     22       .        .
  8.3    100      8.519  31.818    24.75     6.05    1.08    01.1    0.38    09.8   628.3     20       .        .
  8.3    150      7.178  31.760    24.89     5.78    1.28    00.5    0.15    13.3   635.7     23       .        .
  8.3    175T     6.96A  31.763    24.92     5.63    1.63    00.5    0.55    17.8   662.8     32       .        .

                                          STANDARD

          DEP      TEMP     SAL     SIG-T      OXY         SP VOL      DEL D
            0     13.53  24.039    17.88     8.43        979.55       .000
           10     12.01  29.995    22.75     6.65        511.85       .075
           20     12.56  31.181    23.56     6.38        434.29       .122
           30     11.33  31.531    24.06     6.32        386.92       .163
           50      9.77  31.705    24.46     6.25        348.90       .236
           75      8.90  31.792    24.68     6.11        328.19       .321
          100      8.51  31.818    24.75     6.05        322.41       .402
          150      7.17  31.760    24.89     5.78        309.07       .560
```

```
AC   CRUISE 246 CONSECUTIVE STATION NO.    1.   YAK  7     27/ 7/77
---------------------------                                 20.5 HOURS GMT

  LATITUDE = 59  40.0N   LONGITUDE = 139  59.5W   SONIC DEPTH =  172 M

  1-DIGIT WEATHER CODE IS (X1) AND INDICATES PARTLY CLOUDY
  CLOUD TYPE --- (3) ---ALTOCUMULUS
  CLOUD AMOUNT --- (4) ---4/8
  VISIBILITY --- (6) ---4-10 KM
--------------------------------------------------------------------------
I            DIRECTION          SPEED                                     I
I WIND       245 - 254 DEGR      7 KNOTS                                  I
--------------------------------------------------------------------------
I            DIRECTION        HEIGHT       PERIOD                         I
I SEA        215 - 224 DEGR   1.0 M.          SECS                        I
I SWELL          -     DEGR      M.           SECS                        I
--------------------------------------------------------------------------
I TEMPERATURES -DRY =          DEGR C.   BAROMETRIC PR. =1019.3 MB        I
I              -WET =          DEGR C.   TRANSPARENCY    =        M       I
--------------------------------------------------------------------------

                                   OBSERVED

 TIME     DEP      TEMP      SAL     SIG-T     CXY    PO4    NH3    NO2    NO3     NO    SIO3    PH     T ALK
 20.5      0         .     24.634      .       7.57   0.10   00.2   0.06   00.4   679.4    8      .       .
 20.5     10       .008    30.485      .  0    6.46   0.39   00.4   0.09   00.5   681.2   12      .       .
 20.5     20     11.580    31.194   23.76      6.38   0.70   00.7   0.19   03.1   597.5   14      .       .
 20.5     30         .     31.521      .       6.33   0.80   01.2   0.26   05.6   615.5   15      .       .
 20.5     50      9.714    31.790   24.54      6.37   0.91   01.3   0.30   06.9   630.8   18      .       .
 20.5     75      8.998    31.880   24.72      6.26   1.03   01.2   0.35   08.8   638.1   21      .       .
 20.5    100      8.858    31.928   24.78        .    0.95   01.1   0.29   10.1           19      .       .
 20.5    150      8.455    31.929   24.84      6.16   1.22   01.6   0.32   11.9   657.1   25      .       .
 20.5    165T     8.344    31.926   24.86      6.15   1.23   01.7   0.31   11.4   651.7   25      .       .

                                   STANDARD

          DEP      TEMP      SAL     SIG-T     CXY        SP VOL      DEL D
            0       .00    24.634      .       7.57          .          .
           10       .00    30.485      .       6.46          .          .
           20     11.59    31.194   23.76      6.38      415.94         .
           30     10.83    31.521   24.14      6.33      379.32         .
           50      9.71    31.790   24.54      6.37      341.67         .
           75      8.99    31.880   24.72      6.26      324.45         .
          100      8.85    31.928   24.78      6.20      319.17         .
          150      8.45    31.928   24.84      6.16      314.07         .
```

```
AC   CRUISE 246 CONSECUTIVE STATION NO.    4.   YAK-9       28/ 7/77
-----------------------------                                 18.5 HOURS GMT

  LATITUDE = 59  40.0N   LONGITUDE = 139  59.5W   SONIC DEPTH =  158 M

  1-DIGIT WEATHER CODE IS (  ) AND INDICATES NOT RECORDED
  CLOUD TYPE --- ( ) ---NOT RECORDED
  CLOUD AMOUNT --- ( ) ---NOT RECORDED.
  VISIBILITY --- (6) ---4-10 KM
----------------------------------------------------------------------
I           DIRECTION           SPEED                                I
I WIND          -        DEGR      KNOTS                             I
----------------------------------------------------------------------
I           DIRECTION       HEIGHT      PERIOD                       I
I SEA       195 - 204 DEGR  0.5 M.          SECS                     I
I SWELL         -     DEGR      M.          SECS                     I
----------------------------------------------------------------------
I TEMPERATURES -DRY =        DEGR C.   BAROMETRIC PR. =1013.3 MB     I
I              -WET =        DEGR C.   TRANSPARENCY   =       M      I
----------------------------------------------------------------------

                                OBSERVED

 TIME   DEP    TEMP     SAL     SIG-T    OXY   PO4    NH3    NO2    NO3    NO    SIO3   PH   T ALK
 18.5     0   13.56A  24.429   18.17    7.58  0.06   00.2   0.09   00.3  679.4    8    .      .
 18.5    10   14.06A  30.324   22.61    6.36  0.35   00.5   0.05   00.3  570.5   11    .      .
 18.5    20   12.09E  30.990   23.51    6.41  0.58   01.4   0.19   05.5  621.8   14    .      .
 18.5    30   11.06A  31.396   24.01    6.39  0.66   01.4   0.20   03.4  601.1   14    .      .
 18.5    50    9.00A  31.861   24.71    6.21  1.08   00.9   0.35   09.3  638.1   21    .      .
 18.5    75    7.88A  31.939   24.93    5.83  1.34   01.3   0.59   13.8  644.7   27    .      .
 18.5   100    7.769  31.966   24.97    5.79  1.40   01.3   0.56   13.8  641.1   27    .      .
 18.5   150    7.44A  31.977   25.02    5.52  1.51   01.5   0.78   14.0  618.8   33    .      .

                                STANDARD

        DEP    TEMP     SAL     SIG-T    OXY       SP VOL     DEL D
          0   13.56   24.429   18.17    7.58      951.18      .000
         10   14.06   30.324   22.61    6.36      525.51      .074
         20   12.09   30.990   23.50    6.41      439.93      .122
         30   11.06   31.396   24.00    6.39      392.33      .164
         50    9.00   31.861   24.71    6.21      325.66      .235
         75    7.88   31.939   24.93    5.83      304.28      .314
        100    7.76   31.966   24.97    5.79      300.94      .390
        150    7.44   31.972   25.02    5.52      296.82      .539
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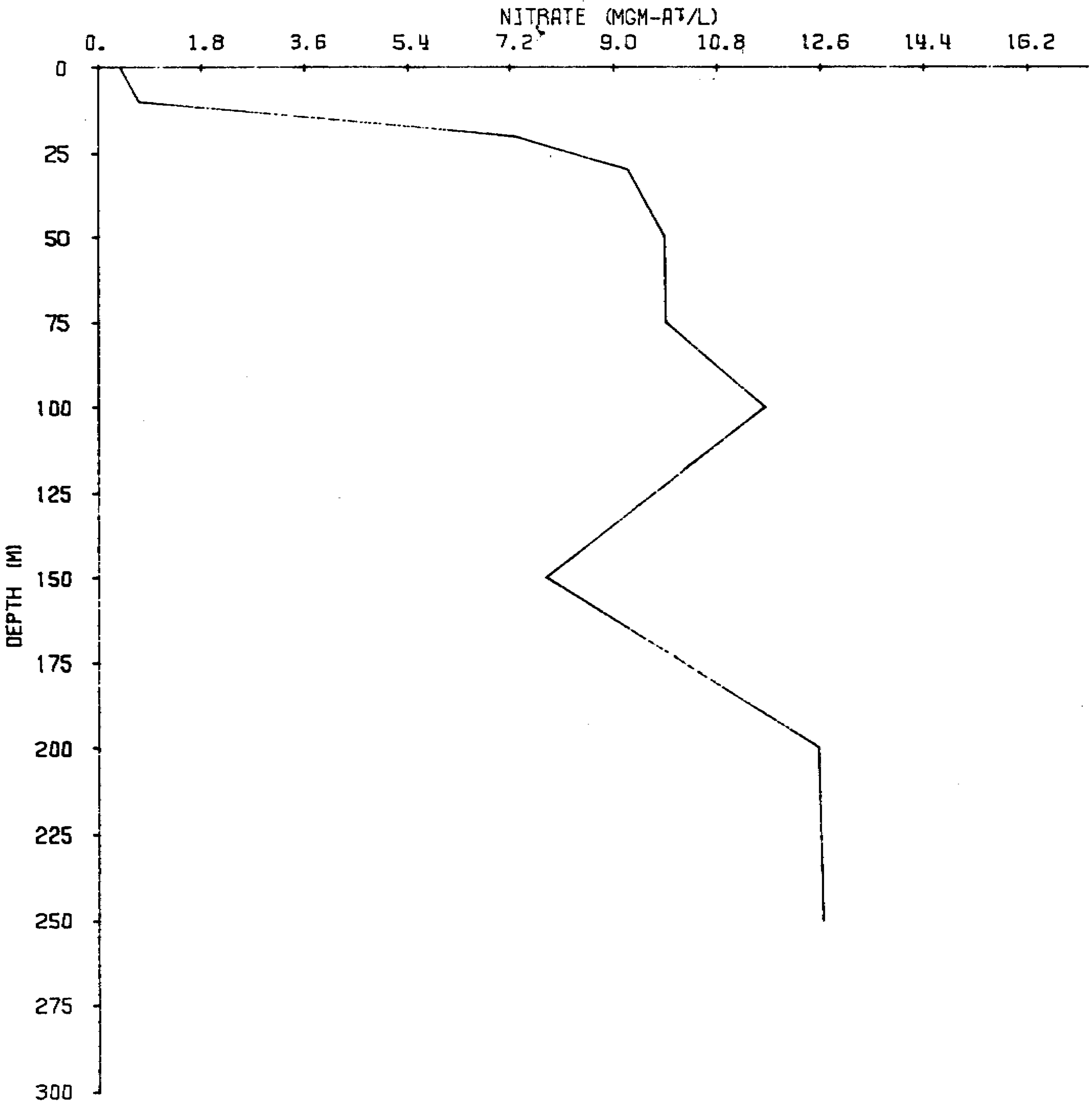

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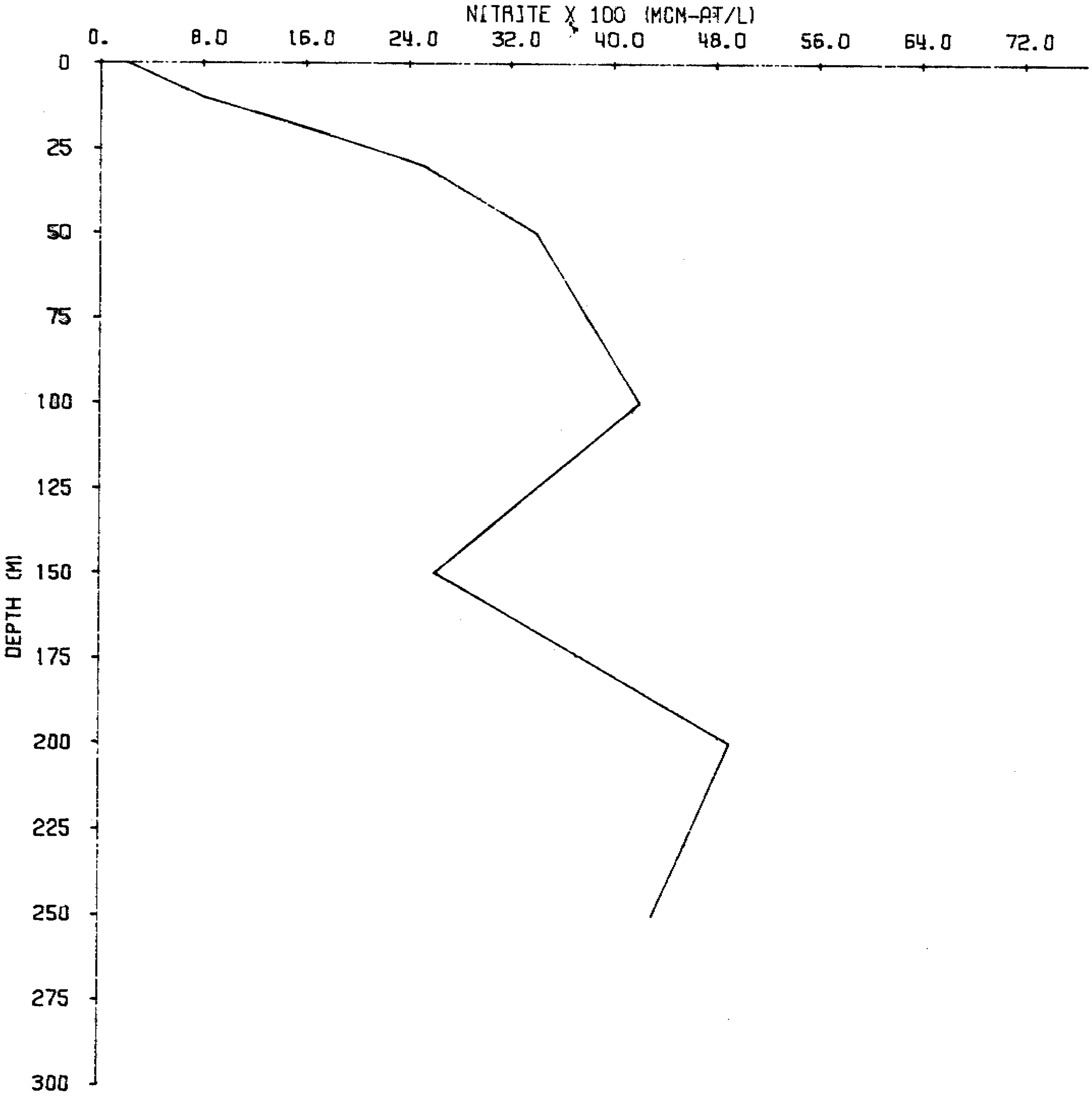

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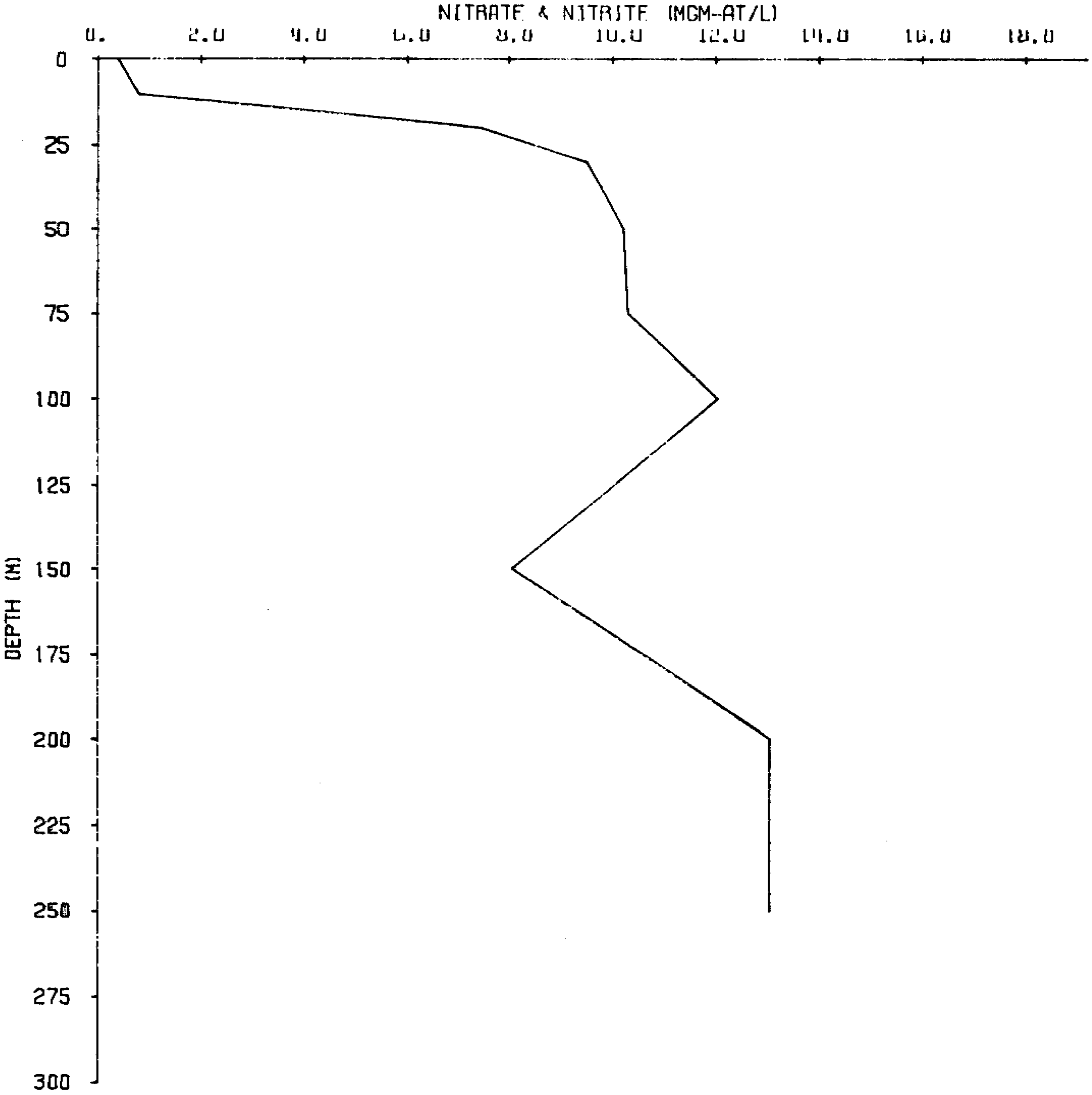

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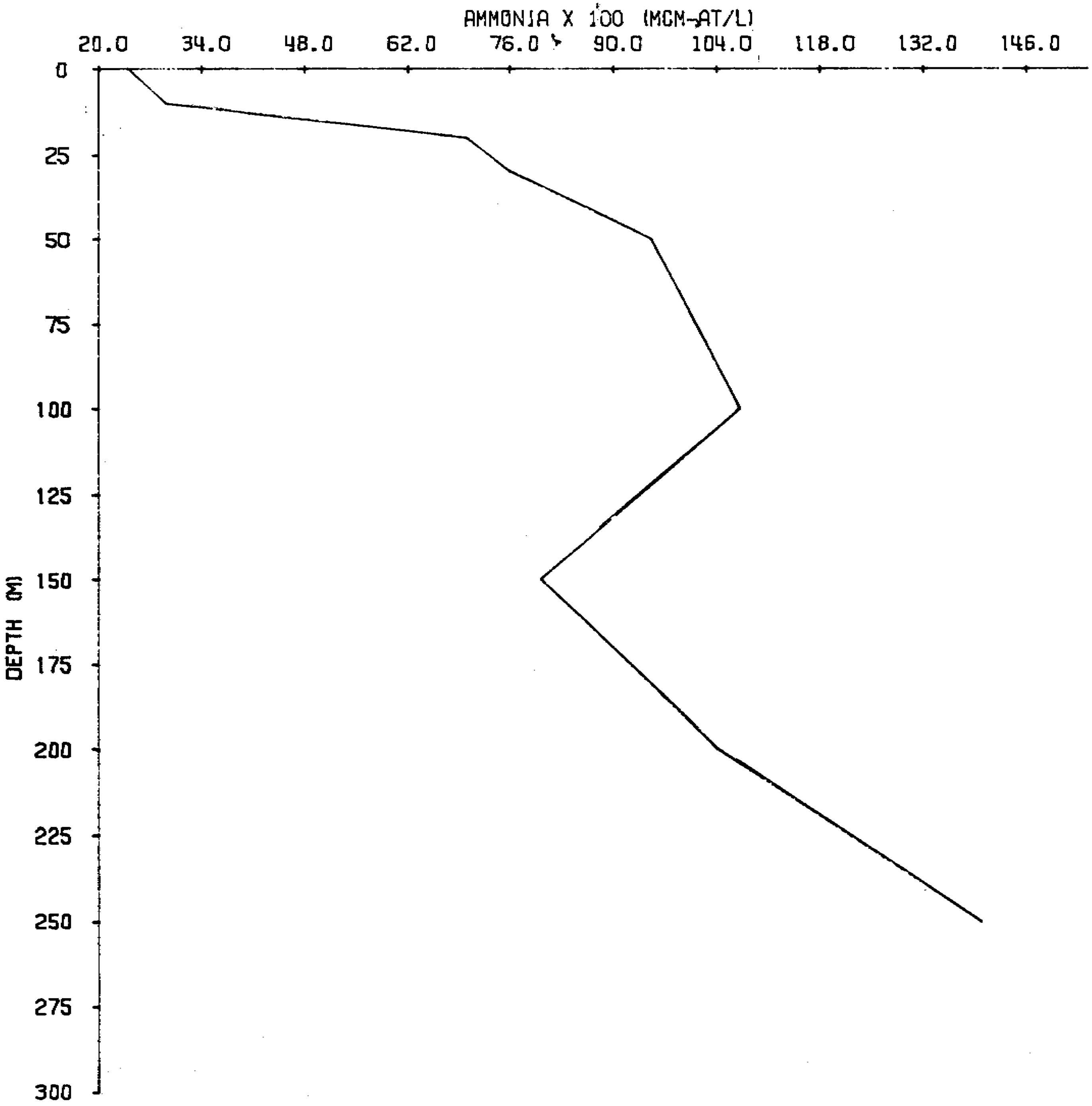

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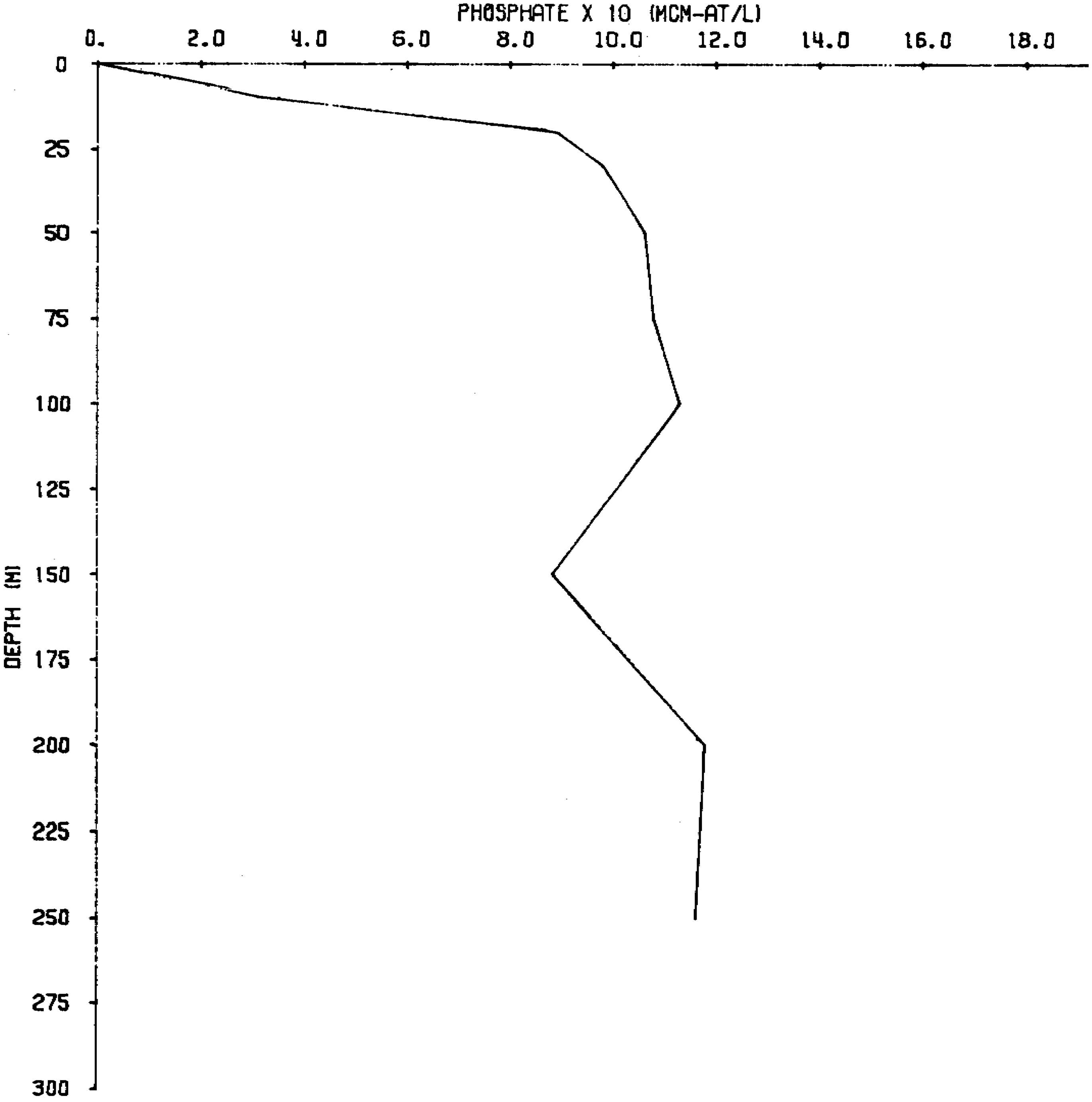

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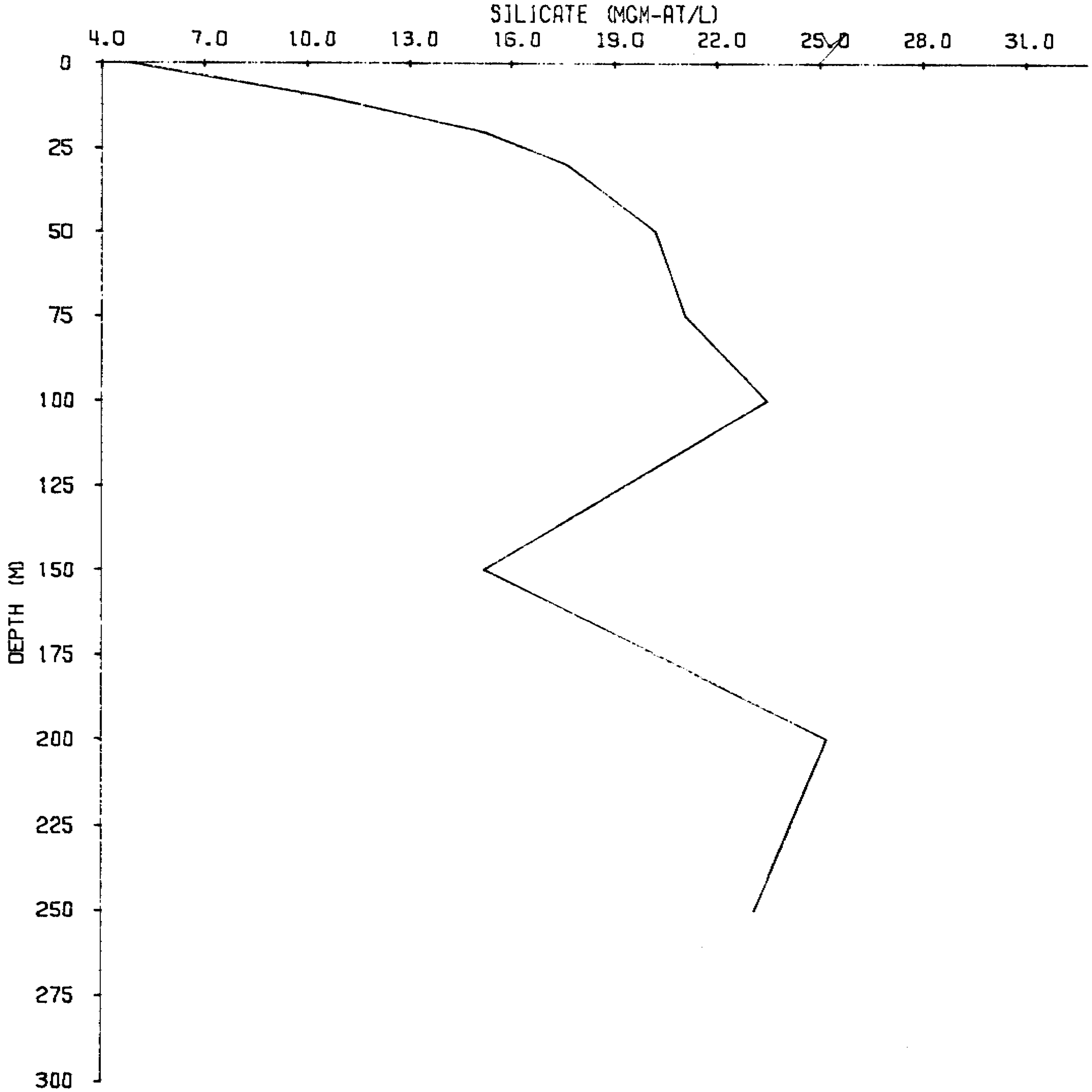

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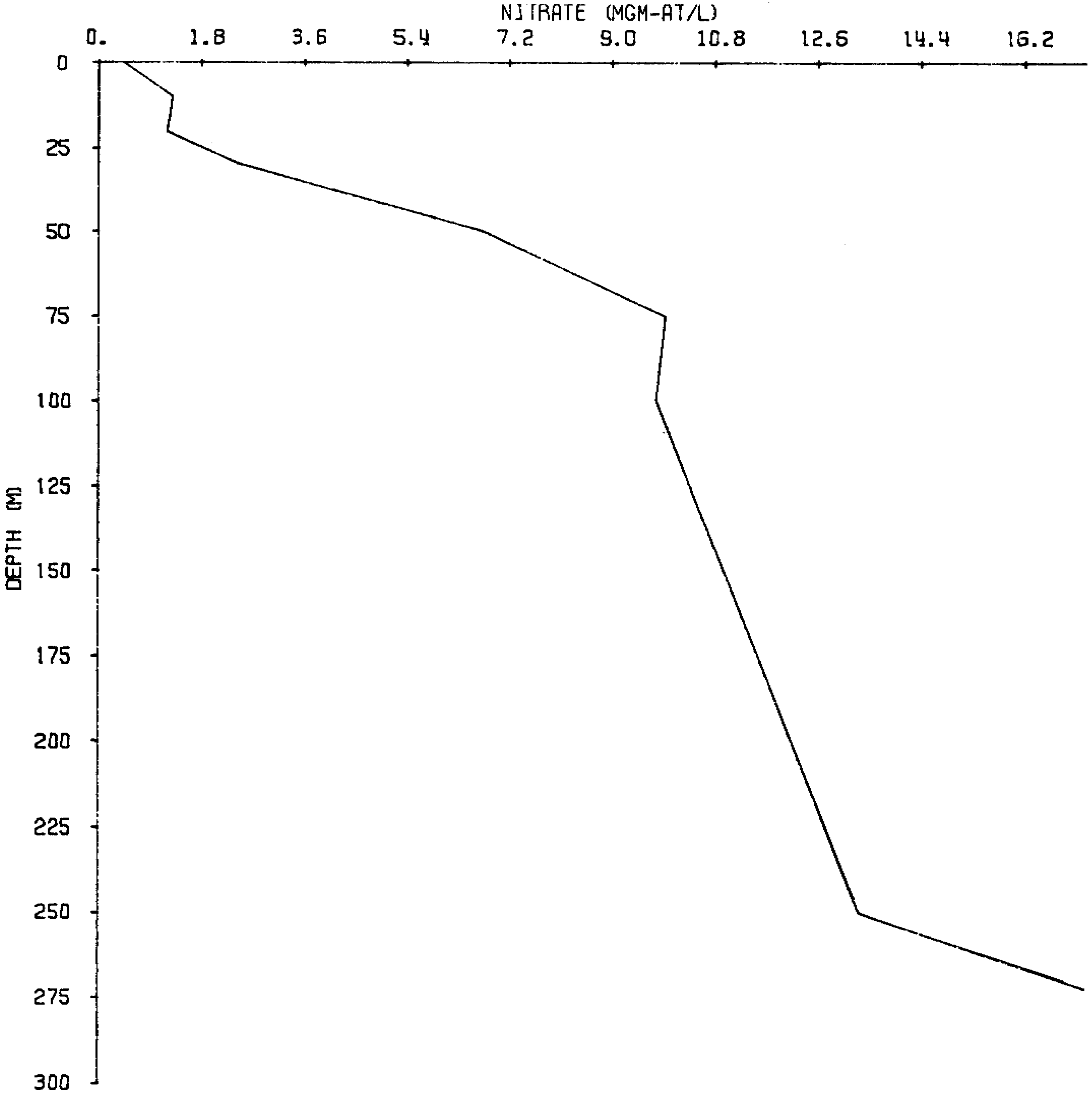

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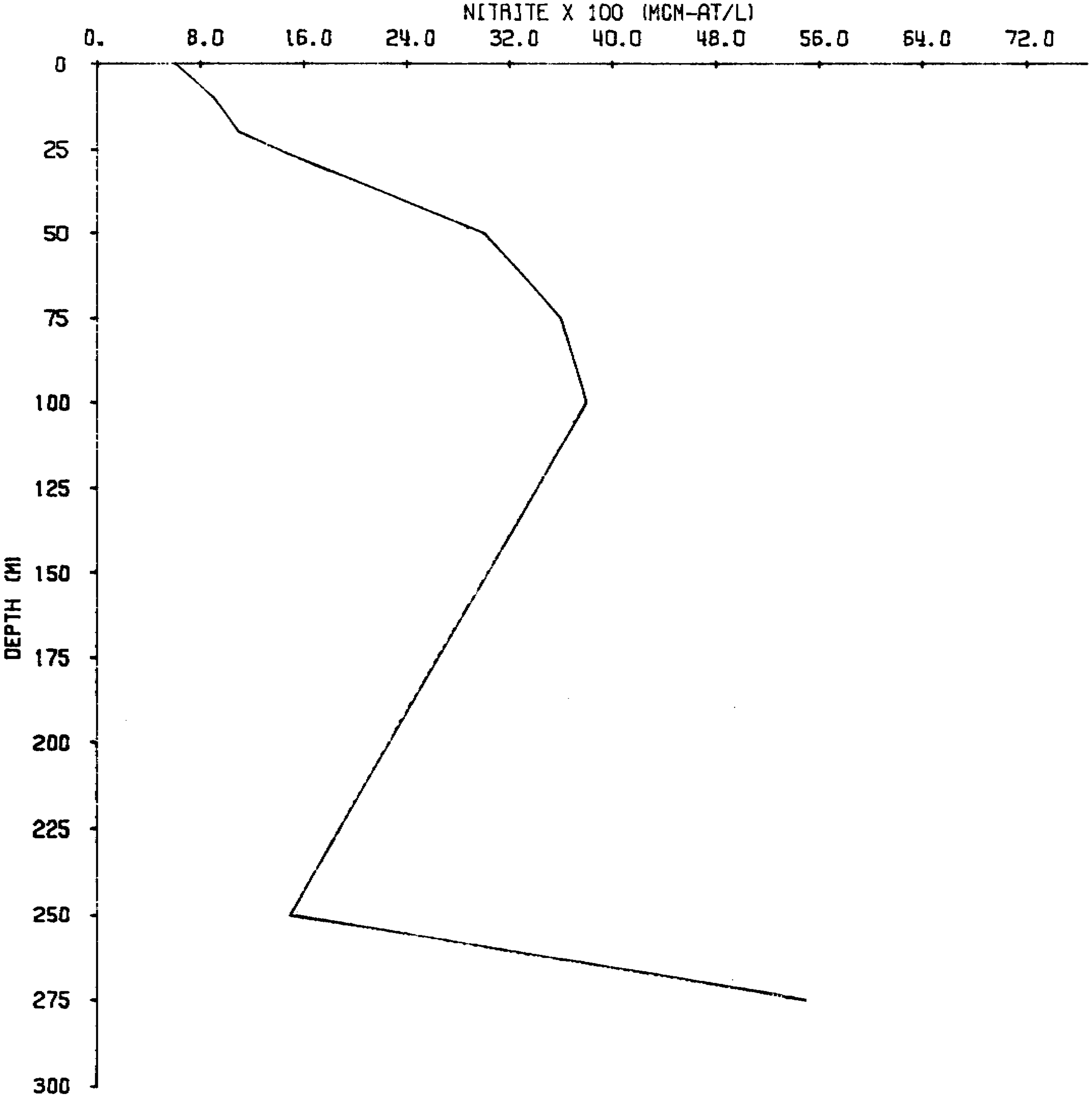

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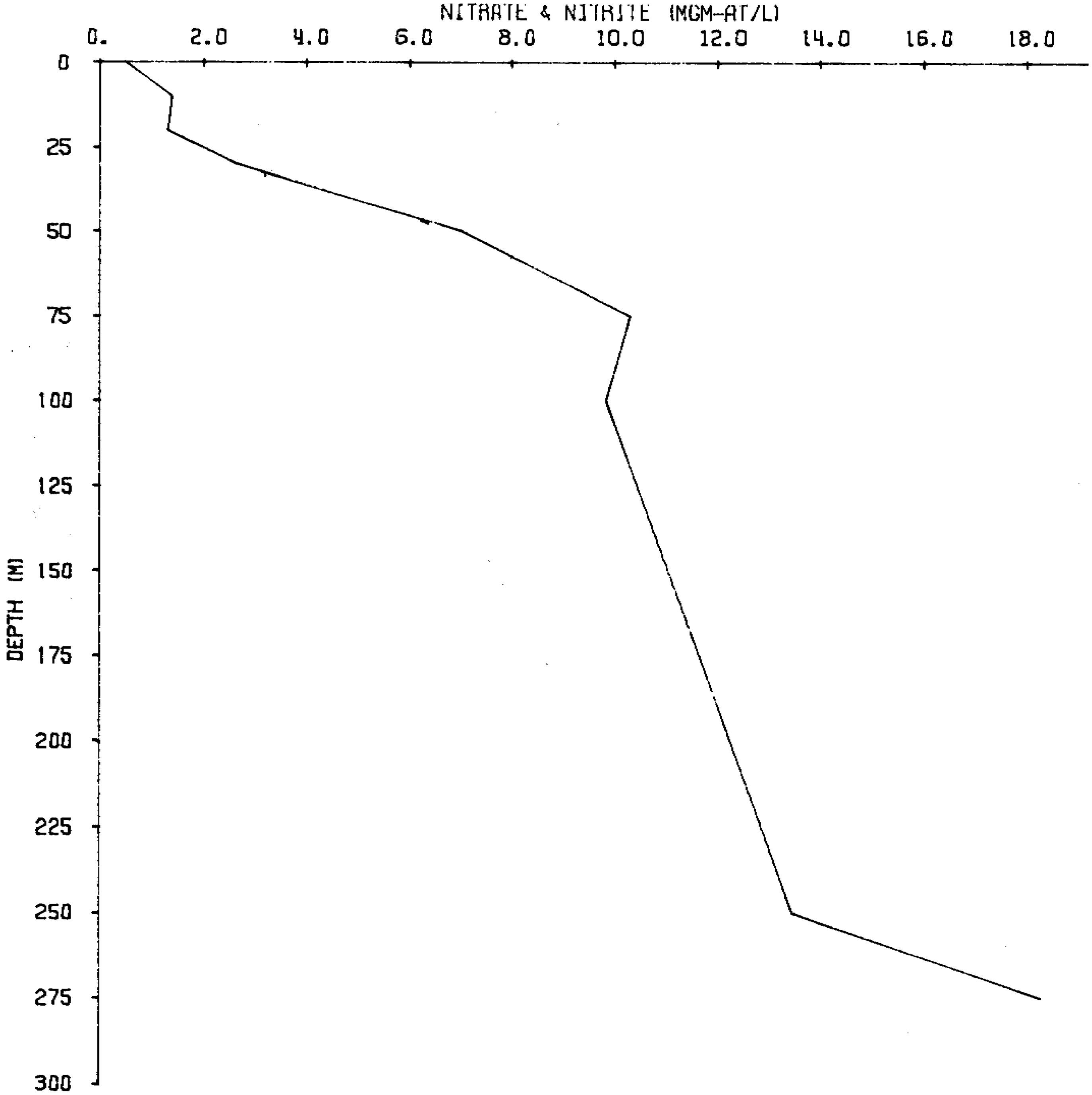

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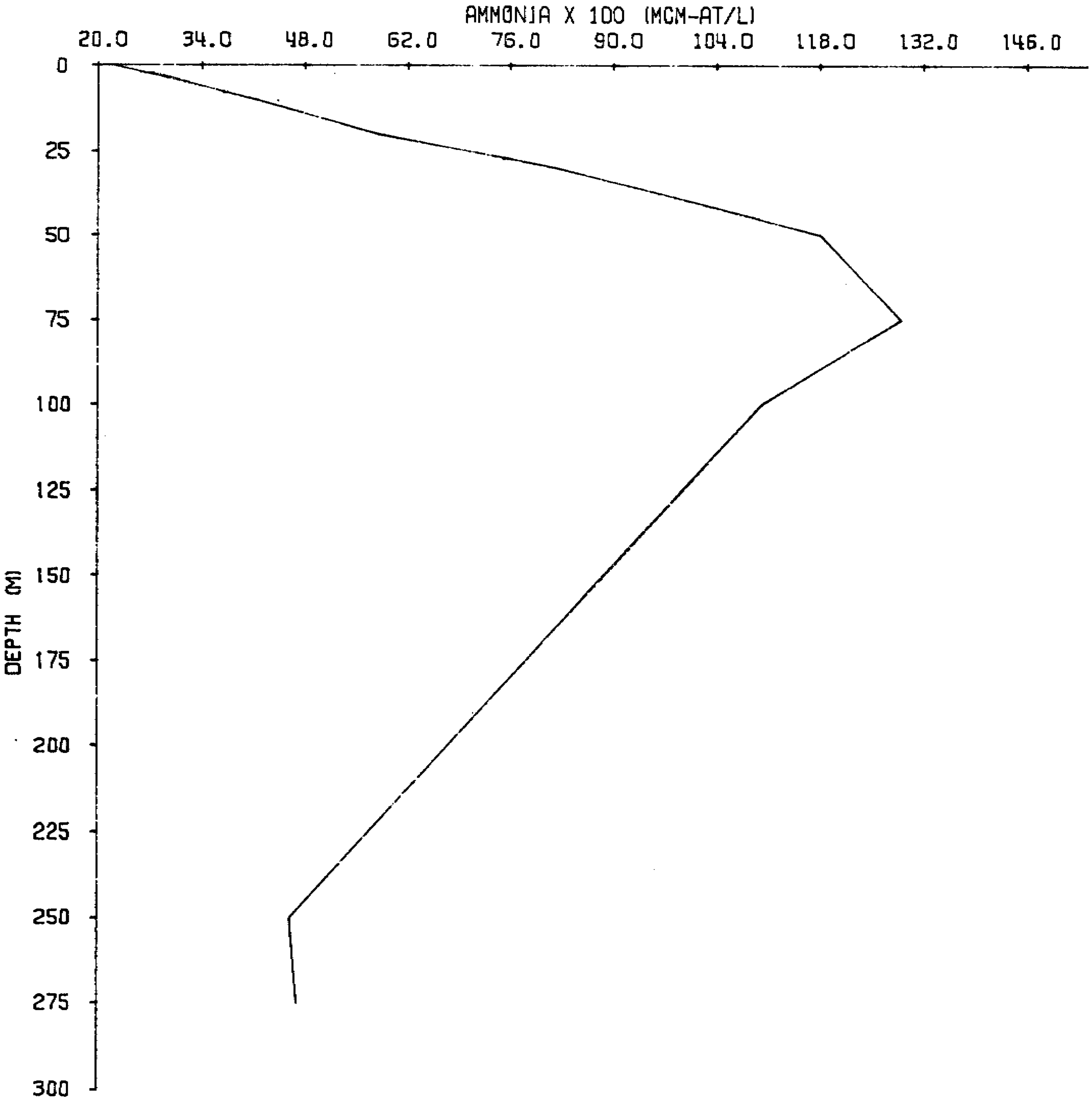

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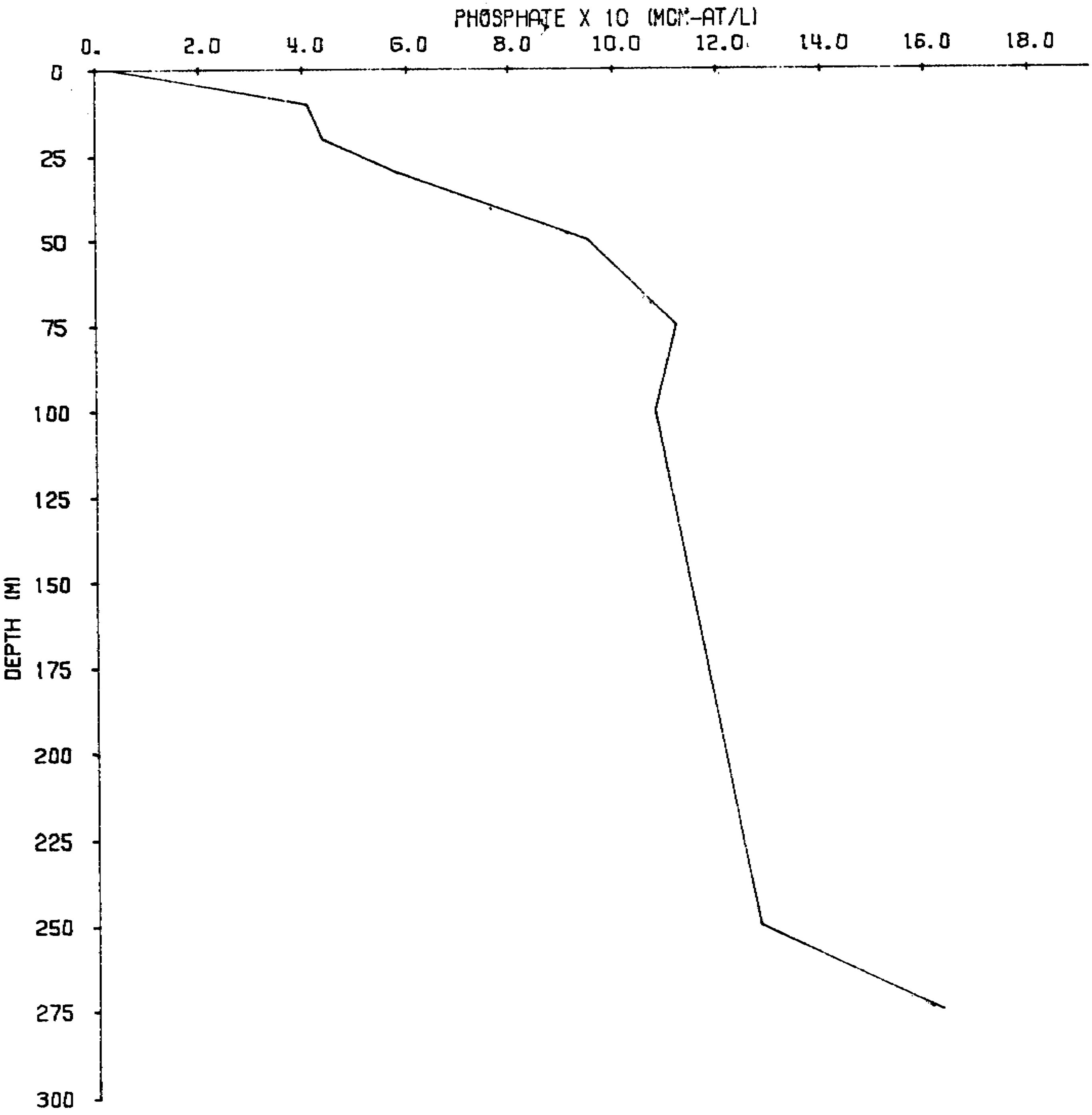

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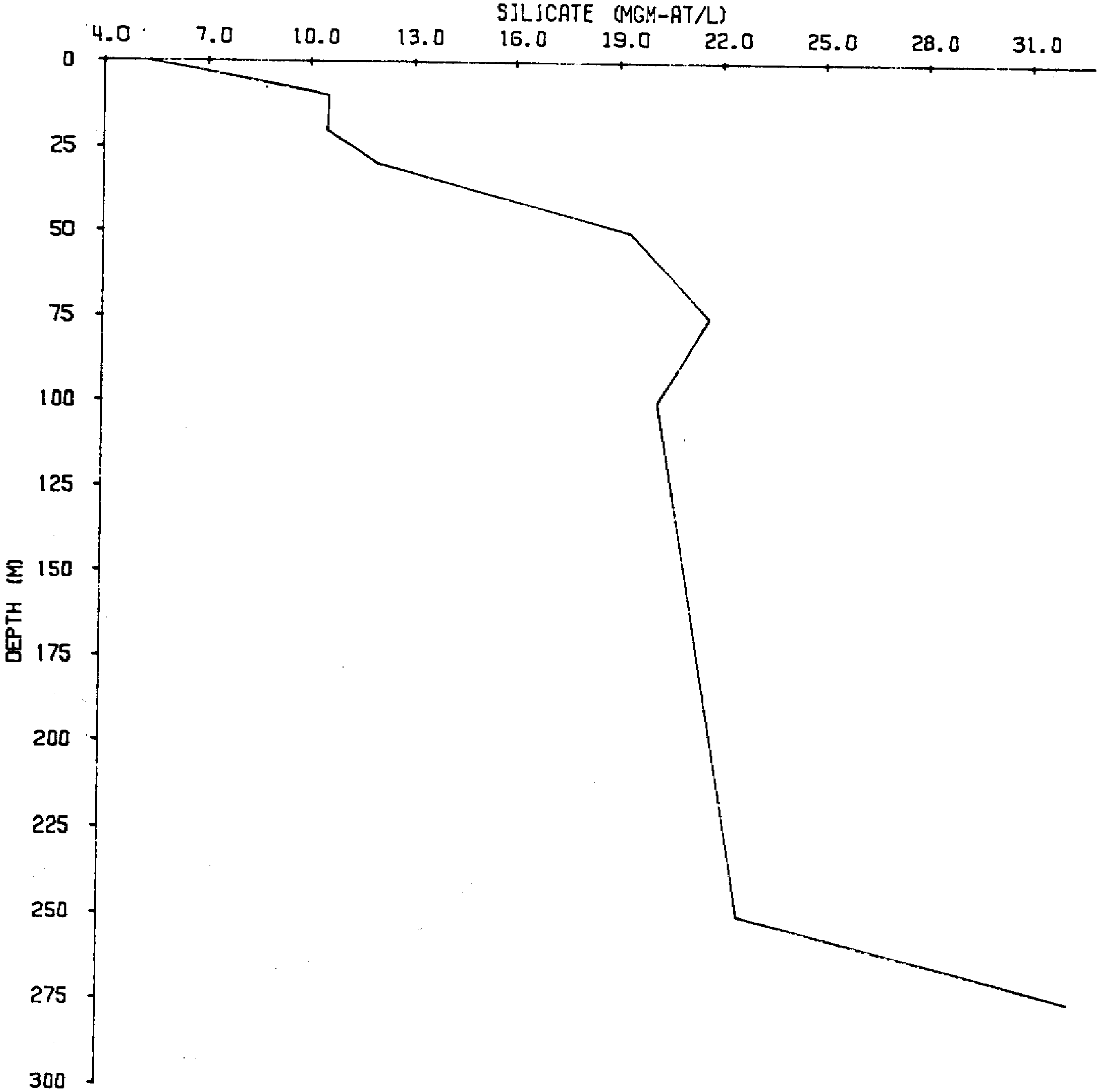

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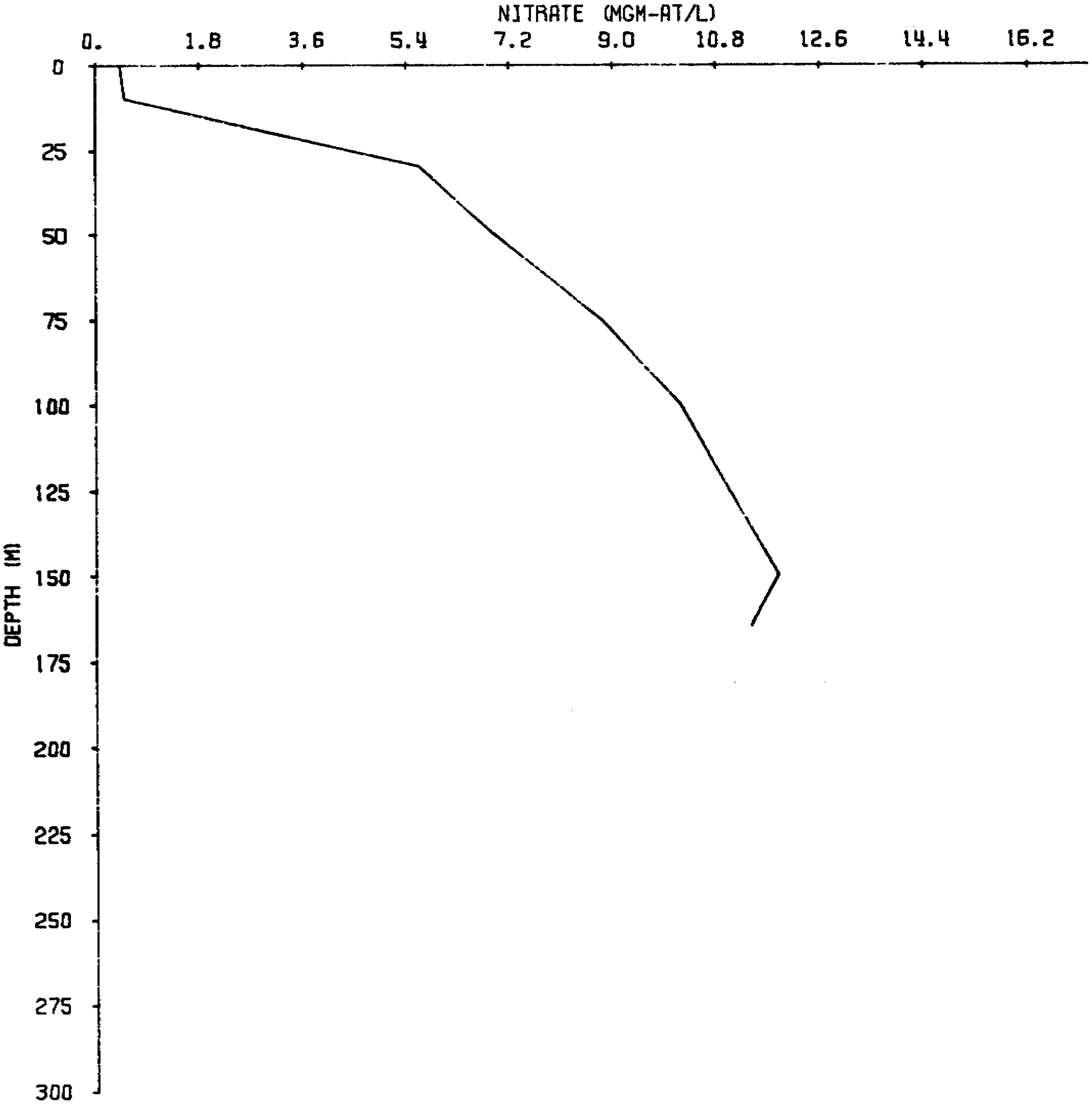

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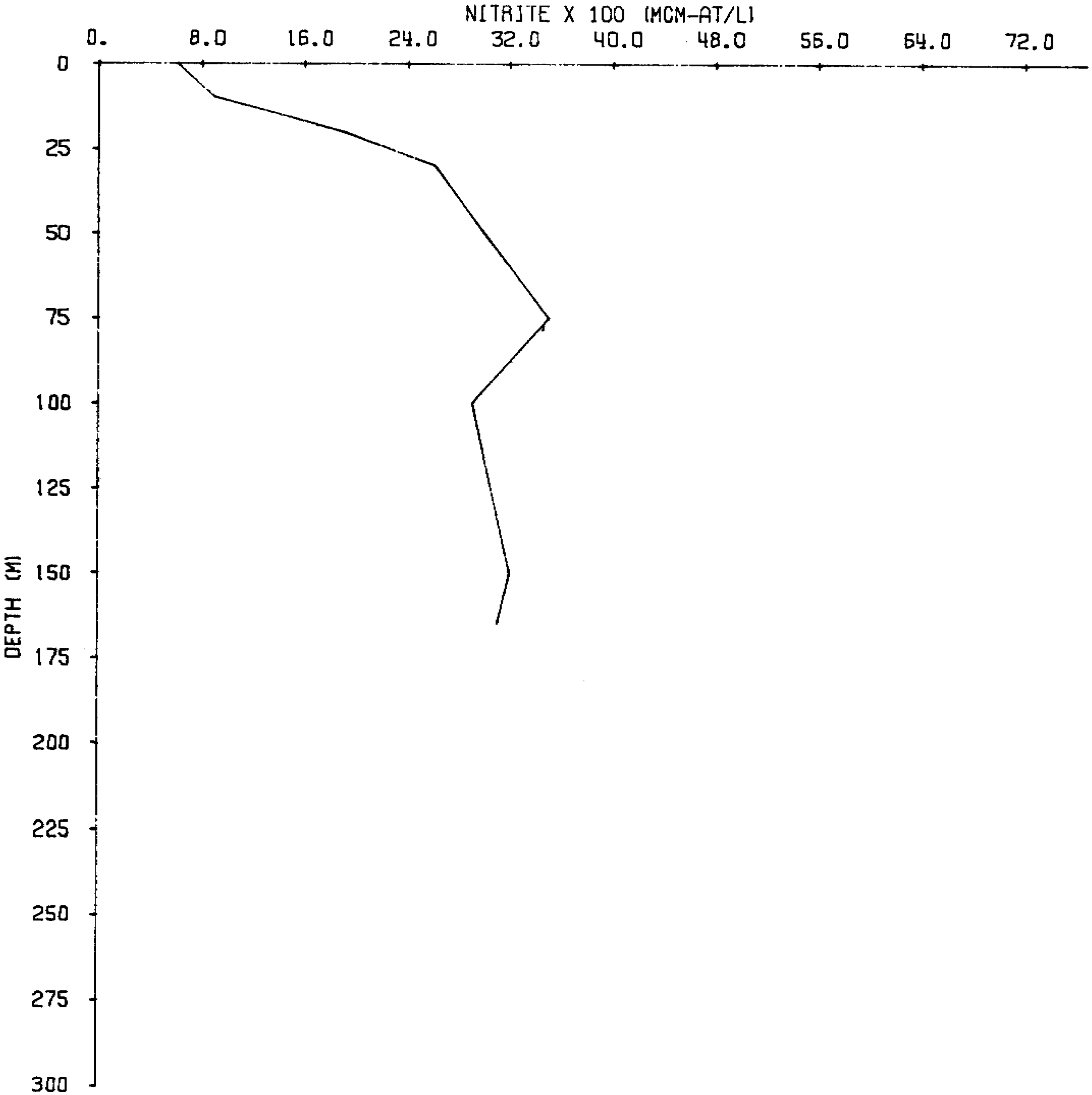

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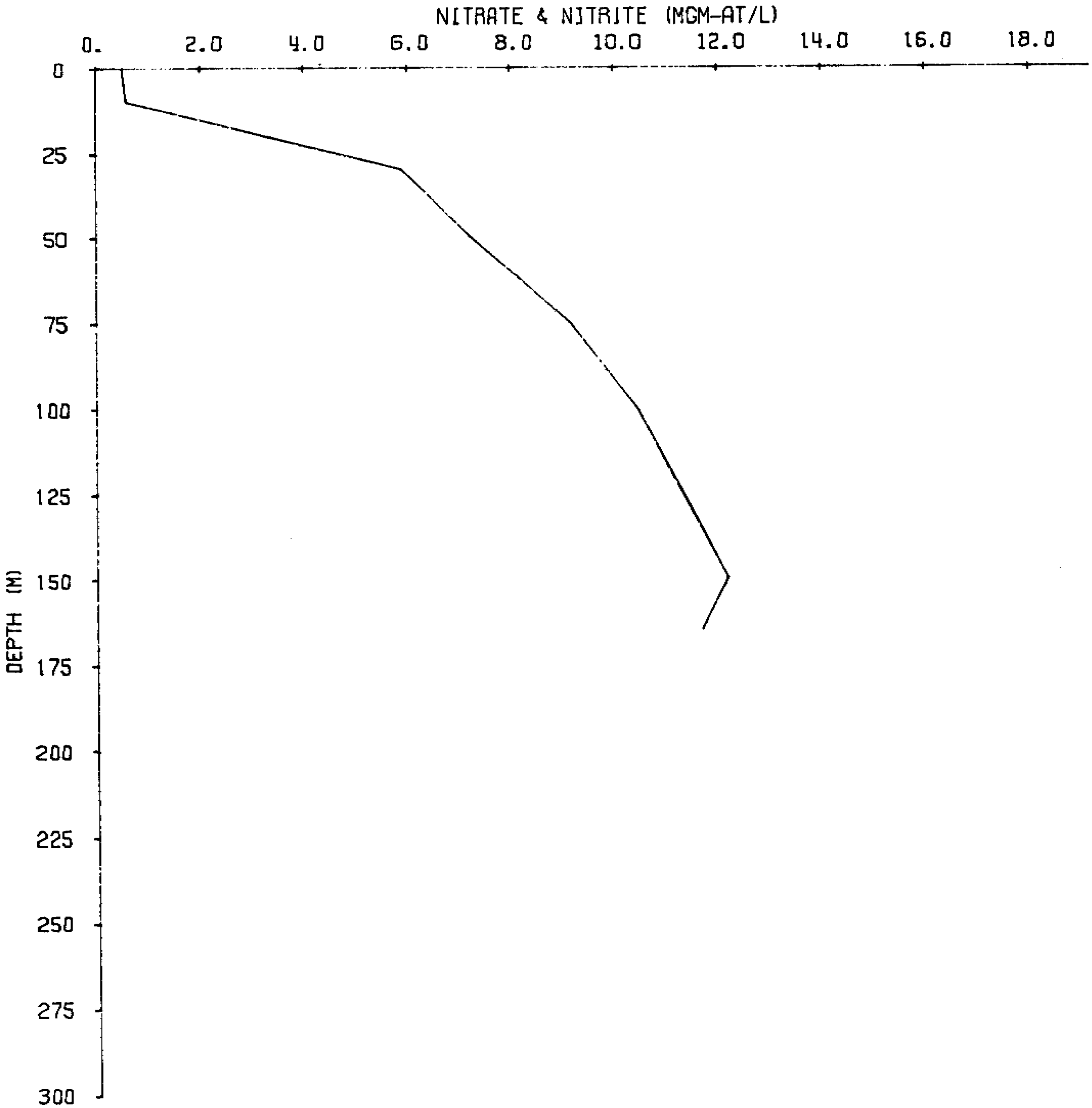

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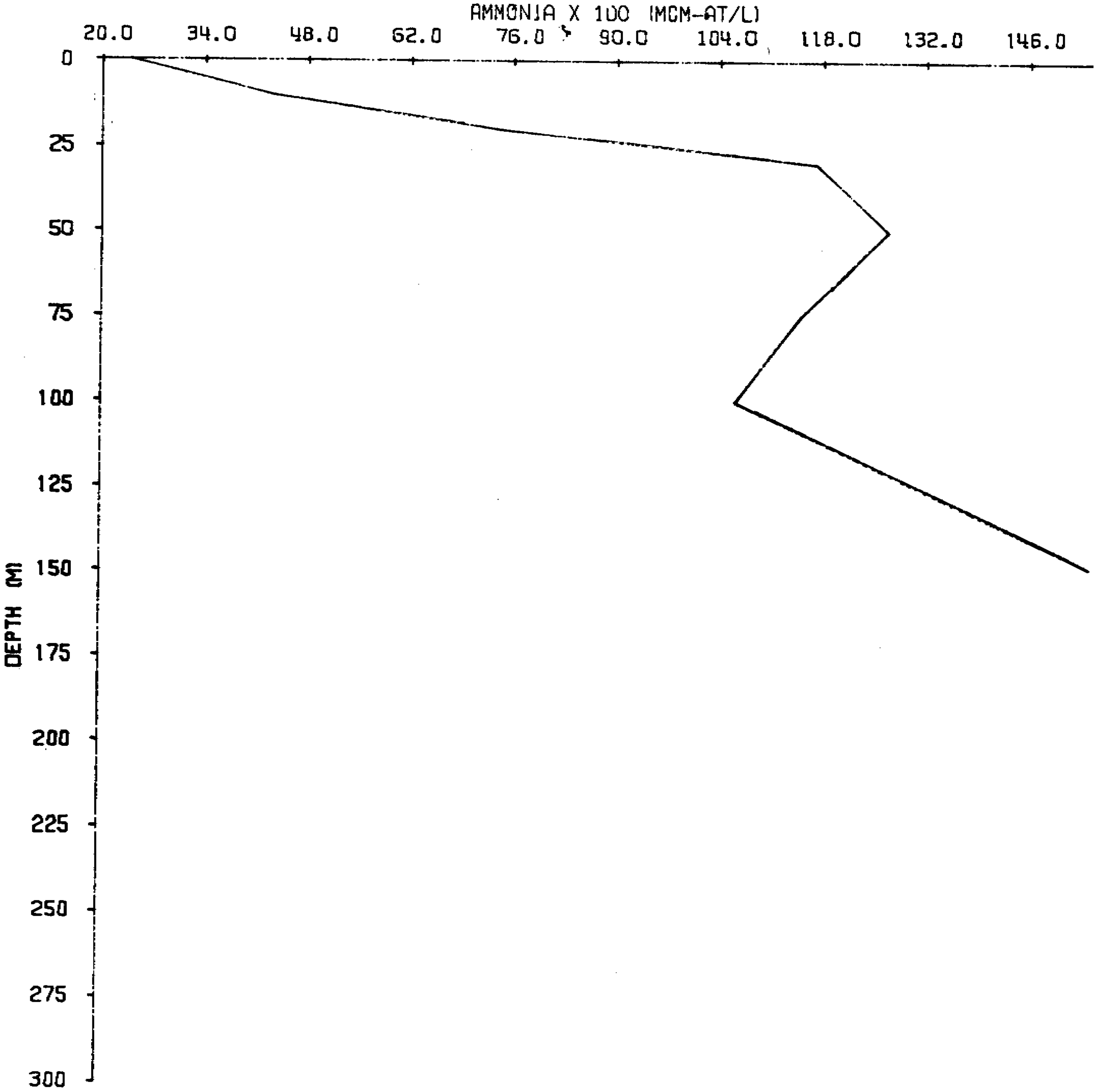

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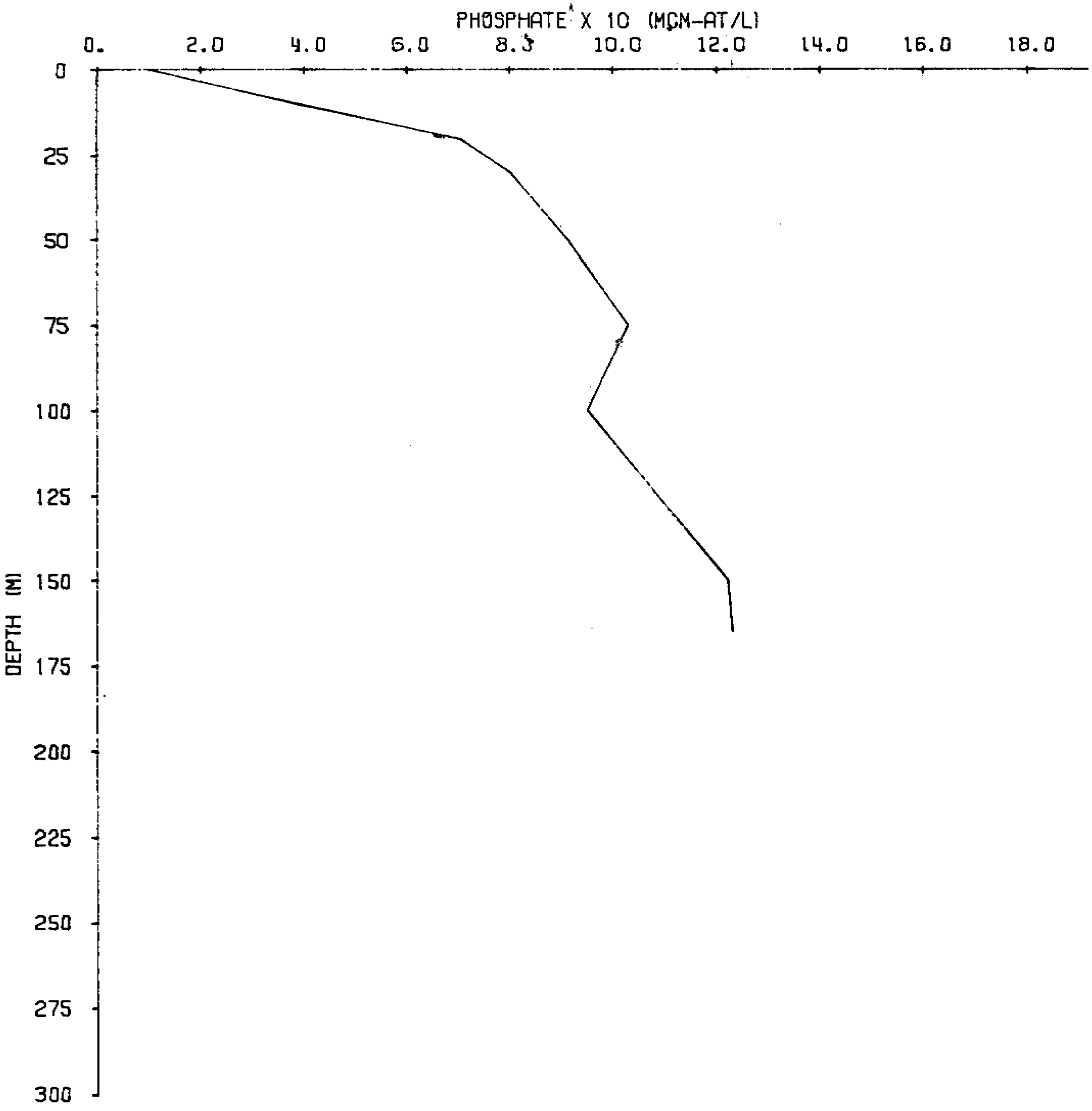

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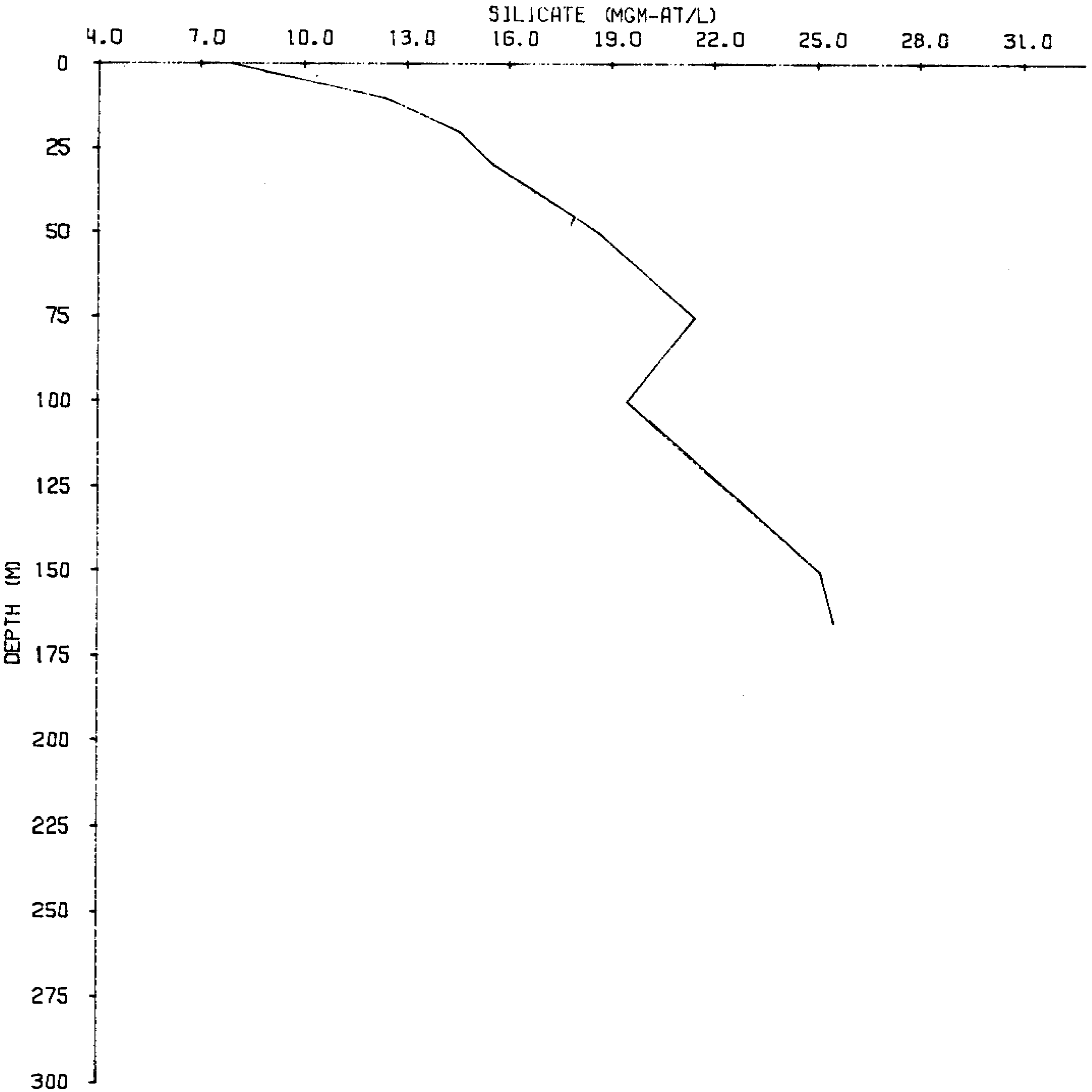

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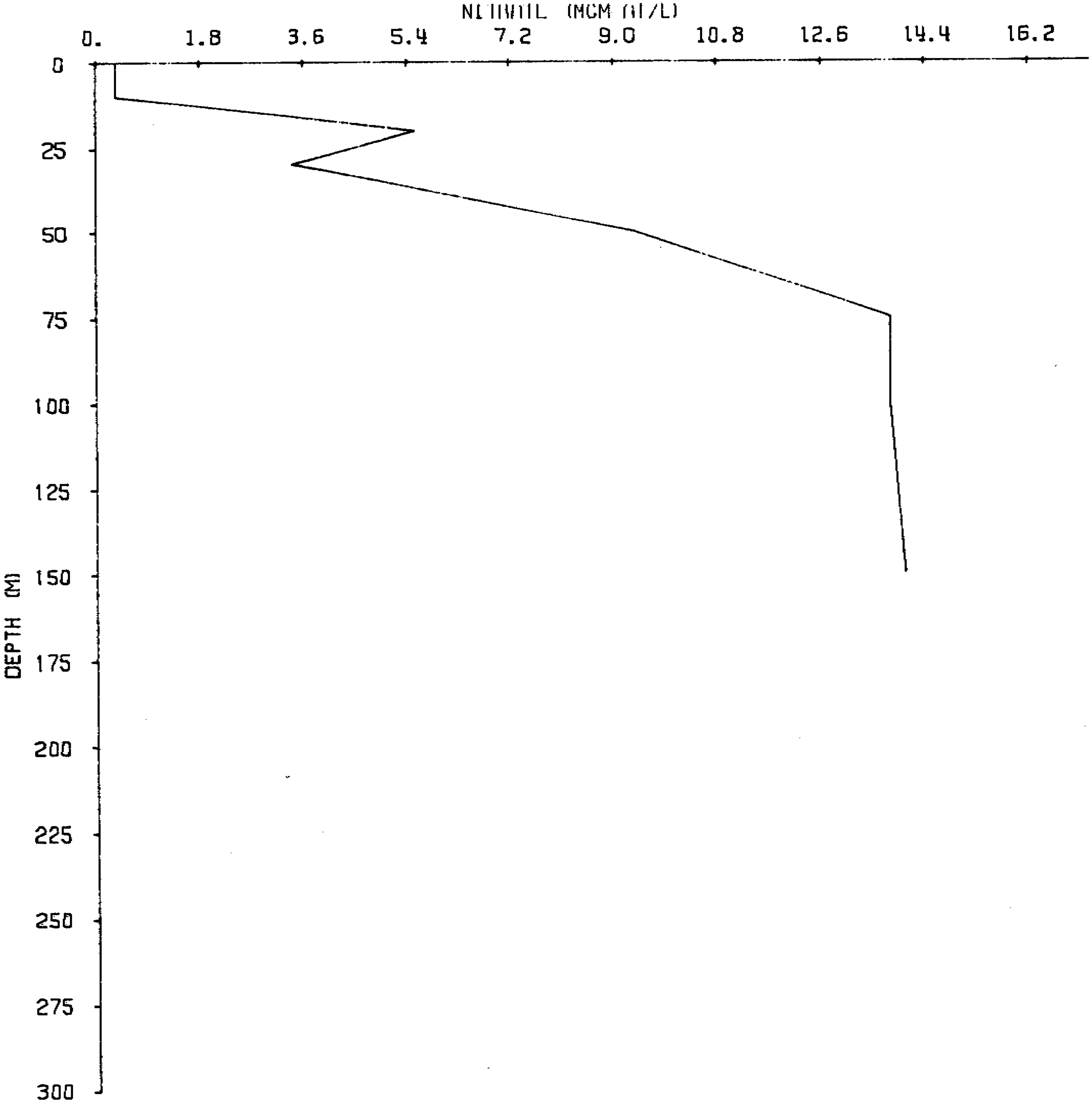
246



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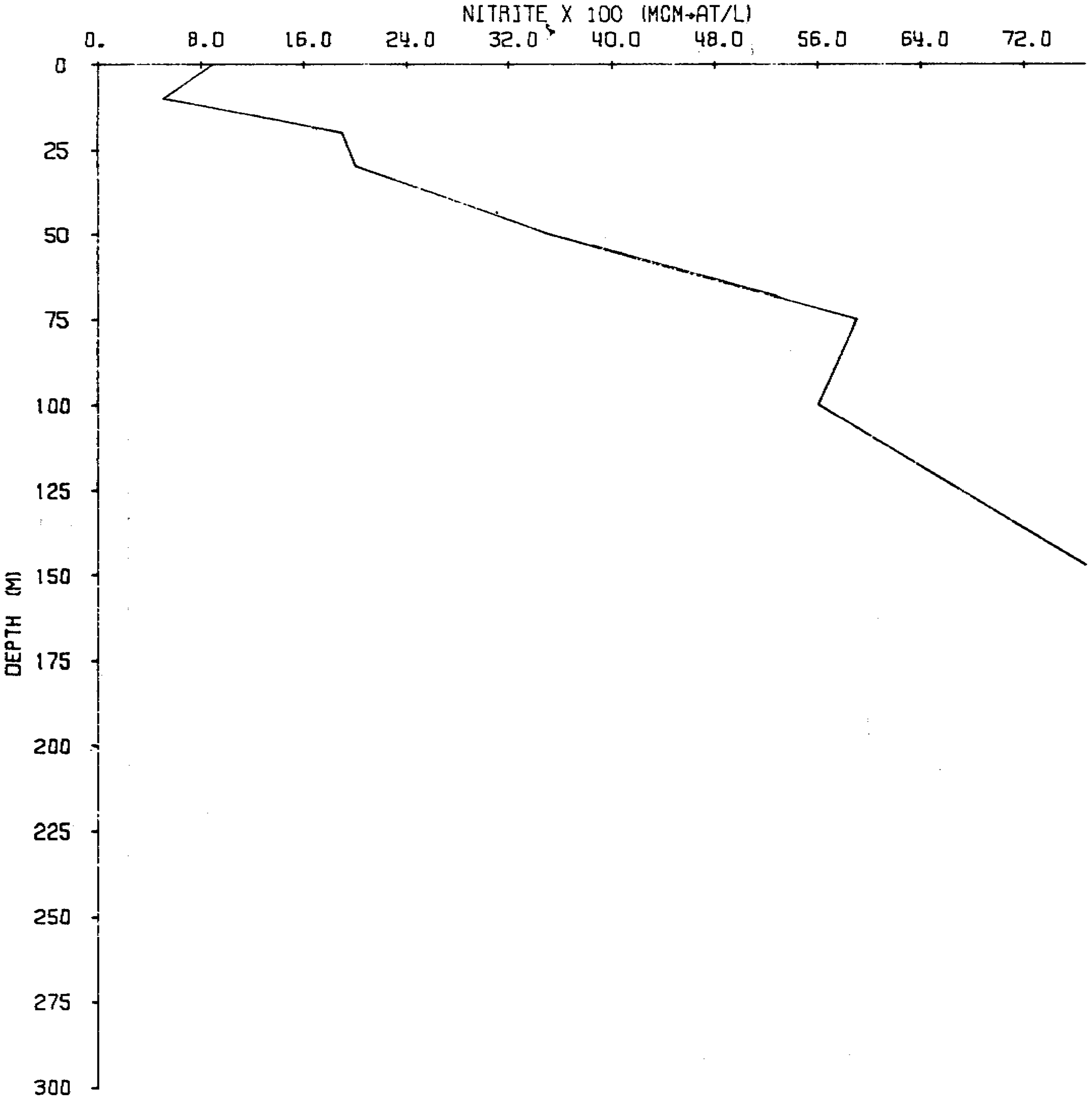

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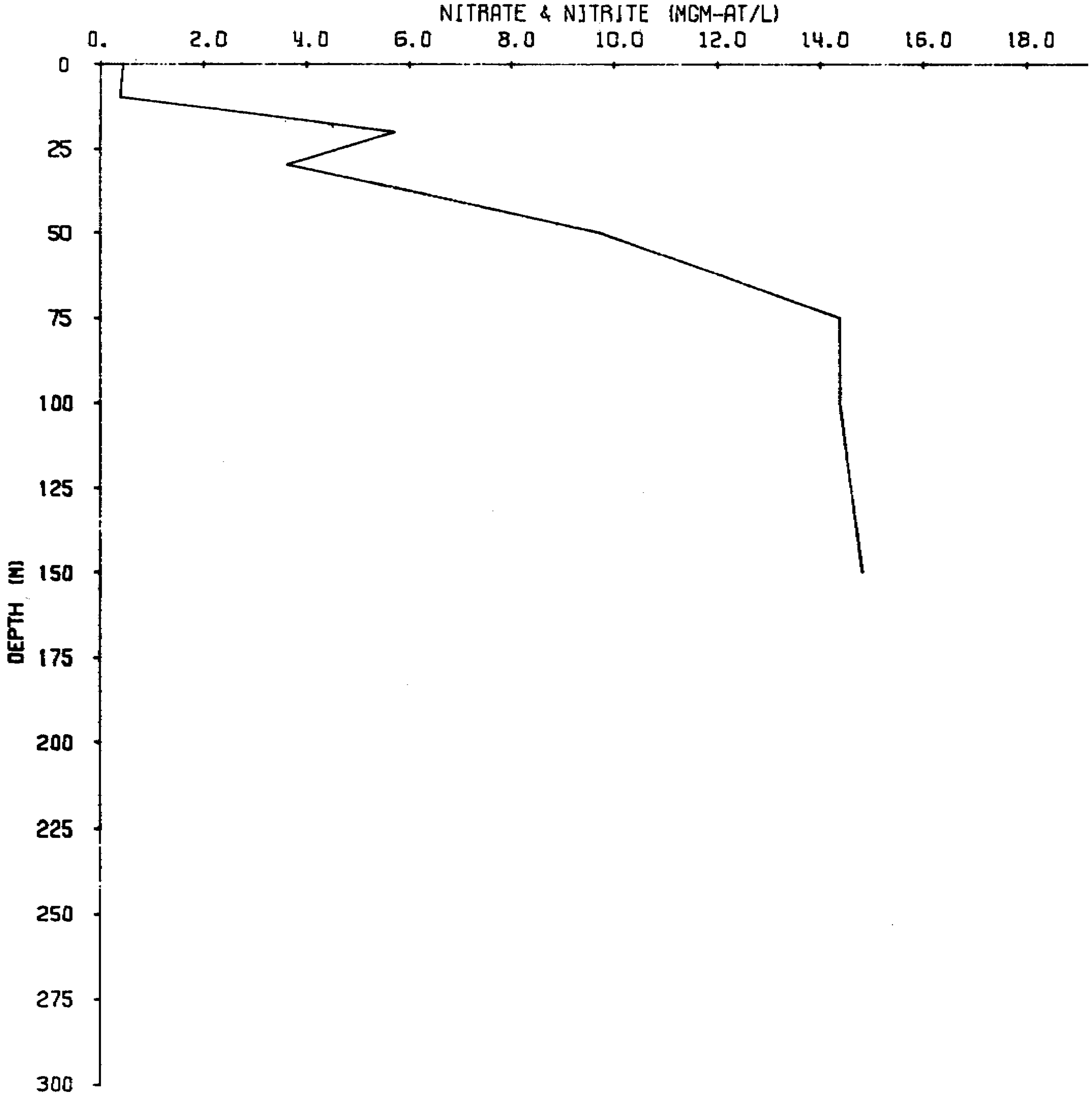

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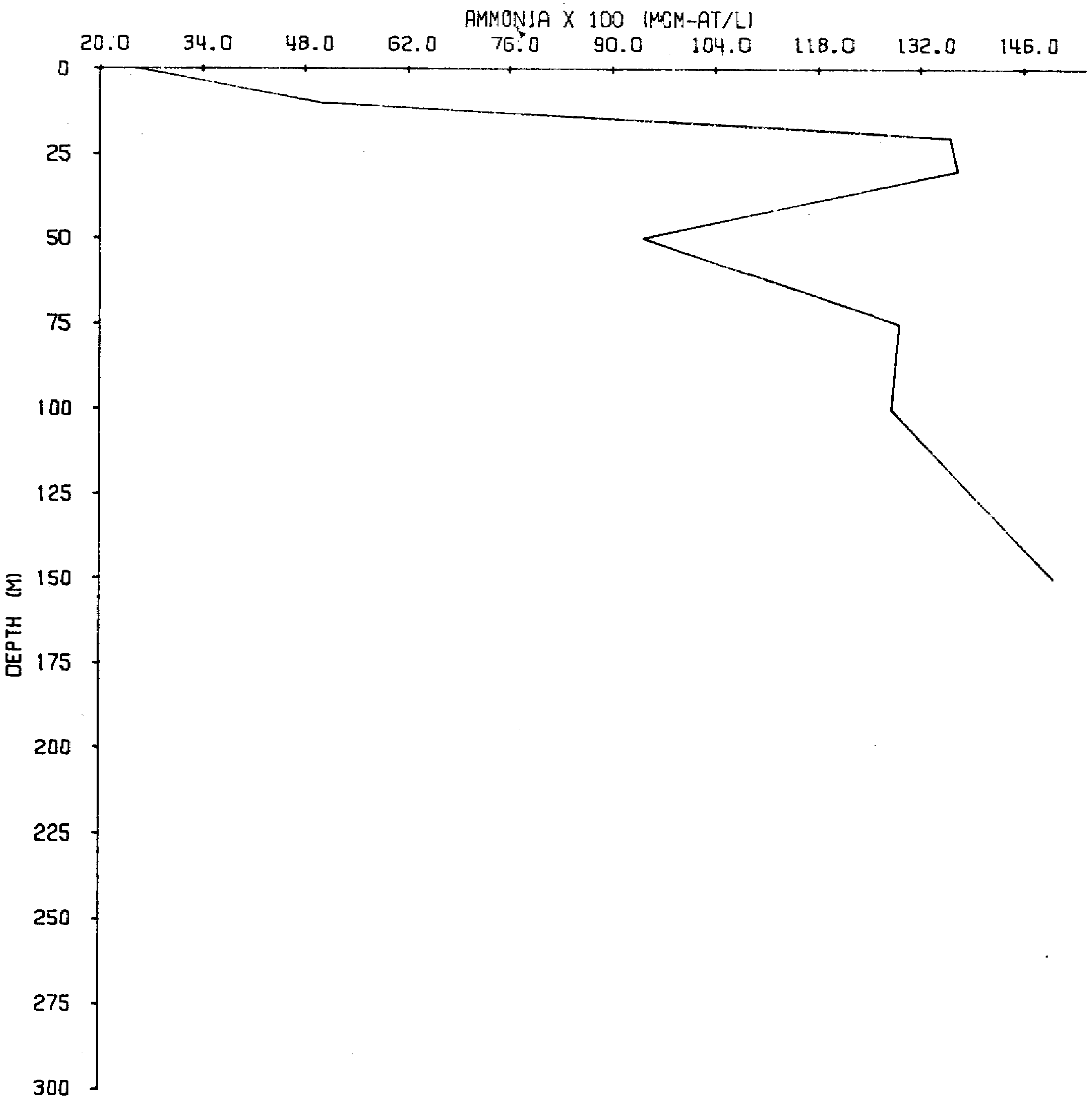

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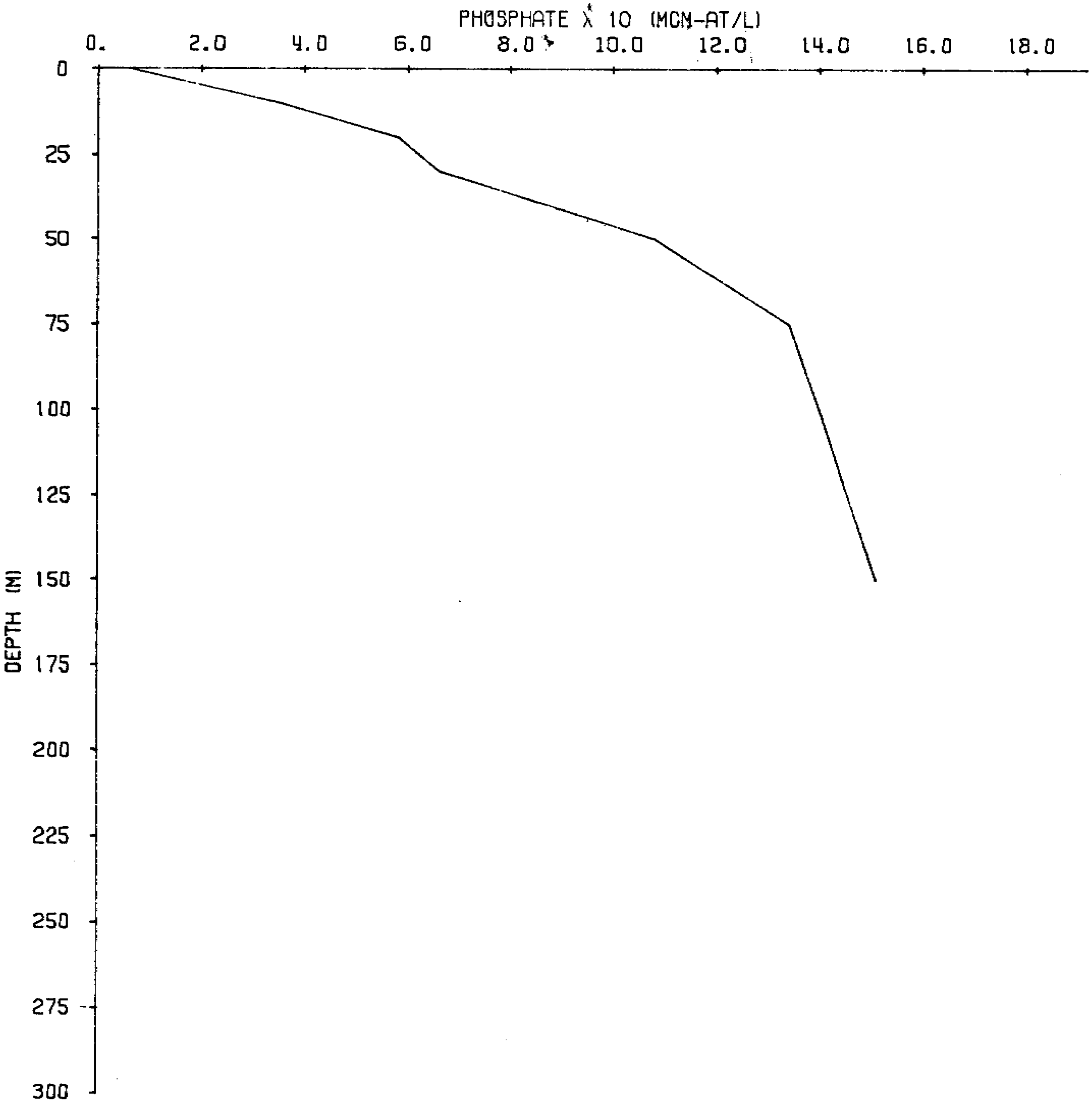

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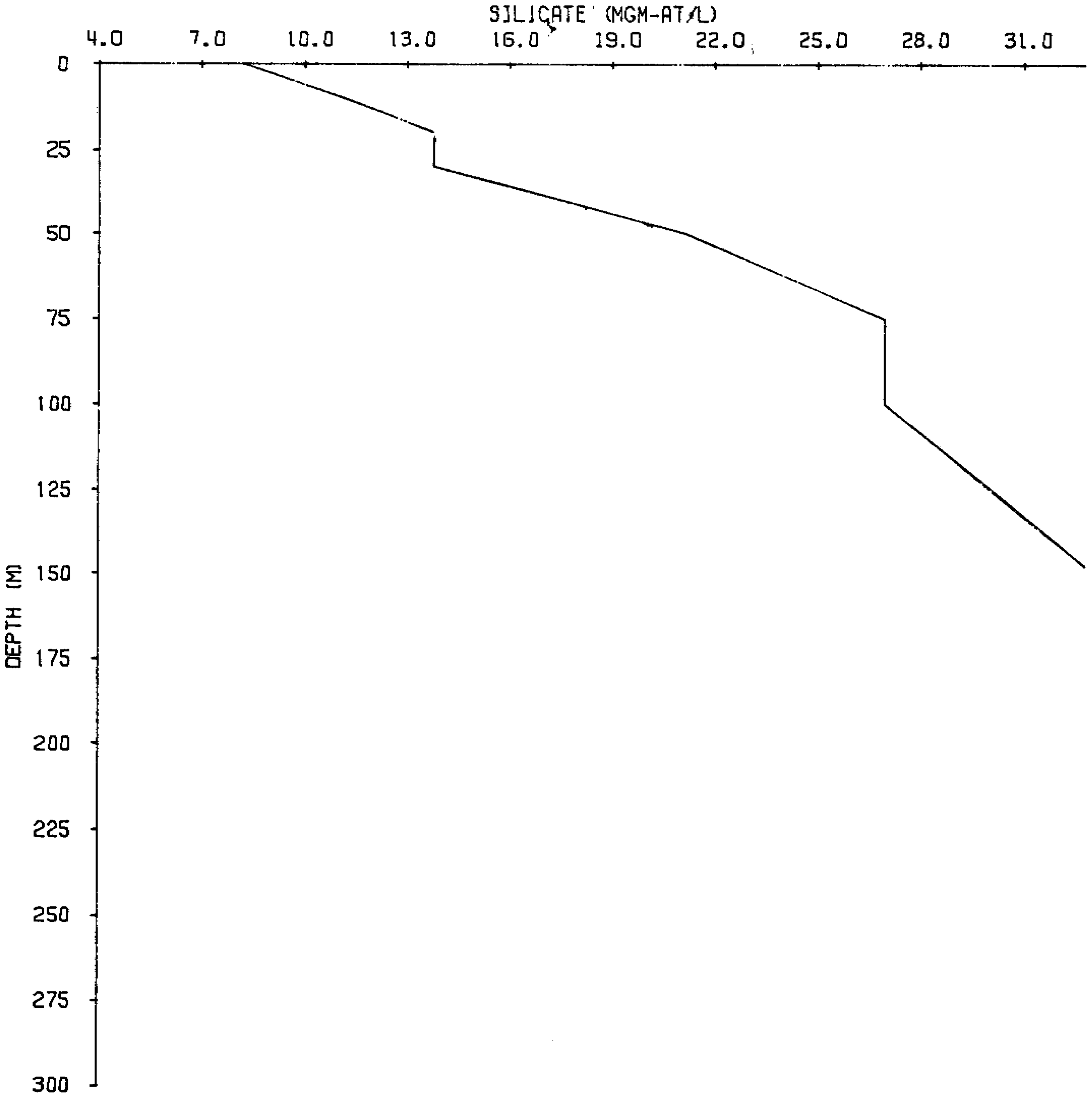

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ANNUAL REPORT

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HYDROCARBONS: NATURAL DISTRIBUTION AND DYNAMICS ON THE ALASKAN OUTER CONTINENTAL SHELF

D. G. Shaw, Principal Investigator

In Collaboration With

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G. Mapes, D. McIntosh, J. Schwartz,
E. Smith, and J. Wiggs

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March 1978

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SECTION I. SUMMARY

This Annual Report presents work completed in our study of the distribution and dynamics of hydrocarbons on the Alaskan outer continental shelf during the period April 1977 through March 1978. A striking finding is the observation that sediments from the Beaufort Sea and from Cook Inlet contain suites of aromatic hydrocarbons. The data indicate that the sources of these hydrocarbons are multiple and complex. It appears that anthropogenic pyrolysis may be a contributing source. This is the first hint that the Alaskan marine environment may not be generally pristine.

We also report studies of the variability involved in hydrocarbon measurement. We report a preliminary statistical treatment of multiple determinations of hydrocarbons in sediment. Although this treatment is not complete, important conclusions can be reached about the relationship of present analytical variability to natural environmental variability. A smaller study of the variability of hydrocarbon determination in biota is also reported.

We report in detail on a study of the interaction of hydrocarbons with suspended sediments of Southcentral Alaska. We present quantitative information about this process, which has been the subject of considerable speculation. Our data show that this is not an efficient process for the transport of hydrocarbons under the conditions investigated.

We also report additional reconnaissance studies of the kinds and amounts of hydrocarbons in the biota of the Bering Sea and Cook Inlet. We also provide information about our intra- and inter-laboratory performance assessments and review previous year's OCSEAP work.

SECTION II. GENERAL INTRODUCTION

This is the third annual report in a continuing study of the distribution and dynamics of hydrocarbons in the Alaskan outer continental shelf. It includes information about hydrocarbons in biota and sediments of the Bering Sea, the Beaufort Sea, and Cook Inlet. The proportion of purely reconnaissance data is smaller than in previous annual reports to OCSEAP. More of the data forms discreet sets from which it is possible to draw general conclusions about hydrocarbons in the Alaskan marine environment. In order to more easily distinguish these data sets and to facilitate their interpretation, a report format has been chosen in which each separately interpretable data set is presented as a Section. This groups all the information (Introduction, Methods, Results, Discussion and References) about a data set together for easier interpretation than the standard OCSEAP format would allow. To put the present work in perspective with this Research Unit's previous results, an appendix is included which summarizes the prior two years.

SECTION III. AROMATIC AND ALIPHATIC HYDROCARBONS IN NEARSHORE BEAUFORT SEA SEDIMENTS

Introduction

Previous work in this laboratory supported by OCSEAP and other agencies showed the presence of aromatic hydrocarbons in sediments of the Beaufort Sea. However, information about the abundance and extent of this class of compounds was sketchy because of the small number of samples examined and variations in analytical procedures. Obtaining a more comprehensive data set on this subject was given a high priority since aromatic hydrocarbons are generally not thought to be associated with pristine environments. It was important to establish how widespread and abundant aromatic hydrocarbons are in this environment before OCS activities.

To meet this objective we collected a suite of nearshore sediment grab samples between Elson Lagoon and Barter Island. The composition of aromatic as well as aliphatic hydrocarbons in these sediments is reported here. Because the presence of these aromatics was somewhat unexpected and because authropogenic sources were an *a priori* possibility, the available information concerning the sources of these materials is discussed in detail. The present work is limited to nearshore sediments; another OCSEAP investigator has collected a suite of offshore sediments.

In recent years there has been increasing interest by organic geochemists and environmental scientists in the distribution of aromatic hydrocarbons in marine and other sedimentary environments (Blumer and Youngblood, 1975; Hites *et al.*, 1977; Hase and Hites, 1976a; Hites and Biemann, 1975; Hites *et al.*, 1977; Youngblood and Blumer, 1975). It has been shown that sediments may contain extremely complex arrays of aromatic hydrocarbons including three, four and five ring aromatic nuclei and zero to ten substituant alkyl carbon atoms. Many isomeric substances exist within this class of components. These isomers are so numerous and so similar that their complete analysis is well beyond the power of analytical chemistry. However, based on the partial characterization which is possible, considerable progress has been made toward understanding their sources.

Youngblood and Blumer (1975) discussed the differences in relative abundances characteristic of fossil hydrocarbons and pyrolytic products of incomplete combustion, two potential sources of aromatic hydrocarbons to sediments. Pyrolysis leads to a kinetically controlled distribution wherein, within a homologous series of alkyl substitution, the unsubstituted aromatic ring system is most abundant and relative abundance drops off quickly and monotonically with increasing alkyl substitution. Low temperature diagenetic processes taking place over geologic time lead to a more thermodynamically controlled distribution in which, within a homologous series, the most abundant member has two to five substituent alkyl carbon atoms and the decrease, particularly toward higher substitution, is more gradual and not necessarily monotonic. Thus, aromatic hydrocarbons from fossil sources such as petroleum or oil shale on one hand, and aromatic hydrocarbons produced during combustion on the other, have quite different relative abundances.

In discussing these homologous series it has become accepted to refer to a series not by the names of parent rings but by specifying the quantity Z where the parent's molecular formula is expressed as C_nH_{2n+z}. Thus, the homologous series based on the isomers anthracene and phenanthrene ($C_{14}H_{10}$) is refered to as "the minus eighteen series" since Z = -18. Youngblood and Blumer (1975) noted that for several sediments whose aromatic hydrocarbons generally had a pyrolytic distribution, the -18 series was anomolous. They suggested that the observed distributions might be the result of overlapping series possibly containing sulfur.

Hase and Hites (1976a) have presented evidence which suggests that aromatic hydrocarbons associated with aquatic sediments are modified in their relative abundances by partitioning into overlying water. This results in dimunition of lower molecular weight, more soluble members of a homologous series.

Hites and co-workers (1977) examined the distribution and abundance of aromatic hydrocarbons in a dated sediment core from Buzzards Bay, Massachusetts Sections dated 1850, 1900 and 1970 all showed pyrolytic distributions; the earliest showed one order of magnitude less total aromatics than the more recent sections. From this it was concluded that, at least in Buzzards Bay, the bulk of the aromatic hydrocarbons are the result of anthropogenic combustion rather than natural fires. The order of magnitude concentration increase in the last century indicates that organisms are currently being exposed to concentrations of these compounds for which they have not had sufficient time to adapt. Blumer *et al.* (1977) have presented data which suggests a link between sedimentary aromatic hydrocarbons and human cancer mortality.

Several reports suggest that complex mixtures of aromatic hydrocarbons in sediments might result from microbial activity. This suggestion was countered on a theoretical basis by Youngblood and Blumer (1975) with the argument that the enzymatically controlled processes of microbes (and other biota) would be expected to lead to only one or a few aromatic structures and that the great variety of structures observed was more characteristic of non-enzymatic geochemical reactions. Hase and Hites (1976b) in careful experimentation with a mixed culture of anaerobic bacteria collected from a sedimentary environment known to contain a complex mixture of aromatic hydrocarbons showed bioconcentration but not biosynthesis.

Some marine sediments have been investigated which contain one aromatic hydrocarbon: perylene. Brown *et al.*(1972) determined perylene in a 35 m core from Saanich Inlet, British Columbia. Four analyses showed concentrations increasing with depth from 0.3 to 2.4 ppm giving evidence of *in situ* formation. Aizenshtat (1973) has demonstrated the existance of perylene in a variety of marine sediments and discussed possible pathways for its geochemical conversion from biosynthetic pigments.

Methods

A suite of van Veen grab samples was collected in August 1977 at the stations shown in Table III-I and Figure III-1. In the laboratory each sediment sample was extracted for 48 hours with equal parts methanol and benzene in Soxhlet apparatus. The extract was partitioned into hexane, backwashed with aqueous sodium sulfate. After concentration to 10 ml, free sulfur was removed by reaction with elemental copper. The sample was carefully concentrated to near dryness and taken up in hexane for column chromatography on silica gel (5% water). The column was eluted with hexane to obtain an aliphatic fraction and with 40% benzene in hexane to obtain an aromatic fraction. Each fraction was first analyzed quantitatively by flame ionization gas chromatography (FIGC) (Hewlett Packard Model 5710) using a 50 m by 0.7 mm i.d. support coated open tubular (SCOT) column in which the stationary phase was OV-101 together with a lesser amount of

TABLE III-1

BEAUFORT SEA STATIONS

	N. Latitude	W. Longitude	Depth (m)
1. Plover Islands	71°14'	155°30'	7
2. Smith Bay	70°58.6'	154°30.1'	5
3. Pitt Point	70°56.5'	153°15.3'	5
4. Cape Halkett	70°46.8'	151°56.3'	7
5. Atigaru Point	70°36.7'	151°33.5'	5
6. Colville River Delta	70°33.4'	150°25.0'	5
7. Oliktok Point	70°32.0'	149°55.5'	3
8. Simpson Lagoon	70°31.8'	149°39.0'	2
9. Pingok Island	70°34.5'	149°29.0'	11
10. Egg Island	70°27.1'	148°43.7'	3
11. Stump Island	70°24.1'	148°32.6'	2
12. Sagavanirktok River Delta	70°22.3'	148°07.6'	2
13. Cross Island	70°29.5'	148°02.8'	9
14. Stockton Island	70°18.0'	147°02.0'	4
15. Maguire Islands	70°11.8'	146°27.2'	3
16. Canning River Delta	70°03.4'	145°18.0'	8
17. Anderson Point	70°01.6'	144°32.3'	8
18. Hulahula River Delta	70°05.7'	144°05.0'	5
19. Barter Island	70°07.9'	143°48.0'	8
20. Tapkaurak Entrance	70°08.3'	143°11.3'	4

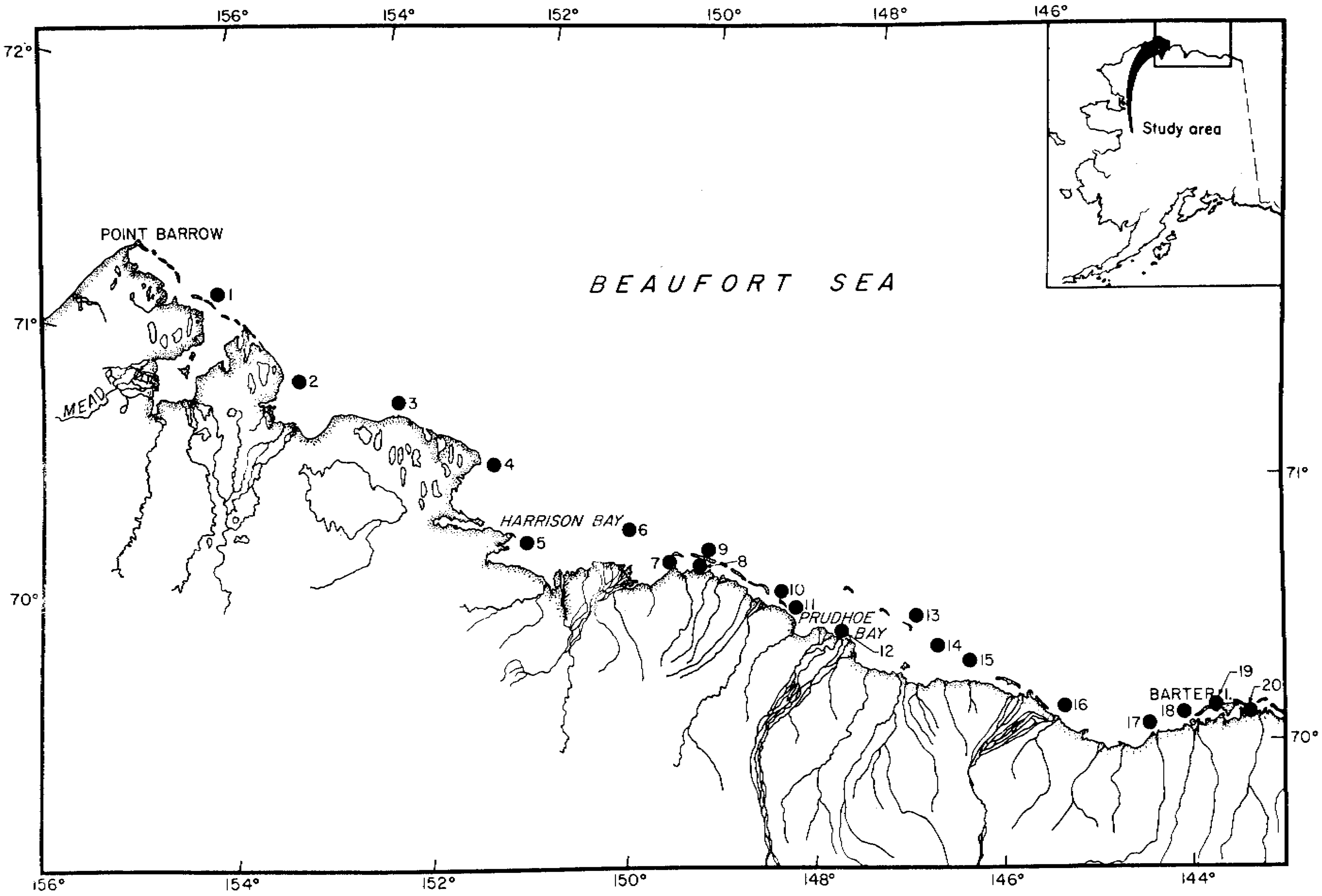

Figure III-1. Beaufort Sea sediment collection locations. Station names are given in Table III-I.

Carbowax 20M. Quantification was accomplished by a digital integrater (Hewlett Packard model 3380 or 3385). Quantitative results have been corrected for percent recovery.

Further analysis of the aromatic fractions was accomplished using a gas chromatograph-mass spectrometer (GC-MS) system consisting of a Hewlett Packard 5710 gas chromatograph, a Hewlett Packard 5930 mass spectrometer and a Hewlett Packard 5933 data system. Samples were injected unsplit onto a SCOT column similar to the one described above. The total effluent was introduced into the ion source of the spectrometer. Ionization was achieved with a beam of 70 volt electrons. The scan rate was 108.3 amu sec^{-1} from 80 to 350 amu for the first 20 minutes and thereafter from 80 to 500 amu. Mass spectral data was computer processed and presented as plots of total ionization versus time, and as plots of single ion intensities versus time (mass chromatograms). Amounts of alkylated and unsubstituted aromatics were estimated from the mass chromatograms of the molecular ions by integrating with the computer the appropriate peak or group of peaks. Individual mass spectra corresponding to peaks in the total ion plots and mass chromatograms were examined and compared to spectra of authentic compounds from our laboratory or to published spectra.

The estimations of relative abundance are semi-quantitative at best in that they are based on the assumption uniform intensity of the molecular ions of all of the compounds analyzed. This is probably not a bad assumption since aromatic hydrocarbons as a group have strong molecular ions. However, it is also probable that it leads to a systematic underestimation of higher alkyl homologs since it is in the alkyl portions that fragmentation is more ready. While no information on the relative intensities of alkylated aromatic hydrocarbons exists which is completely applicable to the mass spectral conditions and compounds of this study, the available data (Schiller 1977) suggests that these differences in sensitivity may be minor. In any case, samples of potential source materials have been analyzed under the same mass spectral conditions to ensure the validity of comparisons.

Aliphatics

Results

Most samples contained detectable quantities of all normal alkanes with between 17 and 31 carbon atoms (Table III-II). In a few samples of coarser sediments, such as Canning River Delta, Sagavanirktok River Delta, and Tapkaurak Entrance some of these compounds were undetectable or present in trace amounts. In most samples heptacosane was the most abundant compound being 10% to 20% of the total aliphatics. All aliphatic fractions were dominated by odd chain length normal alkanes having 23 to 31 carbon atoms. Pristane and phytane were present in detectable quantities, their ratio generally being in the range 1 to 3 with pristane more abundant. Heptadecane was frequently more abundant than the adjacent normal alkanes. The mean total aliphatic concentration in these 20 samples was 4.7 $\mu g\ g^{-1}$; all values were in the range 0.1 to 12.5 $\mu g\ g^{-1}$.

Discussion

The picture of aliphatic hydrocarbons in nearshore sediments of the Beaufort Sea which emerges from these analyses is of an environment dominated by biogenic compounds with few abiotic and no anthropogenic components. This is indicated by the dominance of odd chain length normal alkanes with 23 to 31 carbon atoms. These compounds, important constituents of higher plant waxes, typically occur in nearshore marine sediments as the result of inputs of terrigenous detritus. Biogenic origin is also indicated by the presence of heptadecane and pristane, two compounds characteristic of many marine plankton. Phytane is thought to be produced geochemically from the phytol side chain of chlorophyll in anaerobic environments or micro-environments of recent sediments. Thus, the presence of phytane may be the result of a minor abiotic alteration of biosynthetically produced organic material. In short, the major aliphatic hydrocarbons of these sediments can simply be attributed to modern biogenic sources. This is in contrast to the more complex array of aromatic hydrocarbons considered next.

TABLE III-II

HYDROCARBONS IN BEAUFORT SEA SEDIMENTS (ppm dry weight)

Sample ID	Total Saturates	Total Unsaturates	C_{14}	C_{15}	C_{16}	C_{17}	Prist.	C_{18}	Phyt.	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	C_{32}	Peryl.*	Comments
Plover Island	11.5	2.3	.10	.12	.13	.16	.14	.18	.05	.31	.26	.97	.50	1.43	.55	1.22	.31	1.63	.16	1.17	.39	1.08	.16	.45	Contained sulfur, sandy sed., bottom of sample jar cracked
Smith Bay	0.9	0.1	–	–	–	.02	.02	.02	.01	.03	.02	.05	.04	.09	.03	.09	.02	.09	.01	.07	.03	.06	–	–	Sandy with small rocks
Pitt Point	3.0	<.01	–	–	–	.03	.07	.09	–	.10	.08	.21	.15	.43	.12	.38	.08	.47	.05	.34	.08	.26	–	–	
Cape Halkett	1.1	0.1	–	–	–	.08	–	.05	–	.04	.03	.08	.06	.13	.04	.12	t	.14	t	.11	t	.08	–	–	Sandy sediments
Atigaru Point	4.7	<.01	–	–	–	.08	.09	.09	.04	.14	.11	.25	.15	.41	.13	.37	.12	.52	.18	.47	.30	.36	–	–	
Colville Delta	12.5	7.3	.18	.20	.22	.25	.22	.21	.08	.33	.25	.62	.41	1.47	.37	1.26	.26	2.49	.16	1.08	.39	1.00	.19	1.71	Contained sulfur
Oliktok Point	12.1	1.7	–	–	–	.15	.13	.15	.05	.23	.07	.45	.31	.91	.30	.90	.26	1.46	.40	1.43	.95	1.37	t	–	
Simpson Lagoon	6.0	1.9	.04	.05	.06	.08	.07	.06	.02	.15	.15	.36	.20	.60	.21	.59	.14	.77	.06	.55	.38	.57	.14	.44	Contained sulfur
Pingok Island	7.8	2.3	.03	.04	.04	.06	.06	.04	.01	.09	.08	.24	.14	.36	.16	.36	.09	.48	.05	.35	.16	.04	.07	.62	Contained sulfur, used pressure to run column
Egg Island	4.9	1.8	.03	.05	.06	.09	.07	.06	.02	.12	.11	.41	.20	.53	.18	.55	.12	.74	.07	.57	.22	.04	.14	.32	Contained sulfur, sandy sed.
Stump Island	7.3	0.2	t	t	t	.10	.07	.08	.03	.14	.22	.28	.18	.51	.17	.52	.16	.81	.31	.92	.51	.87	–	–	
Sagavanirktok Delta	0.5	0.1	–	–	t	.01	.01	.02	.01	.02	.03	.03	.02	.03	.01	.02	.01	.03	t	.02	t	.02	–	–	Sandy sediment
Cross Island	2.6	0.1	t	t	t	.04	.01	.05	.02	.07	.06	.21	.07	.17	.06	.18	.05	.26	.06	.33	.13	.25	t	–	
Stockton Island	4.2	0.2	t	t	t	.12	.08	.09	.03	.14	.09	.30	.16	.39	.13	.43	.09	.53	.05	.48	.12	.33	t	–	
Maguire Island	3.8	0.7	.02	.05	.07	.09	.09	.10	.03	.12	t	.29	.17	.38	.18	.40	.10	.58	.06	.46	.19	.33	.13	.14	
Canning Delta	0.1	<.01	–	–	–	t	–	t	–	–	–	t	t	t	–	t	–	t	–	t	–	–	–	–	Sandy sediment
Anderson Point	4.7	1.8	.02	.06	.04	.10	.07	.05	.02	.13	.09	.41	.18	.44	.22	.49	.11	.75	.08	.63	.23	.47	.14	.37	
Hulahula Delta	3.9	1.2	–	.02	.01	.09	–	.02	–	.08	.05	.21	.13	.34	.11	.33	.08	.62	.05	.53	.02	.44	.20	.32	
Barter Island	1.7	0.5	–	–	t	.06	t	.04	t	.07	.63	.11	.07	.19	.04	.21	.04	.34	t	.24	.10	.17	t	–	
Tapkaurak Entrance	0.2	0.1	–	–	–	–	–	–	–	–	t	.03	.01	.03	.03	.03	t	.05	t	.03	–	.02	–	.05	Contained sulfur, sandy sed., used pressure to run column

* Approximate amount

t means there is a visible peak but the integrator did not report an area

Aromatics

Results

The concentrations of total aromatic hydrocarbons determined by FIGC are shown in Table III-II. Mass chromatograms of parent peaks of aromatic ring systems and their alkyl homologs revealed the presence of complex mixtures of these compounds in each of the 17 samples examined. The remaining three samples, Canning River Delta, Sagavanirktok River Delta, and Tapkaurak Entrance had insufficient material for this analysis. The relative abundance of various homologous series for each sample are shown in Table III-III. These distributions are fairly uniform, at least compared to the range in variability shown by potential source materials in Table III-IV.

Prudhoe Bay crude oil was included among the potential source materials since it is the only available North Slope crude. There have been no major oil field accidents in which this material has been lost to the Beaufort Sea. Furthermore, it is produced from a well pressurized formation; natural seepage is unlikely. We obtained and analyzed asphaltic material from a natural seep area on shore near Cape Simpson, northwest of Smith Bay. However, the aromatic fraction of that material contained only structures with higher degrees of alkyl substitution than any of the sediments or other potential source materials. Diesel exhaust particulates were obtained by trapping on a glass wool plug material from a stationary engine. Coal collected from an outcrop on the Mead River (Fig. III-1) is assumed to be representative of the coal beds which are known to occur onshore in the western portion of the study area (Smith and Mertie 1930). An aromatic extract of particulates in winter air of Fairbanks, Alaska was prepared by a procedure similar to that described above and analyzed by the methods described here.

The relative abundances of alkyl homologs within homologous series were also determined. These results for the sediment samples are presented graphically in Figures III-2, III-3 and III-4; and for the potential source materials in Figure III-5. As discussed below, much useful information can be gained by interpretation of these homolog plots. However, because of the abundance of isomers (both in the larger ring systems and in alkyl

TABLE III-III

RELATIVE ABUNDANCE OF HOMOLOGOUS SERIES OF AROMATIC HYDROCARBONS FROM BEAUFORT SEA SEDIMENTS

	(-12)	(-16)	(-18)	(-22)	(-24)	(-28)
Plover Island	37.0	9.7	27.5	12.2	5.7	8.0
Smith Bay	47.6	7.7	17.2	13.7	7.1	6.7
Pitt Point	42.2	3.7	35.3	11.3	4.4	3.0
Cape Halkett	29.1	15.5	26.4	14.8	7.1	7.3
Atigaru Point	39.5	13.6	25.6	12.9	6.8	0.2
Colville Delta	42.0	8.7	25.9	12.1	4.5	7.0
Oliktok Point	48.2	9.3	16.0	11.7	7.5	7.3
Simpson Lagoon	32.3	9.0	30.8	13.4	6.1	8.3
Pingok Island	27.4	10.3	28.0	14.6	7.4	12.3
Egg Island	27.2	10.2	28.8	14.1	7.7	11.9
Stump Island	55.5	7.0	16.8	12.3	5.1	3.2
Cross Island	38.9	9.4	27.6	16.0	7.4	0.5
Stockton Island	41.2	11.8	21.3	17.1	8.1	0.4
Maguire Island	26.7	11.5	33.5	13.2	7.0	8.2
Anderson Point	28.1	8.7	33.6	10.5	6.0	13.3
Hulahula Delta	62.9	6.5	23.1	4.8	1.0	0.8
Barter Island	51.1	7.5	17.6	9.1	6.5	8.3

TABLE III-IV

RELATIVE ABUNDANCE OF HOMOLOGOUS SERIES OF AROMATIC HYDROCARBONS FROM POTENTIAL SOURCE MATERIALS

	(-12)	(-16)	(-18)	(-22)	(-24)	(-28)
Prudhoe Crude Oil	76.5	7.5	12.2	2.7	1.0	0
Diesel Fuel	92.3	4.3	3.4	0	0	0
Diesel Exhaust	39.0	8.4	28.4	21.6	0.8	0
Mead River Coal	18.8	17.6	18.9	28.4	12.0	4.3
Fairbanks Air	1.9	0.3	16.4	39.4	27.2	11.6

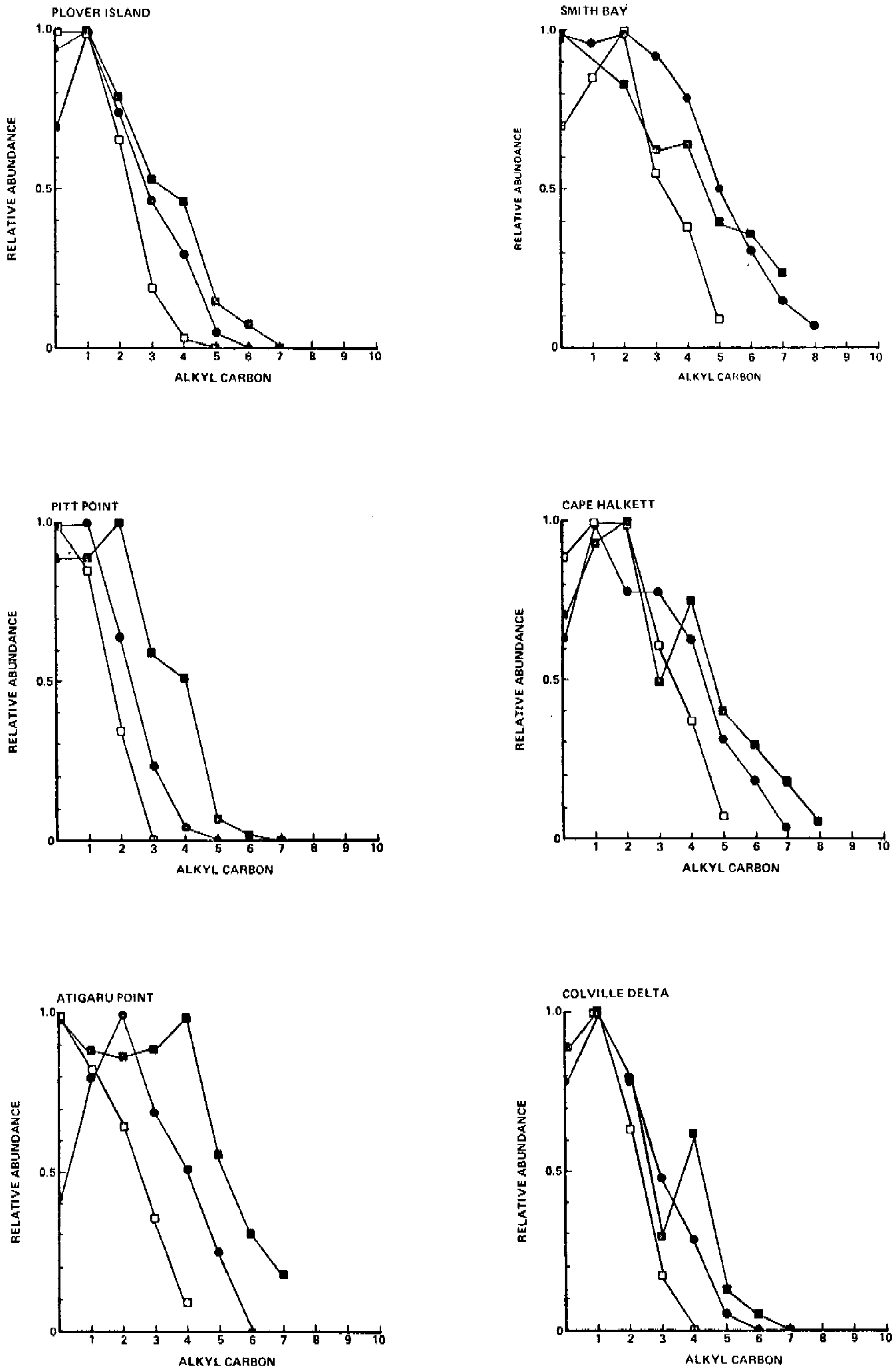

Figure III - 2. Relative abundances of polycyclic aromatic hydrocarbons and their alkyl homologs for nearshore Beaufort Sea sediments. Solid squares represent the -18 series; solid circles, the -22 series; and open squares the -24 series. Each series is separately normalized.

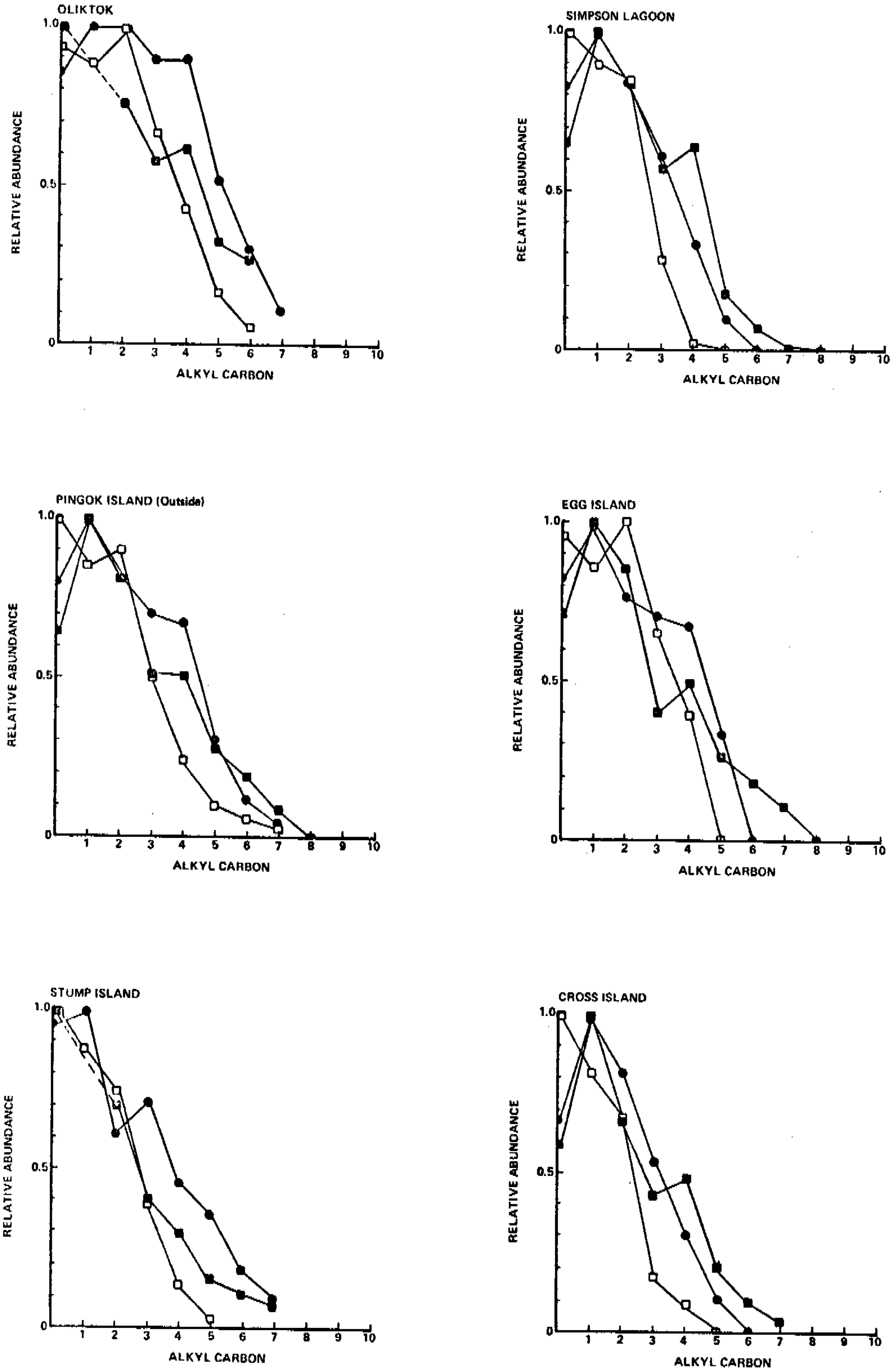

Figure III - 3. Relative abundances of polycyclic aromatic hydrocarbons and their alkyl homologs for nearshore Beaufort Sea sediments. Solid squares represent the -18 series; solid circles, the -22 series; and open squares the -24 series. Each series is separately normalized.

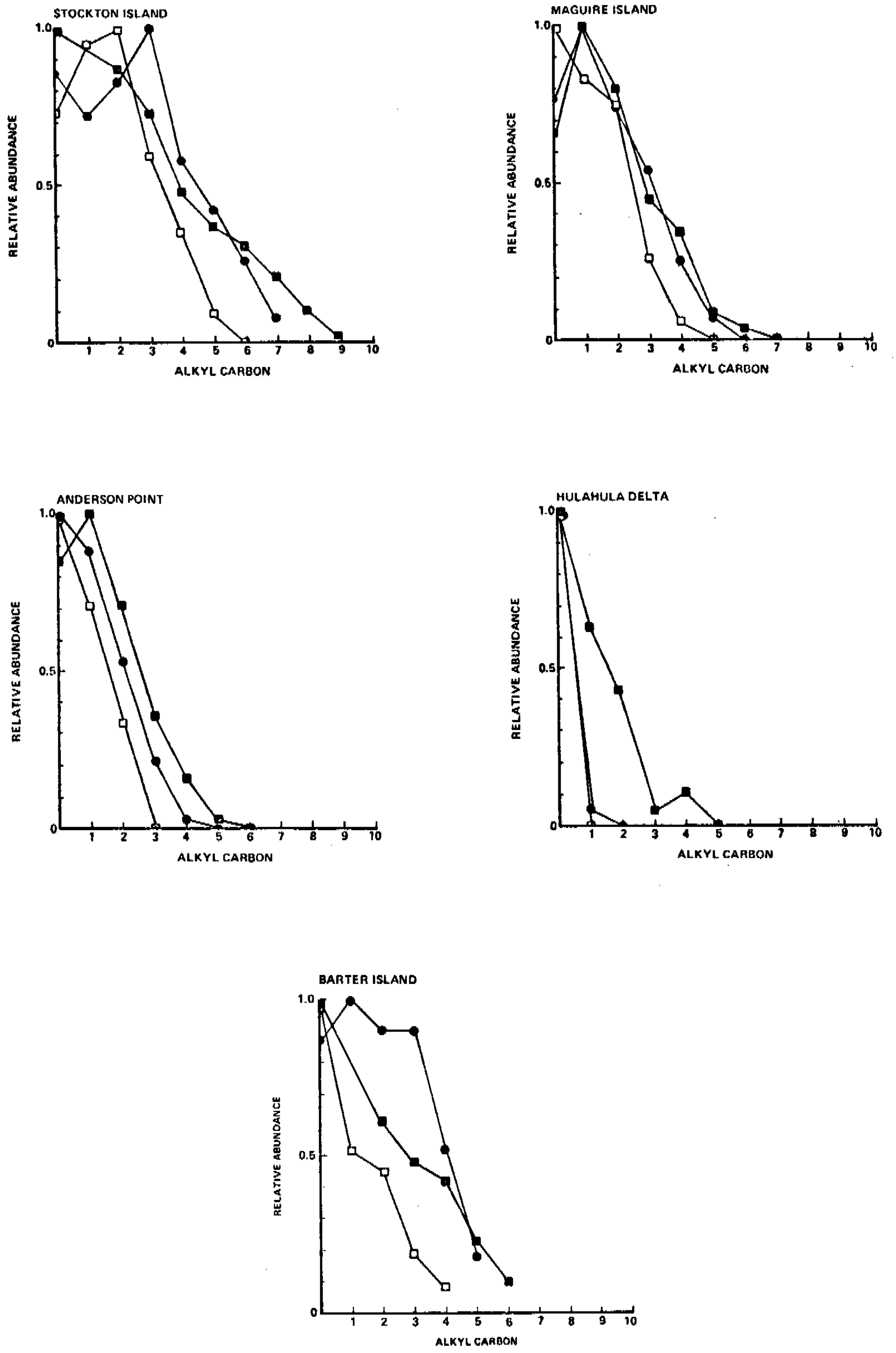

Figure III - 4. Relative abundances of polycyclic aromatic hydrocarbons and their alkyl homologs for nearshore Beaufort Sea sediments. Solid squares represent the -18 series; solid circles, the -22 series; and open squares the -24 series. Each series is separately normalized.

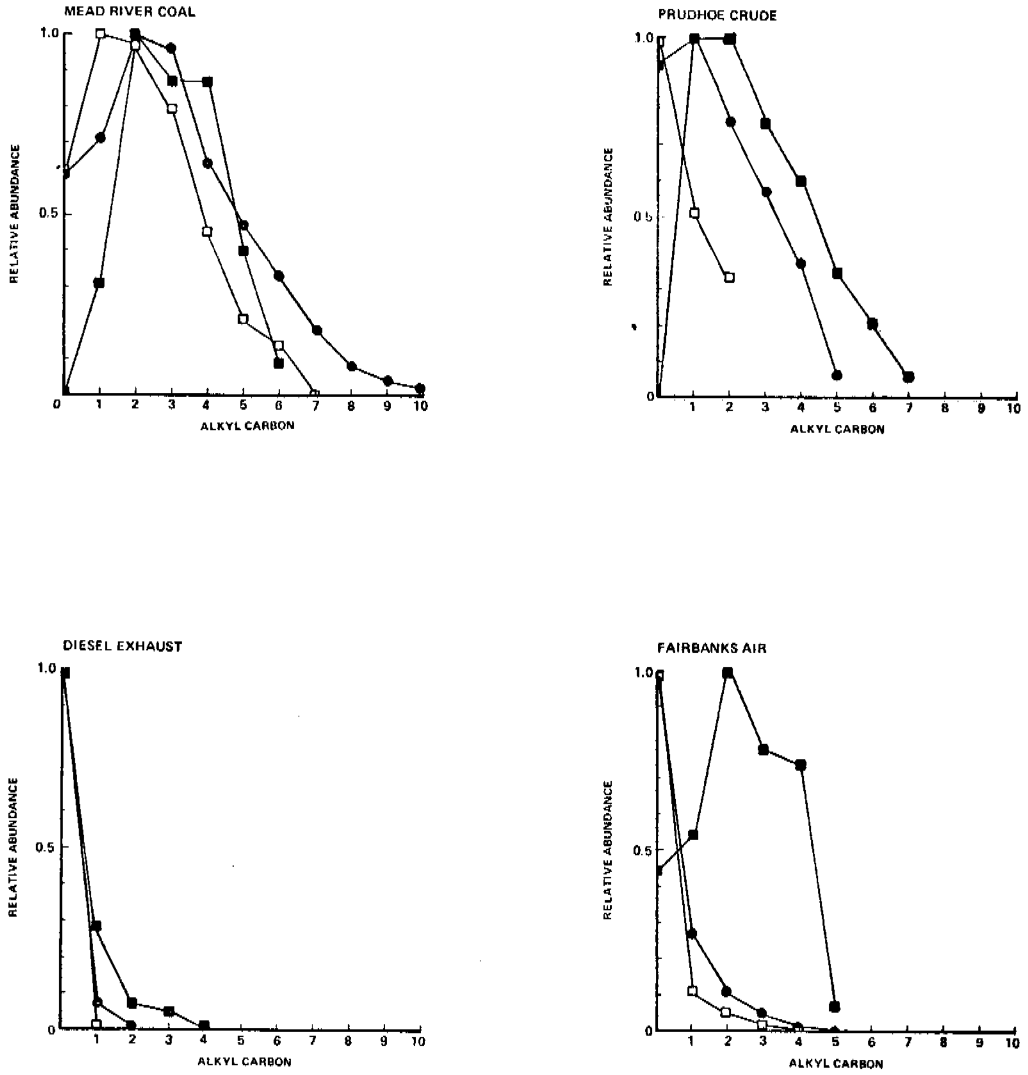

Figure III - 5. Relative abundances of polycyclic aromatic hydrocarbons and their alkyl homologs for potential source materials. Solid squares represent the -18 series; solid circles, the -22 series; and open squares the -24 series. Each series is separately normalized.

substitution patterns) these plots do not deal with individual structurally defined compounds. In a few cases we have been able to identify individual aromatic hydrocarbons derived from compounds synthesized by terrestrial plants. Cadalene (1,6-dimethyl-4-isopropylnaphthalene) was identified in all 17 samples subjected to mass spectral analysis. Identification was based on the fact that the mass spectrum of the found material was indistinguishable from a spectrum of cadalene published by Bendoraitis (1974), who identified the substance in crude oils. Cadalene is thought to result from the diagenetic alteration of cadinene and other sesquiterpenes from higher plants. We also found cadalene in Mead River coal but not in Prudhoe Bay crude oil. Two well known products of the diagenesis of the diterpene abietic acid, another constituent of higher plants, were found. One of these compounds, retene (1-methyl-7-isopropylphenanthrene) was identified by the indistinguishability of the found material's mass spectrum from the published spectrum of authentic material (Simoneit, 1977). Retene was found in all sediment extracts, Mead River coal, Prudhoe Bay crude oil and even Fairbanks air. In several samples the abundance of retene was great enough to produce a distinct peak at the C_4 homolog in the -18 series. This is most striking in the homolog plot for Colville Delta sediment (Fig. III-2) and is present in several other plots. The other abietic acid derivitive, simonellite (1-methyl-7-isopropyl-1,2,3,4-tetrahydrophenanthrene), was also identified based on indistinguishability of the observed and authentic mass spectra. In this case the authentic spectrum was supplied by B. Simoneit (personal commun.). Simonellite was found in most sediment samples. Mass spectrometry of several sediments showed several other compounds with molecular ion m/e ratios of 256, 268, 270, and 274. These were not identified but probably were diterpenoid and possibly related to abietic acid.

Discussion

A striking feature of the relative abundances of the various homologous series shown in Table III-III is the substantial fraction of the -12 series (naphthalenes) in most sediments. Selective removal by aqueous solution of this most soluble series as suggested by Hase and Hites (1976a) is not effectively controlling the relative abundance of aromatic hydrocarbons in this environment. This may be a reflection of arctic environmental conditions where water temperatures are always cold and the ocean is ice covered for nine months of the year, both of which would tend to retard solution into the water column and transfer to the atmosphere. In addition, it cannot be ruled out that the rate of input of aromatic hydrocarbons to the nearshore Beaufort Sea is simply great enough to make up for solution losses.

Further information comes from the abundance of the -12 series in the sediments when these data are compared to those for the potential source materials shown in Table III-IV. The -12 series comprises 35-50% of most sediments. Thus, Mead River coal and atmospheric particulates appear to be insufficient sole sources of the sedimentary aromatics, since it is unlikely that any important natural process will result in the relative enrichment of the most soluble homologous series. A mixture of petroleum or some other source rich in the -12 series seems a more likely way to explain the concentration of the -12 series observed in these sediments.

The homolog plots for sediments and potential source materials, Figures III-2 - III-5, have many characteristics in common with similar plots reported by Youngblood and Blumer (1975). The plots of Prudhoe Bay crude oil and Mead River coals are quite similar to plots for petroleums and oil shales of Youngblood and Blumer. All have the characteristic distribution of low temperature, thermodynamically controlled formation described above. Similarly, the diesel exhaust plot in Figure III-5 is very much like Youngblood and Blumer's plot for wood pyrolysate, both showing the kinetically controlled homolog distribution. The Fairbanks winter air homolog plot (Fig. III-5), however, has the pyrolysate distribution for the -22 and -24 series but a fossil hydrocarbon distribution for the -18 series. This type of distribution is also seen in several of the plots reported by Youngblood and Blumer for recent New England sediments. Mass spectral analysis of the Fairbanks air extract indicated the probable presence of retene. The source of this material may be uncombusted coal soot entering the Fairbanks air at a coal fired electrical generating plant about 1 km from the sampling site. Mixture of such soot with combustion products of petroleum and coal might give rise to the observed distribution. Youngblood and Blumer suggested that the enhanced abundance of C_4 of the

-18 series (m/e 234) particularly observed in soil samples might be due to the presence of substituted thiophenes. We suggest that their observed enhancement at m/e 234 may have been in part due to retene either produced *in situ* from abietic acid or associated with the historical use of coal in New England. The presence of retene and its abietic acid derived cogeners appears to be a reasonable explanation of the fossil hydrocarbon distribution of the -18 series in New England sediments where the -22 and -24 series and the temporal distribution (Hites *et al.*, 1977) suggest pyrolytic sources. This same mixture of retene to an otherwise pyrolytic homolog distribution is shown for the Hulahula Delta extract (Fig. III-4) and to a lesser extent by the extracts from Anderson Point (Fig. III-4), Pitt Point (Fig. III-2) and Plover Island (Fig. III-2). The major regional centers of human activity, fuel consumption and thus pyrolysis products are Barrow and Prudhoe Bay (Fig. III-1). If these locations were the sources of the observed pyrolysates we would expect concentration gradients away from them (which were not observed) and the pyrolytic signature near these sources. Another possible source of pyrolytic materials is long distance transport from lower latitude sources.

The homolog plots for the remaining 13 sediments show distributions which suggest greater inputs of fossil hydrocarbons. The presence of cadalene, retene and simonellite in detectable quantities further supports the importance of fossil sources. These three terpenes are more abundant in Mead River coal than Prudhoe Bay crude oil. In fact, cadalene could not be detected the latter material. But, Mead River coal cannot be the sole source of these aromatic hydrocarbons based on its low relative abundance of the -12 series discussed above. Another potential source of cadalene, retene and simonellite are the onshore peat beds of the area which are eroding into the sea. Retene and simonellite have been isolated from other peats (Streibl and Herout 1969). However, peat is not a likely source of the wide range of -12, -18, -22, and -24 series aromatic hydrocarbons present in these sediments. In addition, other potential sources exist which have not yet been evaluated. Fragments of oil shale have been reported in the Mead River (Smith and Mertie 1930). It is not unlikely that undiscovered coal or oil shale outcrops or oil seeps exist in the nearshore Beaufort Sea. Fossil hydrocarbon inputs from the Mackenzie River are also possible since its drainage includes oil of the Athabasca tar sands and the east to west longshore current in the Beaufort Sea could carry discharged materials into the study area. Each of these materials would possess a somewhat different aromatic hydrocarbon distribution but each with the characteristic fossil rather than pyrolytic pattern.

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SECTION IV. AROMATIC AND ALIPHATIC HYDROCARBONS IN SOUTH CENTRAL ALASKAN SEDIMENTS

Introduction

One of the questions raised by our finding of aromatic hydrocarbons in nearshore Beaufort Sea sediments (Section III) was whether this class of compounds could be detected in other Alaskan marine sediments, and if so, what sort of distribution was present. To provide a preliminary answer to this question we selected for analysis five sediments from those already collected.

A subtidal sample was taken near Bluff Point in outer Kachemak Bay because we suspected that its hydrocarbon composition might be influenced by the presence of coal outcrops on adjacent coastal cliffs and because of the importance of the area to juvenile tanner crab populations. Visual inspection of the sediment revealed the presence of small black flecks which we believe to be detrital coal particles. Another sample came from Kasitsna Bay in southeastern Kachemak Bay; a site somewhat removed from the Bluff Point coal outcrops. Two samples came from Kamishak Bay. One was collected intertidally in Iniskin Bay, an area reported to contain natural petroleum seeps. The other was taken at a subtidal location off Shaw Island, another area of importance to crab populations. The fifth sample was collected in Port Valdez before operation of the trans-Alaska pipeline. This is an area of no known natural inputs of fossil hydrocarbons.

Methods

The Bluff sample was collected in November 1977 during a cruise of the NOAA ship *Surveyor*. The other three Cook Inlet samples were collected during a cruise of the R/V *Acona* in June 1977. The Port Valdez sample was taken during a cruise of the R/V *Acona* in August 1977. Subtidal samples were extracted and analysed by the procedures described for nearshore Beaufort Sea sediments (Section III).

Results and Discussion

Aliphatics

Table IV-I shows the aliphatic hydrocarbon concentrations of the five sediments. All show odd carbon dominance among the normal alkanes with 23

TABLE IV-I

CONCENTRATIONS OF HYDROCARBONS IN SOUTHCENTRAL ALASKAN SEDIMENTS ($\mu g\ g^{-1}$)

Sample	Location	Total sat.	Total un.	C_{15}	C_{16}	C_{17}	pr	C_{18}	ph	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	C_{32}
Port Valdez	60°05.5'N 146°36.9'W	1.1	1.3	-	-	.03	.12	.02	.01	.03	.01	.17	.03	.03	.02	.05	.02	.15	.04	.07	-	-	-
Shaw Island	59°03.1'N 153°23.4'W	0.8	0.9	-	-	-	-	-	-	-	-	-	-	.05	-	.07	.02	.19	.03	.12	-	-	-
Bluff Point	59°38.7'N 151°93.5'W	1.2	1.3	-	-	-	-	-	-	.02	-	.05	.01	.03	.01	.05	.01	.11	.02	.11	-	-	-
Iniskin Bay	59°43.3'N 153°22.1'W	3.7	3.6	.02	.02	.03	.10	.02	.01	.04	.03	.29	.08	.12	.08	.24	.07	.71	.06	.29	.01	.22	.01
Kasitsna Bay	59°28.8'N 151°34.2'W	2.0	1.9	-	.01	.02	.04	.02	.01	.08	-	.27	.04	.06	.02	.10	.01	.12	.04	.10	.08	-	-

to 29 carbon atoms indicating an input of hydrocarbons from terrigenous plant sources, not surprising for intertidal and nearshore sediments. The Port Valdez, Iniskin Bay and Kasitsna Bay sediments also contain heptadecane and pristane indicating algal and other marine contributions. Traces of phytane are also present in these latter three sediments. On the whole these sediments appear to contain only natural hydrocarbons.

Aromatics

The concentrations of total unsaturated hydrocarbons are shown in Table IV-I. Figure IV-1 shows the relative abundances of -18, -22 and -24 series aromatics and their alkyl homologs (see Section III for explanation). These homolog plots are different in important ways from those of Beaufort Sea sediments. The plot for Bluff Point shows rather pyrolytic distributions of the -22 and -24 series but a distorted -18 distribution. The reason for this is clear from Table IV-II which shows the relative abundance of terpenoids in the sediments. The Bluff Point sediment is particularly rich in abietic acid derived arenes. Retene, which contributes to C_4 of the -18 series, is almost 9% of the aromatics in this sample. The Port Valdez sediment is strikingly different in that its homolog plot shows a distinctly pyrolytic distribution for all three series and terpenoid arenes are present at lower relative abundance. The other three sediments are intermediate in composition but more closely resemble Port Valdez than Bluff Point. The lack of a high abundance of terpenoids at Kasitsna Bay indicates the influence of the Bluff Point coal outcrops is quite small in area. The lack of a distinct fossil hydrocarbon distribution at Iniskin Bay and Shaw Island indicates that neither the natural oil seeps of Kamishak Bay nor petroleum production of upper Cook Inlet is resulting in the accumulation of petroleum hydrocarbons in this area.

The ubiquity of the pyrolytic distribution in the homolog plots confirms our conclusion from the Beaufort Sea data that there is a general source of pyrolytically produced aromatic hydrocarbons, possibly atmospheric transport of urban dust from lower latitudes. In order to obtain further information bearing on this question, we are presently attempting to develop quantitative procedures for the determination of aromatic hydrocarbons by gas chromatography-mass spectrometry. We expect that this will be a

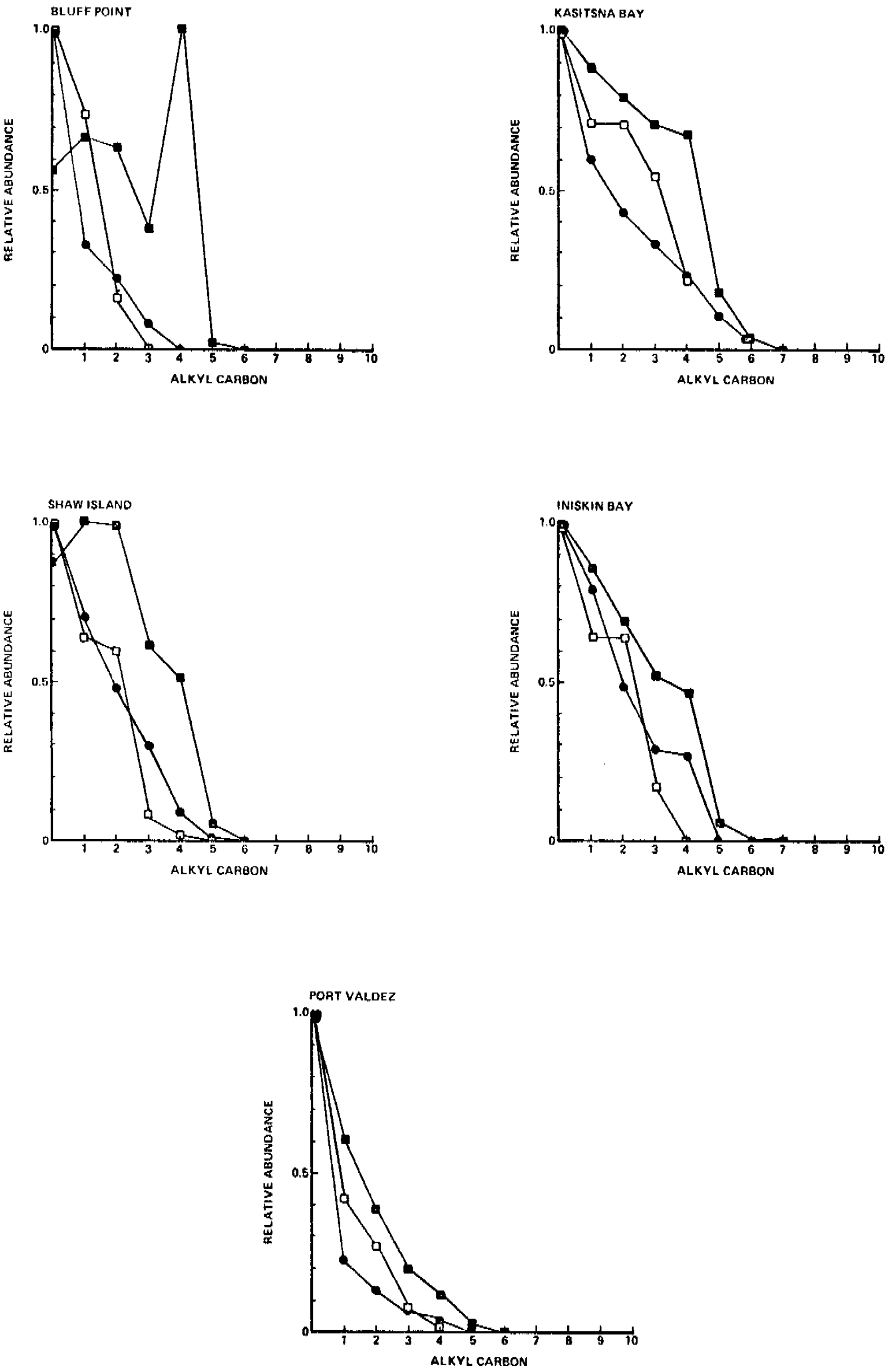

Figure IV - 1. Relative abundances of polycyclic aromatic hydrocarbons and their alkyl homologs for nearshore Southcentral Alaskan sediments. Solid squares represent the -18 series; solid circles, the -22 series; and open squares the -24 series. Each series is separately normalized.

TABLE IV-II

TERPENOID ABUNDANCE AS PERCENT OF TOTAL AROMATICS

Compound	m/e	Kasitsna Bay	Iniskin Bay	Shaw Island	Port Valdez	Bluff Point
Cadalene	198	1.7	1.1	0.90	0	4.9
Retene	234	1.1	1.6	2.4	0.31	8.8
Tetrahydroretene	238	0.61	0.23	0.48	0.13	1.4
Simonellite	252	0.80	0.74	1.5	0	33.3
Dehydroabietin	256	0.76	0	0.02	0.02	0.27
Dehydroabietane	270	0.97	0.04	0.23	0	1.9
	274	1.7	2.0	3.4	0.45	12.0
	292	0.48	1.0	1.6	0.24	5.2

relatively easy task for the parent ring systems where authentic materials are available for use as standards. However the alkyl homologs, which in most cases are complex mixtures of isomers may be beyond quantification.

These analyses show that the sediments of lower Cook Inlet, Port Valdez, and perhaps by implication, much of South Central Alaska contain a complex suite of aromatic hydrocarbons, primarily of pyrolytic origin. As was found to be the case in the Beaufort Sea, local sources of fossil hydrocarbons can mask the pyrolytics.

SECTION V. THE VARIABILITY IN HYDROCARBON CONTENT OF SEDIMENT

Introduction

This project has not sought to produce an intensive baseline characterization of hydrocarbons in the Alaskan OCS environment with statistically validated precision. Rather the approach has been to carry out a preliminary reconnaissance survey of ambient hydrocarbon concentrations and then move on to site specific and process oriented investigations with the objective of developing a predictive understanding of hydrocarbon dynamics. But this approach by no means eliminates the need to measure hydrocarbon variability. As with any measurement there are two sources of variability: natural variation in hydrocarbon content of the materials analysed, and measurement error introduced in the analytical procedure. Within the measurement error above there are two distinct kinds of error, systematic and random. The contribution of systematic error cannot be accurately evaluated since the actual hydrocarbon content of the environmental materials under study is unknown. However, from interlaboratory comparison analyses of reference materials (see Section X) we know that large systematic differences exist between our results and those from other laboratories. We have no reason not to believe that these differences are due, at least in part, to systematic errors in our analytical procedure.

In order to interpret our environmental hydrocarbon data we need to know something about the relative magnitude of environmental variability and analytical error. Suppose that we determine the hydrocarbon content of intertidal sediments from two locations and find different values. We need to know with some confidence to what extent this difference results from environmental variability, and to what extent, random laboratory error.

In order to address this general question for hydrocarbons in intertidal sediments we designed a sampling and analytical program in which at a single intertidal mud flat three plots were investigated. At each plot 10 sites were designated. At each site sediment was collected. For one plot, sediment from each site was analysed separately. For each plot sediment was pooled and repetitively analysed. Two analysts were involved; each performing half of the analyses for each plot.

At the time of this annual report we have begun a statistical analysis of our results. So far we have only considered the variability in total saturates. Our statistical analysis is continuing and will be reported at a later date.

Sampling

A sediment collection plot was chosen, with three rows of sites parallel to shore by three columns perpendicular to the coast. Individual sites in the plot were spaced 2 m apart on the perimeter, with a duplicated central site. Sites of the upper row were numbered 1-3, middle sites 4-7 (with 5 and 6 equivalent) and lower sites 8-10. On December 16, 1976, a portion of mudflat (59°39.83'N-151°26.00'W) east of Homer, Alaska on inner Kachemak Bay, accessible from 3.1 mile Kachemak Drive, was chosen for collection. Collection plots were selected on a seaward transect perpendicular to shoreline, with the first plot (A) 60 m below mean high tide line, the second plot (B) 40 m below plot A, and the third plot (C) in the midtidal zone, 40 m seaward from plot B. Plots A and B were sampled on December 16; C on December 17, 1976.

Sediment from individual sites was spooned into 8-oz jars, labeled with the plot, individual category, and site number. For each plot two 32-oz jars were filled with sediment as a composite of all sites.

Laboratory Procedure

Sediment samples (approximately 60 g dry weight) are extracted for 48 hours in pre-cleaned Soxhlet apparatus with 150 ml each of methanol and benzene. In charging the apparatus, methanol is added to the sediment before the benzene in order to remove water. The sediment is stirred half way through the extraction procedure. Fifty ml of water is added to the methanol-benzene and the resulting solution is extracted three times with 100 ml hexane and dried overnight with Na_2SO_4. Next the hexane extract is concentrated to 50 ml and free sulfur is removed by reaction with elemental copper. The hexane extract is further concentrated to 2 ml and the weight of extractable lipid is determined on an aliquot.

Column chromatography was performed as described in Section VIII of this report; gas chromatography and quantification as in Section III.

Results and Discussion

Table V-I shows the quantification of total saturates, total unsaturates and eleven individually identified compounds in sediments from the three plots. Normal alkanes with between 23 and 31 carbon atoms were observed with a strong odd carbon dominance. In addition compounds with retention indices of 1950, 1960, 1980, and 2090 were respectively characterized as fichtelite, molecular weight 276 with undetermined structure, iosene, and simonellite. The relationship of these compounds to terrestrial plant sources has been discussed in Sections III and IV of this report and by Simoneit (1977).

A statistical analysis was applied to the total saturated hydrocarbons determined by analysis of composites using a single classification analysis of variance (ANOVA). The ANOVA provides information about the variability among groups, and within groups. The variance components were estimated as percents in order to determine the relative amount of variance within groups (error variance) and the amount of variance among groups. There was a highly significant difference ($P<.01$) between plots A, B, and C. Approximately 43.5% of the variation was among the plots, and 56.5% of the variation was within the plots. Intuitively, this implies that any detectable difference between plots is being obscured by within plot variation.

The variance of ten individual samples from plot A was compared to the variance of the composites from plot A. There was no significant difference between the two variances. A t-test was then applied to the two sets of data to test the hypothesis that the two sample means are equal. There was no significant difference between the mean value of the composites and the mean value of the individual samples, indicating that the replicates from plot A are adequately representing the actual distribution of total saturates in plot A.

Because two experimenters analyzed half the replicates in each plot, their individual data sets were compared to one another to see if one was contributing the same variance as the other. The alternative hypothesis is that the two variances are unequal, and we have no reason to suppose that one set of replicates should be more variable than the other. Hence, this is a two tailed test, and variances are calculated as a ratio (greater

TABLE V-I

HYDROCARBONS IN SEDIMENT (μg/g)

Sample	Analyst	Total saturates	Total unsaturates	1950	1960	1980	2090	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{29}	C_{31}
AC1	1	8.0	6.6	.7	0.4	1.3	2.2	.37	.13	.41	.1	.9	.7	.5
AC2	1	13.6	6.7	.5	4.1	2.0	1.8	.31	.10	.46	.1	1.1	1.1	.6
AC3	1	15.3	14.9	.6	1.3	1.9	3.3	.52	.19	.77	.2	1.6	1.7	1.1
AC4	1	11.2	3.6	.8	0.6	1.5	1.6	.46	.16	.59	.1	1.3	1.1	.7
AC5	1	9.6	3.3	.5	0.3	1.1	2.1	.46	.15	.64	.1	1.3	1.3	.8
AC6	2	16.0	11.0	.5	-	1.0	3.0	.56	.28	1.1	.3	2.5	2.7	-
AC7	2	18.0	8.1	.5	.3	1.5	1.7	.59	.32	1.2	.4	2.6	2.8	-
AC8	2	17.0	7.9	.5	.4	0.9	1.6	.54	.30	1.1	.4	2.5	2.6	-
AC9	2	15.0	7.4	.5	.4	1.6	2.0	.59	.25	1.1	.3	2.3	2.5	-
BC1	1	19.9	4.7	.5	.3	1.2	.8	.41	.21	.51	.5	1.4	1.6	1.5
BC2	1	13.6	4.4	.6	.4	1.2	.8	.25	.15	.44	.1	.9	1.3	.7
BC3	1	13.2	9.8	.6	.4	1.2	1.0	.20	.15	.29	.1	.7	.7	.5
BC4	1	24.4	9.0	.7	.5	1.7	2.0	.43	.22	.81	.4	1.9	2.7	2.0
BC6	2	11.0	-	.4	.4	1.2	-	.33	.24	.60	.2	1.3	1.6	-
BC7	2	18.0	7.3	.5	.5	2.1	1.4	.75	.44	.80	.7	1.8	2.2	-
BC8	2	8.2	9.7	.3	.2	.7	1.1	.43	.17	.57	.3	1.4	1.5	-
BC9	2	12.0	9.1	.4	.8	1.7	1.1	.41	.22	.63	.2	1.4	1.5	-
BC10	2	8.8	10.0	.3	.3	1.1	1.2	.37	.19	.59	.2	1.3	1.1	-
CC1	1	19.1	5.0	.7	.4	2.2	1.7	.71	.52	1.0	-	1.9	2.1	1.3
CC2	1	19.4	9.6	.6	1.4	4.0	2.0	.63	.39	.64	.3	1.6	1.5	.7
CC3	1	16.7	5.4	.6	.7	1.9	1.4	.51	.37	.94	.2	1.9	2.2	1.4
CC4	1	23.8	11.5	.6	.5	2.6	1.4	.49	.39	.93	.3	2.0	2.4	-
CC5	1	23.7	6.7	.5	.4	1.5	1.9	.40	.19	.83	-	1.8	2.6	1.7
CC6	2	12.0	16	.5	.5	1.7	2.4	.43	.18	.80	.3	2.1	1.7	-
CC7	2	33.0	27	.7	.7	2.5	2.9	.85	.50	1.9	.8	4.4	4.8	-
CC8	2	23.0	15	.9	.4	2.6	2.9	.89	.48	1.5	.3	3.2	3.4	-
CC9	2	44.0	15	1.5	8.2	3.2	2.8	.89	.54	1.6	.7	4.2	4.8	-
CC10	2	32.0	7.5	.8	.8	2.6	1.3	-	.66	2.0	.9	3.4	3.6	-
AI2	1	24.7	4.8	.5	.4	1.6	1.4	.76	.25	1.1	.28	2.5	2.5	1.7
AI4	1	17.3	2.4	.8	.5	1.6	1.1	.69	.23	.9	.21	1.8	1.9	1.2

TABLE V-I

CONTINUED

Sample	Analyst	Total saturates	Total unsaturates	1950	1960	1980	2090	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{29}	C_{31}
AI6	1	28.1	8.6	1.1	.6	2.3	5.7	.93	.38	1.7	.39	3.6	4.3	2.5
AI7	1	21.7	4.3	.5	1.3	1.3	2.0	.54	.18	.77	.23	1.9	2.3	1.4
AI9	1	13.7	12.2	.7	.5	2.9	3.1	.36	.12	.4	.10	.8	1.0	.7
AI1	2	18.7	-	.3	.2	.8	.7	.27	.21	.5	.17	1.0	1.2	.6
AI3	2	19.4	-	.6	.4	4.3	1.5	.40	.34	.81	.26	1.6	1.9	.8
AI5	2	18.4	-	.5	.4	2.1	2.2	.51	.51	.98	.21	2.0	2.2	.9
AI8	2	20.6	-	1.1	.5	1.8	2.5	.73	.58	1.37	.52	2.5	2.7	-
AI10	2	18.9	-	.7	.3	2.7	1.5	.40	.38	.79	.27	1.5	1.6	.7

divided by lesser) and compared to the F-distribution. There was no significant difference in the variance between experimenter one and two in plots A and B. There was a significantly ($P<.05$) greater variance in the replicates of experimenter two within plot C, when compared to the replicates of experimenter one. This added variance of the second experimenter's replicates may be decreasing the within group precision.

Next, each experimenter's replicates were tested separately with an ANOVA to see if they were obtaining similar precision among the plots as they were within plots. Experimenter one had a highly significant difference ($P<.01$) among the plots with 42.6% of the variation within each plot, and 57.4% variation among plots. Experimenter two detected a significant difference ($P<.05$) among plots, with 44.9% variation within plots, and 55.1% variation among plots:

Experiment 1	Experiment 2
F_s^{**} ($P<.01$)	F_s^{*} ($P<.05$)
42.6% within	44.9% within
57.4% among	55.1% among

Although both experimenters had approximately the same percent-variations, these values are relative to the level of variation that is initially detected. The precision of the experimenters are the same, but experimenter one was able to detect variability with higher sensitivity (i.e., confidence) than experimenter two. Let us now return to plot C where we detected a significantly higher variability with the replicates of experimenter two.

All of the replicates from plot A and all of the replicates from plot B were compared to the first experimenter's replicates from plot C with the ANOVA. There was a significant difference among plots ($P<.05$). However most of the variation was within the plots (67.6%; 32.4% was among plots). This is to be expected, since within the amount of precision available, little variability is detectable among the plots.

We now perform the same analysis, only this time we use the second experimenter's replicates from plot C. Now, there is a highly significant difference ($P<.01$) among plots, with 46.7% variation within, and 53.3% variation among plots. It should be noted that the mean value from the second experimenter's replicates from plot C is twice as high as the mean values from the combined replicates of plots A and B ($A_{\bar{y}1\&2} = 13.70$; $B_{\bar{y}1\&2} = 14.34$; $C_{\bar{y}1} = 20.54$; $C_{\bar{y}2} = 28.80$). This results in a greater difference among plots, hence a larger detectable percent difference in-variance, the within plot variance making up the remainder to total 100%.

Furthermore, the added variance of the replicates by experimenter two in plot C has a compounding effect. Namely, there is now a highly significant difference in the variance among plots. It may be inferred from this result that the replicates of experimenter two in plot C are contributing an additional variation to the data for some unknown reason. This could be due to the higher values that exist in these replicates, overall.

SUMMARY OF STATISTICAL FINDINGS

1. If analyzed without considering experimenters there is significant variation among plots, but it is being obscured by within-group variability.

2. Compositing of samples from sites within a plot does not lead to results which differ significantly from the mean value for the individual sites.

3. Both experimenters have the same relative precision, but one is able to detect among group variability with more confidence than the other.

4. There is an added variance associated with the second experimenter's replicates in plot C. This reduces the relative percent of within plot variability. However, these replicates are significantly more variable than the first experimenter's replicates in plot C, and thereby decrease the within plot precision, overall.

Conclusion

From this preliminary analysis it appears that our experimental error is roughly the same magnitude as the environmental variability occurring over tens of meters.

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SECTION VI. SEDIMENT HYDROCARBON INTERACTION

Introduction

It is a truism that if petroleum is to impact a particular community of marine organisms, that oil must reach their habitat. This almost trivial statement has some very non-trivial ramifications.

Petroleum introduced into the marine environment is dispersed and degraded by a large number of biological, chemical and geological processes. These include evaporation, solution, ingestion, metabolism, and sedimentation to mention only a few. Their relative efficiency and the selectivity for various chemical constituents of petroleum, determines what happens to oil in the marine environment. For example, if petroleum is introduced at or near the surface and if the processes which carry that oil to the sea bed are very inefficient compared to other dispersion processes, then there is relatively little reason to be concerned about the effect of that oil on benthic biota. On the other hand, if processes that sediment oil are very efficient, then the effect of the oil on benthic biota should be a major concern.

If one hopes to use the results of studies of the biological effects of oil to quantitatively predict impacts of various potential oil spills, it is necessary to have quantitative information about dispersal pathways. We report here on laboratory studies on a potential oil dispersal pathway, adsorption to and sedimentation by suspended sediments. This pathway was selected as particularly worthy of study because a body of data which indicates that once petroleum is incorporated into sediments it may reside there for years continuously effecting organisms (Blumer *et al.*, 1970).

Some information about the interaction of oil and suspended sediments can be found in the scientific literature. Following the Santa Barbara blowout it was observed that areas of high oil incorporation into the bottom were largely coincident with areas of high sedimentation (Kolpack, 1971). Working with a saturated aqueous solution of dodecane, Button (1976) showed no significant decrease in aqueous hydrocarbon concentration following exposure to clay minerals. In a study using radio-labeled hydrocarbons, Lee (1977) has reported considerable association with organic detritus but relatively little with clay particles.

Drawing upon these and other similar reported findings and upon the fact that Southcentral Alaska suspended sediments are dominated by organic poor glacially derived materials, we expected that the interaction between subsaturation hydrocarbon concentrations and suspended sediments in Southcentral Alaskan waters would be slight. Yet this process still needs to be investigated because of the great abundance of these sediments. For instance a single fjord, Port Valdez, has an annual suspended sediment input in excess two million metric tons (Hood *et al.*, 1973). These sediments enter the marine environment largely in summer with peak river runoff. They spread out in large surface freshwater lenses, an ideal configuration for interaction with floating oil.

Our studies have been restricted to hydrocarbon concentrations near or below saturated solution. Another OCSEAP study has considered higher hydrocarbon concentrations. The results of these two studies have been quantitatively different. It does not appear that the results of one can be readily extrapolated to the other. This may indicate that quite different mechanisms of hydrocarbon-sediment interaction are operating at high and low hydrocarbon concentration. The low concentrations considered here are more representative of chronic petroleum discharge conditions than major spills.

Methods and Materials

Suspended sediment was taken from two locations off the Copper River delta during a cruise of the R/V *Acona* 6-10 October 1975 using a continuous run centrifuge (see Table VI-I for location). Surface water was taken by steel buckets and fed into the centrifuge. The centrifuge was opened at the end of the run, sediment scraped into glass jars previously baked at 500°C for 24 hrs and frozen for shipment to the laboratory.

Suspended sediment was also collected from Aialak Bay during a cruise of the R/V *Acona* from 25 June-2 July 1976 (see Table VI-I for location). The sediment was obtained by using the ship's seawater pumping system and continuous run centrifuge. During centrifugation the ship was anchored 2 km from the terminus of the Aialik Glacier.

Sediment treated and untreated with hydrogen peroxide was used in the adsorption experiments. The treated sediment was refluxed for 2 hrs with a

TABLE VI-I

STATION LOCATIONS FOR SUSPENDED SEDIMENT COLLECTION

Station No.	Latitude	Longitude	Date
CR-1	60°11.0'N	145°10.0'W	6-10 Oct. 1975
CR-2	60°14.9'N	145°34.0'W	6-10 Oct. 1975
Aialik Bay	59°56.1'N	149°42.4'W	25 June-2 July 1976

1:1 mixture of distilled water and 30% hydrogen peroxide. After refluxing the sediment was washed three times with distilled water. The sediment was then freeze-dried prior to the adsorption experiments. The raw sediment from Aialik Bay was not treated with hydrogen peroxide but washed three times with distilled water and air dried.

Carbon-14 labelled biphenyl and decane used in the adsorption experiments were purchased from ICN Pharmaceuticals, Irvine, California. Biphenyl arrived in a 1:1 mixture of ethanol and water, had a specific activity of 4.91 m Ci/mmole and a total activity of 1.0 m Ci. The decane arrived as neat liquid with a specific activity of 3 m Ci/mmole and a total activity of 500 μ Ci.

Counting was done on a Beckman LS-100 Scintillation Counter and data corrected for quench. Isotopes were counted in a Triton-X toluene cocktail (700 ml toluene, 300 ml Triton X, 0.1 g 1,4bis [2(5phenyloxazolyl)]-benzene, 4.0 g 2,5-diphenyloxazole) prepared in the laboratory.

The adsorption experiments were carried out at room temperature (24°C) in 16 oz glass jars. Agitation was furnished by a Burrell wrist action shaker. Labelled biphenyl or decane was added by syringe or pipette. In each case 500 ml of distilled or saline water was used to which the labelled hydrocarbon was added. After shaking for 15 minutes a 1 ml aliquot was counted to determine the amount of hydrocarbon in the water. Weighed sediment (usually 0.25 g) was then added and shaken for an additional two hours.

Centrifuging to separate water from sediment was done on an International centrifuge using 250 ml polycarbonate centrifuge tubes. After centrifuging the water was poured off and 1 ml aliquot taken for counting. The sediment in the bottom of the tubes was transferred with an eyedropper into a scintillation vial. Sediment recovery was 85%. The vial was then centrifuged and any remaining water was aspirated off with another eyedropper. Scintillation fluid was then added and the vial shaken to suspend the sediment and allow the fluid to extract the hydrocarbon from the sediment. The sediment was allowed to settle overnight prior to counting.

An adsorption experiment was done using 500 ml distilled water, 3.74 g of biphenyl (100% of the biphenyl saturation) and 0.25 g of H_2O_2 treated sediment. The mixture was then shaken for 2 hrs, filtered and sediment scraped off the filter. Filtration was done using a fritted disc Millipore apparatus with 300 ml funnel and Whatman GFC glass fiber filters. The filters had been baked at 450°C for four hrs and had a median retention size of 0.7 μm (Sheldon, 1972).

The sediment was resuspended in 500 ml of distilled water and shaken for 30 minutes. The sediment and water were again filtered and the sediment scraped off the filter and counted.

Autoclaved and nonautoclaved hydrocarbon solutions were used in the adsorption experiments. Solutions of decane and biphenyl were baked for approximately one hour in an autoclave at a pressure 7 lbs above ambient at a temperature of 150°C and allowed to cool slowly overnight. The solutions were contained in sealed one liter glass ampoules. The slow cooling process was very critical and assured survival of the ampoules.

After cooling the ampoules were broken open, the solution transferred to the 16 oz glass jars, and an aliquot taken for counting. The adsorption experiments were carried out as above.

Size analysis of the sediment was done according to the pipetting procedures of Folk (1968). Times and depths of withdrawl were also determined after Folk. One liter cylinders used in the size analysis were put in a water bath at 27°C and allowed to thermally equilibrate overnight. Approximately 20 g of sample wet weight were used in each analysis. Equal aliquots were withdrawn at the appropriate depths and times with a 20 ml pipette and pipette bulb. The sediment was oven dried overnight at 95°C and cooled prior to weighing.

Mineralogy of the suspended sediment was determined by X-ray diffraction using Cu radiation. The instrument used was made by Philips Electronic Instruments - Norelco Corporation. Samples were allowed to oxidize overnight with 30% hydrogen peroxide. The sediment was then washed three times with distilled water. A slurry was made of the sediment and mounted on an X-ray diffraction slide prior to overnight glycolation. Samples were slow scanned from 2°20 to 2°320.

Results and Discussion

Grain size analysis shows suspended sediment from all three locations to be nearly identical (Fig. VI-1). Ninety-two percent or more of each

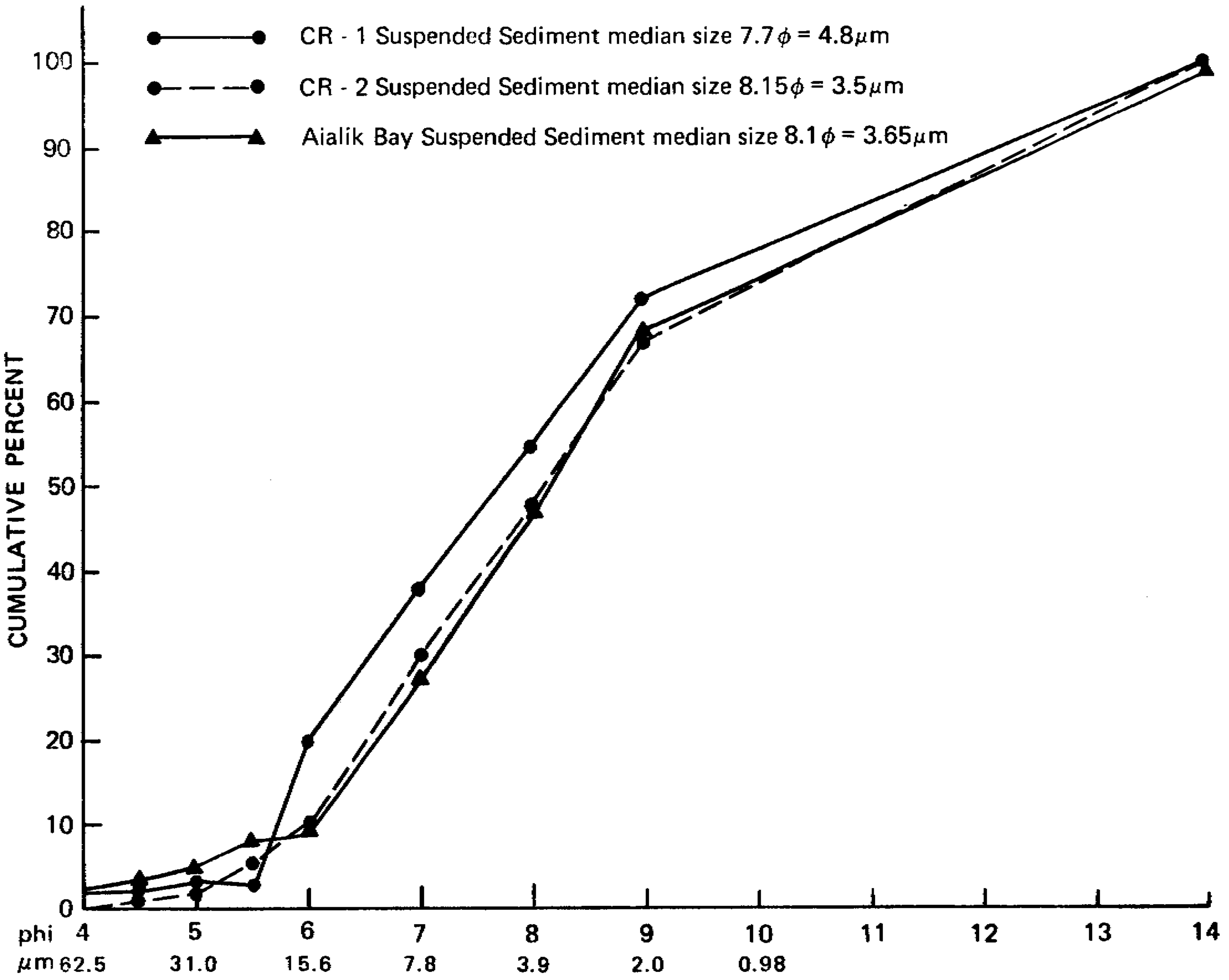

Figure VI-1. Grain size distribution of suspended sediments.

sample is smaller than 22.1 μm (5.5 ϕ). Median grain sizes are as listed in Figure VI-1. Approximately 30% by weight of each sample exists as particles of 2 μm or smaller.

Mineralogically the samples were also found to be very similar in composition. Of the clays present in samples CR-1 and CR-2, 30% (±10%) is chlorite and 70 (±10%) is illite with little or no kaolinite or montmorillinite (expandable clays). The Aialik Bay sample contains roughly equal amounts chlorite and illite with little or no expandable component. Other minerals present are quartz, feldspar, and amphibole.

In short, the above analyses show that there are no large dissimilarities between sediments either in size or mineralogy. The similarity of the samples taken from different areas of the Gulf of Alaska, probably indicates that they are typical of much of the glacial sediment entering the Gulf of Alaska.

A portion of the adsorption experiments was carried out with sediment refluxed 2 hrs with hydrogen peroxide in hope of reducing the natural organic coating of those sediments. Analysis indicated the treatment of sediment in this manner did not detectably alter the sediment either in size or mineralogy.

The adsorption experiments were carried out with the following parameters as independent variables - organic content of sediment, completeness of hydrocarbon dispersion (autoclaving for fuller solution) salinity, sediment concentration and hydrocarbon concentration. The first three parameters did not markedly alter adsorption behavior. Slight increases in adsorption were noted where salinity was increased from 0°/∘∘ to 35°/∘∘ NaCl. Only the changes in adsorption brought about by varying the concentration of sediment and hydrocarbon will be discussed in any detail.

A linear increase in amount of hydrocarbon adsorbed from solutions is obtained by varying the amount of sediment while holding the concentration of hydrocarbon constant. Magnitudes of adsorption and experimental conditions are given in Table VI-II. This linear response is of predictive value and provides a degree of assurance that these experiments are measuring adsorptive behavior of the sediments rather than wall effects of some other artifact.

TABLE VI-II

DECANE ADSORPTION AS A FUNCTION OF AMOUNT OF SEDIMENT AT A DECANE CONCENTRATION OF 16 μg/ℓ (SATURATED SOLUTION)

g of sediment 500 ml of H_2O	μg decane adsorbed
0.13	0.073
0.25	0.244
0.50	0.308
0.75	0.270
1.00	0.593

BIPHENYL ADSORPTION AS A FUNCTION OF AMOUNT OF SEDIMENT AT A BIPHENYL CONCENTRATION OF 0.200 mg/ℓ (2.68% OF SATURATION)

g of sediment 500 ml of H_2O	mg biphenyl adsorbed
0.25	2.12×10^{-4}
0.50	3.20×10^{-4}
1.00	9.40×10^{-4}
2.00	17.30×10^{-4}

Varying the concentration of hydrocarbon reveals three general characteristics of the adsorption system: (1) adsorption is small; (2) there seems to be no point at which zero adsorption occurs; and (3) the most important factor controlling adsorption is concentration of hydrocarbon relative to its concentration in saturated solution.

Adsorption of biphenyl as a function of its concentration is shown in Figure VI-2. A detailed list of values is given in Table VI-III. Adsorption versus concentration is logarithmic at 0°/oo and 35°/oo. The greater adsorption at 100% of biphenyl saturation at 35°/oo probably indicates "salting out" of the hydrocarbon from the water to the surface of the sediment particle.

A graph of decane adsorption versus concentration is given in Figure VI-3. A list of the values is given in Table VI-IV. Adsorption is linear regardless of salinity. There is no apparent enhanced adsorption at the greater salinity, nor is there any evidence of a salting out phenomenon.

The nature of the hydrocarbon dispersion undergoing adsorption is poorly understood. A mixture of water and a hydrophobic material such as these hydrocarbons produces three kinds of hydrocarbon dispersion: (1) hydrocarbon molecules in true solution, (2) a dispersion of tiny droplets of various sizes, and (3) a surface slick. The relative importance of these three kinds of hydrocarbon in associating with sediment is not known.

Resuspension of sediment with adsorbed biphenyl resulted in a 90% loss of the hydrocarbon. Other authors report desorption values of 16% using a fatty acid in which the sediment was resuspended three times in saline water at room temperature (Meyers and Quinn, 1973). This great loss of biphenyl may indicate weaker adsorption forces than those for a fatty acid. It is then probable that a particle can be washed of its adsorbed biphenyl or other hydrocarbon by cleaner water as it falls through the water column.

The data presented in Figures VI-2 and VI-3 show that for a saturated saline solution of either decane or biphenyl the concentration of hydrocarbon adsorbed to sediment (in ppm) is roughly 30% of the original aqueous concentration (in ppm). Since decane and biphenyl are structurally rather different and since together they represent the two major classes of hydrocarbons in petroleum, we assume that this relation holds, at least crudely, for all oil.

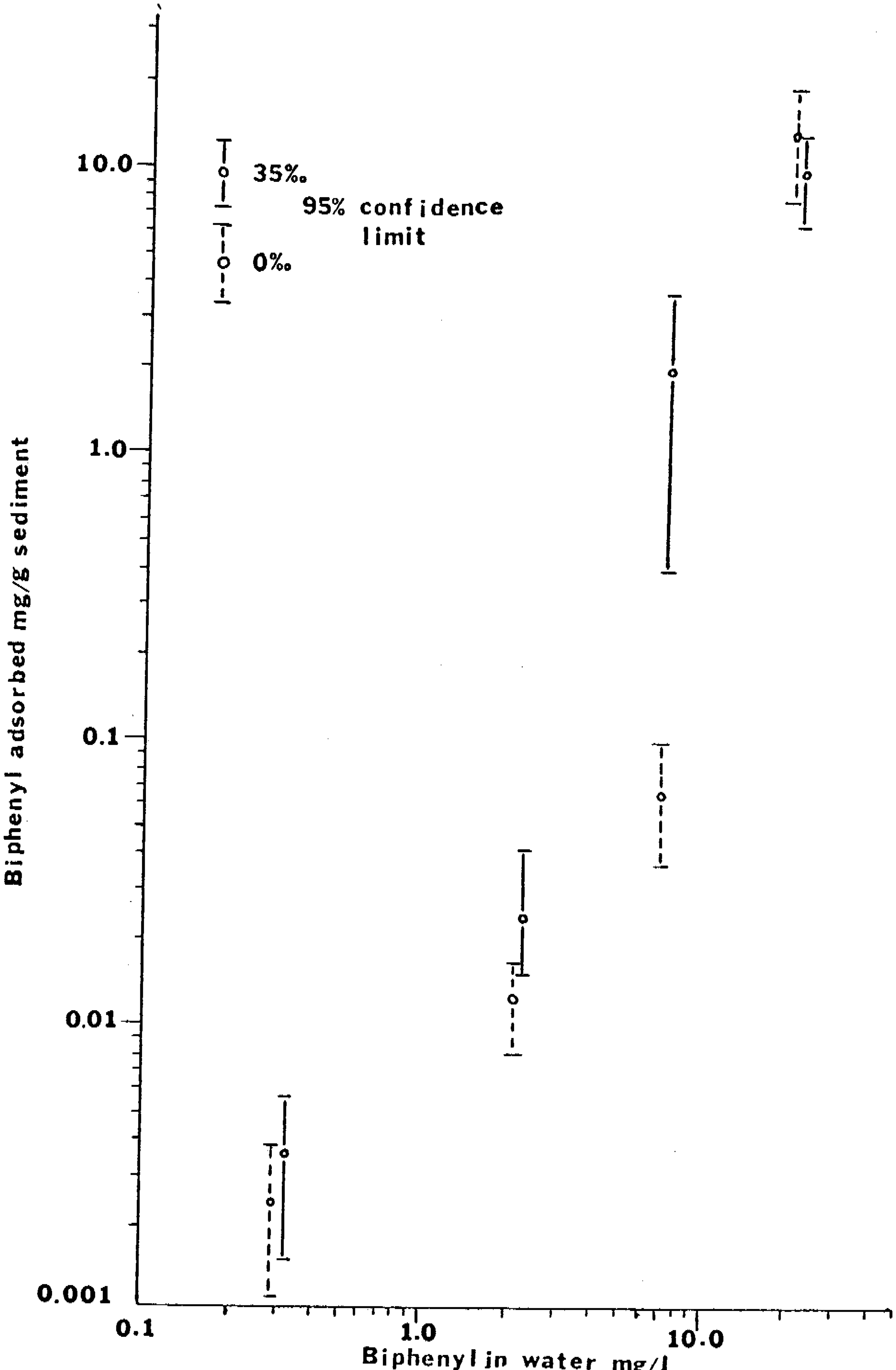

Figure VI-2. Biphenyl adsorption.

TABLE VI-III

BIPHENYL ADSORPTION

Solution Salinity=$35^\circ/_{\circ\circ}$; Results Given at 95% Confidence Limit

Concentration of Biphenyl in H_2O in Percent of Saturation*	Amount Biphenyl on Sediment in μg/g Sediment	
3.98	3.57 x 10^{-3} ± 2.07	(n = 4)
30.88	2.32 x 10^{-2} ± 1.84	(n = 4)
101.2	2.03 ± 1.62	(n = 4)
300.6	10.13 ± 3.70	(n = 4)

Solution Salinity=$0^\circ/_{\circ\circ}$

3.98	2.38 x 10^{-3} ± 1.28	(n = 6)
30.88	1.26 x 10^{-2} ± 0.45	(n = 12)
101.2	6.80 ± 3.12	(n = 7)
300.6	14.08 ± 6.11	(n = 3)

*Saturation = 7.48 mg/ℓ (Bohon and Claussen, 1951)

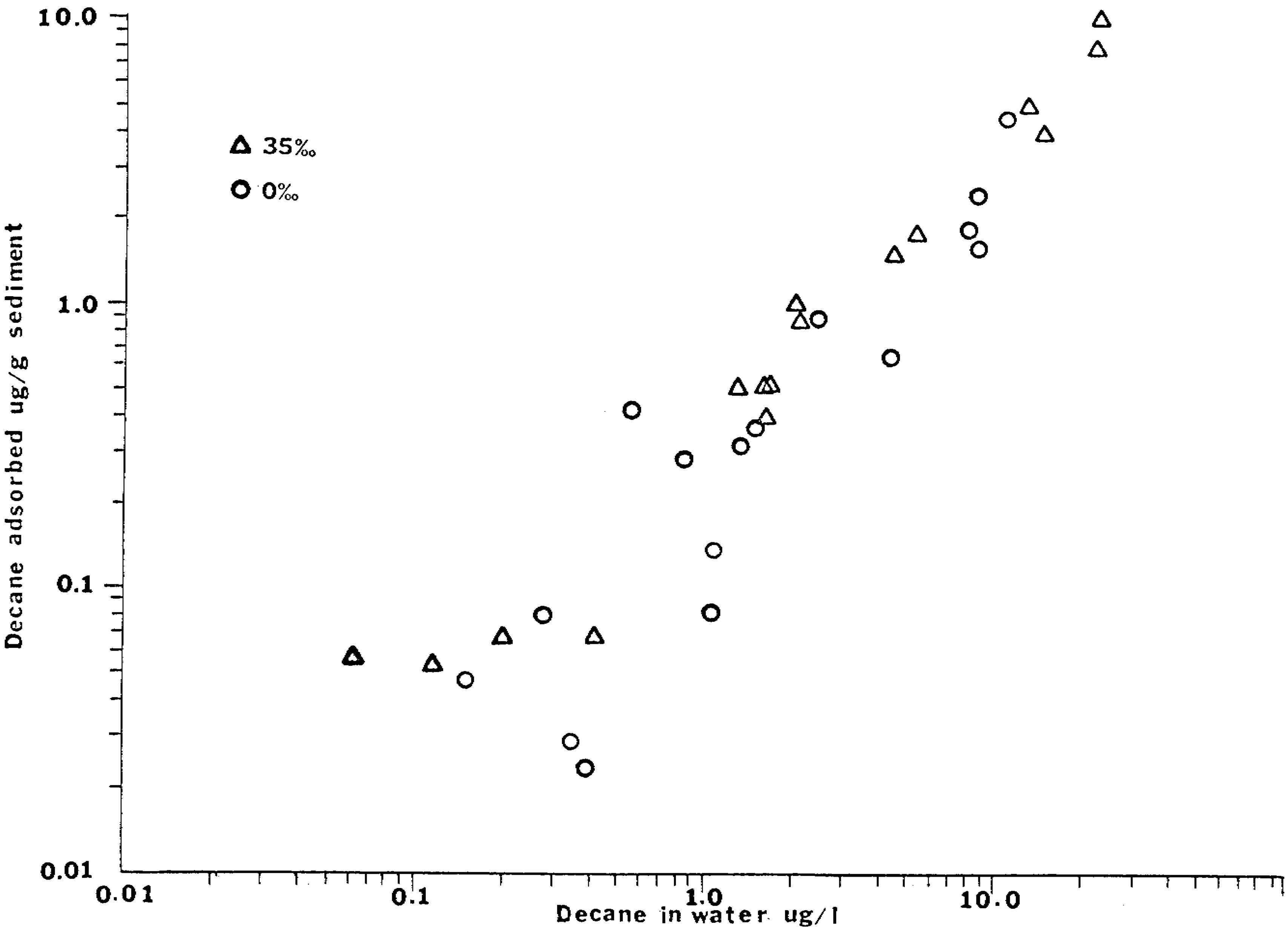

Figure VI-3. Decane adsorption.

TABLE VI-IV

DECANE ADSORPTION

Solution Salinity = 35°/oo

Concentration of Decane in H_2O in Percent of Saturation*	Amount Decane on Sediment in µg/g Sediment
0.40	5.60×10^{-2}
0.76	5.20×10^{-2}
1.33	6.64×10^{-2}
2.66	6.64×10^{-2}
8.74	5.04×10^{-1}
10.50	3.99×10^{-1}
10.81	5.16×10^{-1}
10.90	5.24×10^{-1}
13.25	1.03
14.60	9.12×10^{-1}
29.75	1.55
36.88	1.85
89.25	5.08
101.75	4.04
150.00	8.32
155.00	10.50

Solution Salinity = 0°/oo

0.93	4.60×10^{-2}
1.78	7.56×10^{-2}
2.20	2.80×10^{-2}
2.40	2.27×10^{-2}
3.60	4.10×10^{-1}
5.66	2.82×10^{-1}
7.00	8.76×10^{-2}
7.20	1.36×10^{-1}
8.68	3.25×10^{-1}
10.10	3.70×10^{-1}
16.60	9.00×10^{-1}
29.75	6.88×10^{-1}
54.60	1.89
56.60	2.50
59.50	1.62
79.40	4.56

*Saturation = 16 ug/ℓ (Baker, 1967)

Winters *et al.* (1976) have reported data for four oils which indicates that the solubilities of these materials is about 10 ppm. Based on this figure we can easily calculate that the maximum concentration of petroleum that can be adsorbed from aqueous solution is roughly 3 ppm. Of course, in the immediate vicinity of bulk oil spills, oil droplets may coat sediments and sink, leading to higher concentrations of oil in sediment.

These data are probably more meaningfully applied to chronic permitted discharges where the probability of hydrocarbons being in solution is higher than at spills. For instance we can make a simple calculation of the treated ballast water discharge facility of the transAlaska pipeline at Port Valdez.

For that facility the permitted hydrocarbon concentration is 50 ppb. There we would expect that the concentration of hydrocarbons is sediment to be less than 15 ppb. Less because the 30% factor is for saturated solution and a lower factor should be used at 50 ppb.

Since suspended sediment loads in Southcentral Alaskan marine waters seldom exceed 1 g/ℓ, it appears the process we have investigated cannot be a major (from the mass balance point of view) transport pathway in the dispersal of oil. The scientific study of the chronic effects of petroleum exposure is not sufficiently advanced to understand what, if any, the effects of the sedimented oil are on biological organisms.

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SECTION VII. HYDROCARBON VARIABILITY IN *FUCUS DISTICHUS*

Introduction

We have made a detailed investigation of the hydrocarbon content of *Fucus distichus* (rockweed) at a Cook Inlet intertidal station near Homer. The purpose of this work was to provide an estimate of the variability in observed hydrocarbon content due both to laboratory technique and to actual variation among plants collected in the same vicinity at the same time. Information about these kinds of variability are important to OCSEAP to place reconnaissance measurements in perspective. Elsewhere in this report (and in previous reports) we have presented data showing hydrocarbon concentrations in *F. distichus* and many other species at various locations. Typically, these groups of analyses showed, for each particular species, a general similarity but significant quantitative and qualitative variation between samples. It is important to better understand the sources of this variation in order to distinguish it from pollution induced changes.

Methods

A perennial bed of *Fucus distichus* located 59°39.60'N, 151°26.20'W, on a mudflat of inner Kachemak Bay was chosen as a plant source for the variation study. This location is easily accessible from Kachemak Drive east of Homer, Alaska, and plants could be obtained year-round. The rockweed is clustered on large boulders in the upper intertidal mudflat (area A), and on a series of rocks jutting above the mudflat from upper- to mid-tidal levels (area B).

A grid was adjusted to the rockweed bed in area A December 16, 1976, and collections of *Fucus distichus* were made from ten individual sites (A-1 to A-10) and a composite from all ten sites. Collections were made from seven sites in area B (B-4 to B-10) December 17, 1976, with a composite from all those sites also taken. Collected samples were frozen in clean 16-oz jars until analysed.

Samples A-1 to A-10 from individual sites in the upper intertidal grid were thawed, diced into 1.0 cm^2 pieces, and aliquots were dried from each site to determine dry weights. Samples were weighed into clean flasks and set overnight in 200 ml 4 N aqueous KOH. A sample was spiked with a standard reference mixture of six n-alkanes in hexane. A "blank" of aqueous KOH was also constructed. All the samples were stirred and saponified 24 hours after the addition of stir bars and 50 ml hexane per samples. Samples cooled to room temperature and were hexane extracted 4 x 50 ml. The hexane extracts were washed with 50 ml NaCl saturated water and dried overnight with $Na_2 SO_4$. Extracts were concentrated to about 1 ml and 1% of each sample was air dried to determine hexane extractable lipid content. Column chromatography was done in 9 mm diameter burets with hexane slurries of 5g (5% H_2O-deactivated) silica gel under 5 g (6% H_2O-deactivated) alumina. When samples were on the column, the column was eluted with 20 ml hexane and the eluate collected for saturated hydrocarbons. Columns were then eluted with 20 ml benzene for a second fraction of unsaturated hydrocarbons. These eluates were concentrated for gas chromatography. Peaks were identified by comparison of retention times from n-alkane standards and mass-spectrometry. Peak concentrations were determined by comparison with known standards, recovery from the internal sample spikes, and dry weights of original samples.

Fucus collected for the Composite-A group were thawed and diced into 1.0 cm^2 pieces. This plant material was then divided into 10 subsamples for hydrocarbon analysis (CA-1 to CA-10), plus aliquots for dry weight determination. All other procedures followed those used in analysis of A-individual sites.

Procedures used for rockweed collected in B-individual sites followed those for A-individual sites except in column chromatography. The new chromatography procedure eluted a 9 mm dia. column of 5 g (5%) H_2O-deactivated) silica gel in hexane with 6.8 ml hexane for the saturated hydrocarbon fraction, and 8.5 ml of 40% benzene in hexane by volume for the unsaturated fraction.

Since the variation in the Composite-A samples was large, and some of the heterogeneity might be due to the large (1.0 cm^2) chunks of *Fucus*, we decided to better homogenize Composite-B plants by grinding them into small particles. Plant aliquots were air dried to determine water content, and the remainder of the composite plants were weighed, added to a known weight of powdered $Na_2 SO_4$, and ground with mortar and pestle to a fine, green powder. This powder was then divided into three samples for saponification, and the three samples set overnight in 250 ml 4 N-aqueous KOH. Other procedures of Composite-B samples (CB-1 to CB-3) followed those for the B-individual site samples (B-4 to B-10), including the new column chromatography method.

For analyses, wet weights of *Fucus distichus* ranged from 25 to 60 g per sample, and water content averaged 79%. Total hexane-extractable lipids (determined prior to column chromatography) ranged form 2 to 20 mg. Recoveries from the internal spikes of n-alkanes were from 78-100%. Gas chromagotraphic analysis was carried out as described in Section III.

Results and Discussion

None of the *Fucus distichus* samples analysed contained more than four hydrocarbons; most had only three. The concentrations of pentadecane (C_{15}), heneicosapentane ($C_{21:5}$), heneicosahexaene ($C_{21:6}$) and squalene are shown in Table VII-I. These results can be compared with those of Youngblood *et al.* (1971) and Youngblood and Blumer (1973) who analysed three samples of *F. distichus* and obtained results shown in Table VII-II. In addition to the concentrations of C_{15}, $C_{21:5}$, and $C_{21:6}$ noted in Table VII-II, Youngblood and co-workers identified a few additional hydrocarbons in small amounts, but not squalene. Their non-observance of squalene, which is in contrast to our findings is probably related to differences in column chromatography. Youngblood *et al.* eluted their columns until just before the appearance of the first pigmented band. Our standard elution procedure, which was designed to obtain perylene, resulted in the elution of colored material from *F. distichus* extracts. We expect that squalene was also eluted toward the end of our procedure.

In discussing the variability of hydrocarbon content in *Fucus distichus* and within various other species of marine benthic algae, Youngblood and Blumer (1973) present evidence which indicates that: (1) hydrocarbon concentrations are highest in young plants and rapidly growing tissues; (2) normal alkanes are more abundant in vegetative than reproductive tissue; and (3) $C_{21:5}$ and $C_{21:6}$ are associated with developing tissue.

The variability observed in this work among the individual sites A-1 through A-10 and B-4 through B-10 does not appear unreasonable in view of

TABLE VII-I

HYDROCARBONS IN *FUCUS DISTICHUS* (ppm)

Sample	C_{15}	$C_{21:5}$	$C_{21:6}$	Squalene
A-1	3.17*	-	24.37	4.16
A-2	5.87*	-	20.95	8.20
A-3	5.79*	-	33.26	5.00
A-4	1.97*	-	6.17	.75
A-5	1.59*	-	12.85	1.57
A-6	3.28*	-	24.30	4.56
A-7	.59*	-	6.00	.99
A-8	1.87*	-	8.68	.91
A-9	.76*	-	9.22	2.62
A-10	3.68*	-	31.30	4.88
CA-1	2.07*	.17	9.90	2.22
CA-2	3.01*	.22	14.29	2.21
CA-3	2.67*	.35	11.10	1.93
CA-4	2.06*	.17	12.09	5.41
CA-5	4.88*	.65	29.54	4.61
CA-6	2.09*	5.14	6.80	2.23
CA-7	3.97*	2.54	23.23	4.67
CA-8	2.44*	.19	18.04	4.58
CA-9	2.47*	.82	15.10	3.41
CA-10	5.89*	.47	42.63	7.04
B-4	8.14	-	32.90	10.06
B-5	6.53	-	22.95	8.10
B-6	1.95	-	11.40	4.96
B-7	1.51	-	7.88	5.29
B-8	2.35	-	5.42	3.29
B-9	2.26	-	7.12	2.06
B-10	.47	-	5.32	3.10
CB-1	16.17	-	41.26	29.61
CB-2	21.43	-	27.58	20.93
CB-3	22.62	-	25.82	19.31

*evidence of more than one isomer

TABLE VII-II

LITERATURE HYDROCARBONS IN *FUCUS DISTICHUS* (ppm)

		C_{15}	$C_{21:5}$	$C_{21:6}$
Youngblood *et al.* (1971)		78	-	-
Youngblood and Blumer (1973)	(1)	74	1.5	296
	(2)	63	20	86

these findings. However, the variability in the composite samples CA-1 through CA-10 and CB-1 through CB-3 indicates that laboratory variability is also affecting the results. Peak ratios of the composites also show considerable variation. This indicates that the cause of the variation is not a simple proportional factor such as overall recovery. Another striking variation is the fact that only the CA composite series showed the presence of $C_{21:5}$. This indicates that only one or a few plants contained this compound since it did not appear in the A series which was collected at the same time and place. In an attempt to prepare a more homogeneous sample than the minced material generally used in this work, the plant tissue for the CB composite series was ground to a powder with Na_2SO_4 before extraction. However, variation was still noted in the three replicates run. The actual concentrations of C_{15}, $C_{21:6}$ and squalene were markedly higher for the samples ground with Na_2SO_4 that for the minced samples. Our hypothesis, which is supported by observations with a microscope, is that the higher hydrocarbon yield is the result of a greater extent of cell wall breakage. We have not yet found a procedure that does not leave a substantial portion of the plant cell walls intact. Thus, we suspect that we may not yet have obtained complete extraction.

The variation among the individual samples is greater than that among the composites, showing a degree of environmental variability in keeping with that observed by Youngblood and co-workers. Yet this variability is by no means random. It is largely limited to quantitative differences within a small number of normal hydrocarbons. It is quite simple to distinguish a sample of *Fucus distichus* which has been contaminated with petroleum (see Section IX). However, it would be quite difficult to establish that an environmental stress, such as the presence of petroleum, had led to an alteration in *F. distichus*' metabolic hydrocarbon production since that metabolism is not understood in detail but known to be variable.

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SECTION VIII. HYDROCABONS OF BERING SEA BIOTA

Introduction

In order to obtain a body of general background information about the hydrocarbon composition of animals of the Bering Sea, 34 analyses of plankton, fish, birds and marine mammals have been carried out. Most of the materials analysed were collected for hydrocarbon work in May and June 1977. However, tissue samples from four seal species were materials previously collected and stored frozen by other investigators. Emphasis was placed on pelagic organisms since this ecosystem is unusually productive, supporting both important commercial fisheries and large populations of birds and marine mammals.

Methods

Biota collected expressly for this work are listed in Table VIII-I. Table VIII-II shows the origin of the seal tissues analysed. In the laboratory approximately 10 g of tissue was extracted for 2 hrs at 90° in a capped centrifuge tube containing 10 ml 4 N aqueous KOH and 2 ml hexane. After the extract had cooled to room temperature, an additional 10 ml of hexane was added. Then the tube was shaken well and centrifuged for 15 minutes at 2500 rpm. The hexane phase was removed by pipette and the aqueous phase extracted twice more with hexane in the same manner. The hexane extracts were combined and dried over anhydrous sodium sulfate. The hexane was concentrated to about 5 ml and an aliquot evaporated and weighed to determine the total non-saponifiable lipids. Extracts containing less than 15 mg of lipid are column chromatographed on 5 g silica gel (5% water). Saturated hydrocarbons are eluted first with 8 ml hexane. Next unsaturated hydrocarbons are eluted with 12 ml of 40% benzene in hexane. (The amounts of reagents for column chromatography are approximate. Each batch of silica gel is tested and elution volumes adjusted so that alkanes through dotriacontane appear in the first fraction and aromatics from naphthalene through perylene appear in the second fraction.) Samples containing more than 15 mg lipid are treated using a larger column system, only a portion of the sample or both. Eluates are concentrated to approximately 1 ml for

TABLE VIII-I

SAMPLES COLLECTED - BERING SEA
NOAA SHIP *DISCOVERER* - 5/22/77-6/8/77

Material	Date	Latitude	Longitude	ID#
Chaetognathae	5/22/77	54°42'	165°59'	2-4
Chaetognathae	5/22/77	54°58'	166°43'	3-10
Chaetognathae	5/22/77	55°16'	167°28'	4-14
Chaetognathae	5/22/77	55°33'	168°09'	5-18
Chaetognathae	5/23/77	56°05'	169°40'	7-24
Chaetognathae	5/23/77	58°39'	172°15'	11-28
Chaetognathae	5/23/77	58°39'	172°15'	11-29
Chaetognathae	5/23/77	58°39'	172°15'	11-30
Chaetognathae	5/24/77	60°10'	174°13'	13-33
Chaetognathae	5/28/77	59°31'	174°48'	21-40
Chaetognathae	5/29/77	60°25'	168°44'	30-43
Chaetognathae	6/1/77	60°32'	160°06'	35-46
Chaetognathae	6/6/77	60°21'	169°07'	44-53
Chaetognathae	6/7/77	59°57'	168°56'	46-54
Chaetognathae	6/7/77	59°09'	168°38'	48-57
Euphausiacea	5/22/77	54°42'	165°59'	2-1
Euphausiacea	5/22/77	54°58'	166°43'	3-9
Euphausiacea	5/22/77	55°33'	168°09'	5-19
Euphausiacea	5/23/77	56°05'	169°40'	7-21
Euphausiacea	5/23/77	56°05'	169°40'	7-22
Euphausiacea	5/23/77	56°05'	169°40'	7-23
Euphausiacea	5/28/77	59°31	174°48'	21-38
Euphausiacea	5/29/77	60°25'	168°44'	30-42
Euphausiacea	5/30/77	60°25'	168°44'	31-44
Euphausiacea	6/6/77	60°22'	169°07'	44-52
Euphausiacea	6/8/77	57°59'	168°49'	50-61
Euphausiacea	6/8/77	56°30'	167°41'	52-68
Parathemisto pacifica	5/22/77	54°42'	165°59'	2-2
Parathemisto pacifica	5/22/77	54°58'	166°43'	3-11
Parathemisto pacifica	5/22/77	55°16'	167°28'	4-13
Parathemisto pacifica	5/22/77	55°33'	168°09'	5-16
Parathemisto pacafica	5/23/77	56°05'	169°40'	7-25
Parathemisto pacifica	5/23/77	57°07'	170°58'	9-26
Parathemisto pacifica	5/23/77	58°40'	172°17'	11-31
Parathemisto pacifica	5/24/77	60°10'	174°13'	13-32
Parathemisto pacifica	5/27/77	60°10'	174°29'	T4-34
Parathemisto pacifica	5/28/77	59°31'	174°48'	21-36
Parathemisto pacifica	5/28/77	59°31'	174°48'	21-37,21-39
Parathemisto pacifica	6/7/77	59°09'	168°38'	48-59
Parathemisto pacifica	6/8/77	57°59'	168°49'	50-60
Parathemisto pacifica	6/8/77	56°30'	167°41'	52-67
Hyperia galba	5/27/77	60°10'	174°29'	T4-35

TABLE VIII-I

CONTINUED

Material	Date	Latitude	Longitude	ID#
Anonyx nugax	5/28/77	59°57'	171°55'	27-41
Copepoda-calanus sp.	5/22/77	54°58'	166°43'	3-12
Copepoda-calanus sp.	5/22/77	55°33'	168°09'	5-20
Copepoda-calanus sp.	5/23/77	57°7'	170°58'	9-27
Copepoda-calanus sp.	6/7/77	59°57'	168°56'	46-55
Copepoda-calanus sp.	6/7/77	59°09'	168°38'	48-58
Copepoda-calanus sp.	5/8/77	56°30'	167°41'	52-66
Neomysis rayi	5/31/77	60°26'	168°02'	34-45
Neomysis rayi	6/2/77	60°23'	168°52'	36-49
Neomysis rayi	6/2/77	60°23'	168°52'	36-49
Neomysis rayi	6/2/77	60°27'	170°01'	38-50
Neomysis rayi	6/3/77	60°51'	170°53'	41
Pandalus borealis	5/22/77	54°58'	166°43'	3
Pandalus borealis	5/23/77	57°09'	170°59'	9
Pandalus goniurus	6/3/77	60°52'	170°53'	41
Eualus macilenta	6/3/77	60°52'	170°53'	41
Eualus gaimerdii	6/3/77	60°52'	170°53'	41
Argis sp.	6/3/77	60°52'	170°53'	41
Argis sp.	6/8/77	57°13'	169°32'	51
Crangon dalli	6/7/77	59°32'	168°46'	47
Perigonimus breviconus	5/24/77	60°10'	174°13'	13
Perigonimus breviconus	5/27/77	60°10'	174°29'	T4
Medusae	5/22/77	54°42'	165°59'	2-6
Medusae	5/22/77	55°33'	168°9'	5-17
Medusae	6/8/77	57°59'	168°49'	50-62
Ctenophorae	6/1/77	60°32'	160°06'	35-47
Ctenophorae	6/3/77	60°52'	170°53'	41-51
Janthina pacifica larvae	6/7/77	59°10'	168°38'	48-56
Janthina pacifica larvae	6/8/77	57°59'	169°49'	50-64
Cephalopoda-squid	5/22/77	54°42'	165°59'	2-3
Cephalopoda-squid	5/22/77	54°58'	166°43'	3-8
Cephalopoda-squid	6/8/77	56°30'	167°41'	52

TABLE VIII-I

CONTINUED

Material	Date	Latitude	Longitude	ID#
Fish larvae	5/22/77	54°42'	165°59'	2-5
Fish larvae	5/22/77	54°58'	166°43'	3-7
Fish larvae	5/22/77	55°33'	168°09'	5-15
Fish larvae	5/8/77	56°30'	167°41'	52-65
Mallotus villosus	5/31/77	60°26'	168°02'	34
Mallotus villosus	6/2/77	60°23'	168°52'	36
Mallotus villosus	6/2/77	60°27'	170°01	38
Clupea heringa	5/28/77	59°57'	172°29'	26
Clupea heringa	6/2/77	60°27'	170°01'	38 fingerling
Clupea heringa	6/2/77	60°27'	170°01'	38
Theragra chalcogramma	5/23/77	57°09'	170°59'	9
Theragra chalcogramma	5/28/77	59°57'	172°29'	26
Boreogadus saida	6/2/77	60°35.2'	174°02'	39
Rissa tridactyla†	5/25/77	60°37'	174°38'	GJD-77-31
Rissa tridactyla†	5/25/77	60°37'	174°38'	GJD-77-32
Uria lomvia†	5/25/77	60°37'	174°38'	GJD-77-37
Uria lomvia†	5/25/77	60°37'	174°38'	GJD-77-36
Uria aalge†	5/25/77	60°37'	174°38'	GJD-77-30
Uria aalge†	5/25/77	60°37'	174°38'	GJD-77-28
_Phoca vitulina largha_*	5/25/77	60°37'	174°38'	DIS- 2-77
_Phoca vitulina largha_*	5/25/77	60°37'	174°38'	DIS- 3-77
_Phoca vitulina largha_*	5/25/77	60°37'	174°38'	DIS- 4-77
_Phoca vitulina largha_*	5/25/77	60°37'	174°38'	DIS- 5-77
_Pusa hispida_*	5/30/77	60°25'	168°44'	31-pup
_Pusa hispida_*	5/30/77	60°25'	168°44'	31
_Phoca vitulina richardi_*	5/30/77	60°25'	168°44'	31

† liver only
* blubber only

TABLE VIII-II

ORIGIN OF SEAL TISSUES

Material	Date collected	Latitude	Longitude	ID#
Phoca vitulina largha	3/27/76	56°05'	164°31'	SUV-20-76
Phoca vitulina largha	3/26/76	56°05'	164°31'	SUV-15-76
Phoca vitulina largha	4/24/76	56°05'	162°47'	SUV-30-76
Phoca vitulina richardi	3/25/76	56°08'	164°20'	SUV-12-76
Erignathus barbatus	3/28/76	56°12'	165°29'	SUV-22-76
Histriophoca fasciata	4/19/76	57°21'	172°41'	SUV-24-76

For other information - age, sex, stomach contents, morphology - contact Francis Fay (R.U. 194).

gas chromatography. Gas chromatography and mass spectrometric peak identification are carried out as described in Section IV.

Results and Discussion

Table VIII-III shows the results of the analyses of Bering Sea biota. Pristane is both ubiquitous and abundant. It was identified in 31 of the 34 samples analysed, and in many was the only saturated hydrocarbon present. The presence of pristane in zooplankton has often been reported and its transfer through marine food chains has also been noted (Blumer, 1967). Heneicosahexaene ($C_{21:6}$, structure undetermined) was commonly found in the zooplankton examined, but was not as common in the bird and mammal tissues examined as pristane. This is in keeping with previous observations that $C_{21:6}$ is produced by phytoplankton (Blumer *et al.*, 1971) and by benthic algae (Youngblood and Blumer, 1973) and that higher food web members show markedly different abilities to accumulate this compound from dietary sources (Blumer *et al.*, 1970). Most of the seal tissues analysed contained phthalate esters as the principal unsaturated constituent. Phthalates have recently been reported in marine water, sediment, air and biota (Giam *et al.*, 1978). However, in the present case we cannot exclude the possibility the phthalates were introduced as contaminants after sample collection. These samples were not collected with the intention of using them for hydrocarbon analysis. These samples were collected and saved as part of a study of the general biology and life history of Alaskan marine mammals. The samples had been wrapped in aluminium foil, placed in plastic bags and frozen. We chose to analyse these samples in spite of our reservations about their freedom from contamination. In a first reconnaissance effort it simply was not justifiable to sacrifice more of these large, legally protected mammals for the sake of hydrocarbon analysis. We tend to believe that post-collection contamination is not the only source of these phthalates since the smaller samples analysed did not show higher concentrations as one might expect to be the case if various sized pieces of tissue were contaminated from a constant source such as an outer plastic wrapper. Also, seals have been shown to accumulate chlorinated hydrocarbons (Holden and Marsden, 1967).

All hydrocarbons (chemically, phthalates are not hydrocarbons) identified in the biota of the Bering Sea are biogenic and probably algal in origin. In most organisms this hydrocarbon array is extremely simple consisting of only one or a few compounds. Furthermore, these arrays are quite different from that of petroleum.

TABLE VIII-III

BIOLOGICAL MATERIAL - BERING SEA
ALL BASED ON WET WEIGHT CENTRIFUGE TUBE METHOD
(μg/g)

Material	ID #	Total sat.	Total unsat.	Pristane	$n\text{-}C_{21}H_{32}$	Phthalate
Erignathus barbatus						
kidney	SUV-22-76	<.01	.25	-	-	-
Histriophoca fasciata						
kidney	SUV-24-76	.21	.88	.21	-	.88
Phoca vitulina richardi						
kidney	SUV-12-76	.95	1.1	.52	-	1.1
Phoca vitulina largha						
liver	SUV-30-76	.22	2.2	.22	-	2.2
kidney	SUV-30-76	4.5	5.5	4.5	-	5.5
muscle	SUV-30-76	.85	20	.85	-	20
liver	SUV-15-76-1	66	18	66	-	18
liver	SUV-15-76-2	65	11	65	-	9.3
liver	SUV-20-76-1	30	16	30	.1	14
liver	SUV-20-76-2	43	19	43	-	18.5
blubber	SUV-15-76	104	-	104	-	-
blubber	SUV-20-76	23	140	23	-	-
blubber	SUV-30-76	140	37	101.2	-	37
Uria aalge	GJD-77-30	<.01	<.01	-	-	-
Uria lomvia	GJD-77-37	0.4	0.6	0.4	-	-
Rissa tidactyla	GJD-77-31	220	0.8	220	-	-
Neomysis rayi	38-50	<.01	<.01	-	-	-
Parathemisto pacifica	50-60	70	20	70	-	-
Parathemisto pacifica	21-36	68	4.1	68	3.4	-
Parathemisto pacifica	21-37	20	13	20	-	-
Mallotus villosus	38	10	1.1	10	-	-
Medusae	50-62	2.3	7.5	2.3	1.2	-
Chaetognathae	11-28	8.3	8.3	8.3	.9	-
Chaetognathae	2-4	60.2	10.3	60.2	9.0	-
Chaetognathae	5-18	53.1	2.3	53.1	2.3	-
Chaetognathae	7-24	33.6	8.9	33.6	7.6	-
Chaetognathae	11-29	7.5	0.6	7.5	-	-
Chaetognathae	11-30	11.1	<.01	11.1	-	-

TABLE VIII-III

CONTINUED

Material	ID #	Total sat.	Total unsat.	Pristane	$n\text{-}C_{21}H_{32}$	Phthalate
Euphausiacea	2-1	52	31	52.5	26.9	-
Euphausiacea	7-21	66	150	57.5	-	-
Euphausiacea	7-23	58	100	49	87.9	-
Euphausiacea	21-38	9.5	34	5.7	26.2	-
Euphausiacea	44-52	3.6	34	1.2	-	-
Euphausiacea	50-61	1.0	11	1.0	10.9	-

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SECTION IX. HYDROCARBONS OF LOWER COOK INLET BIOTA

Introduction

We have surveyed the kinds and amounts of hydrocarbons in the biota of Lower Cook Inlet. The organisms examined have included subtidal animals and intertidal plants. We also collected intertidal animals and expect to analyse these in the coming months. In conjunction with our studies of the variability in the hydrocarbon composition in *Fucus distichus* and sediment in Kachemak Bay (see Sections V and VII) we selected this area as our primary intertidal collection area. Most of the biota contained only biogenic arrays of hydrocarbons. However a sample of *F. distichus* collected near the town of Homer contained what appears to be diesel fuel and a red alga collected near Bluff Point coal associated suite of compounds.

Methods

Three collecting trips were made to Lower Cook Inlet. The materials obtained are listed in Tables IX-I, IX-II, and IX-III. Sediment samples collected at some of the same sites as the biota are also indicated in these tables. The subtidal animals were analysed as described in Section VIII. A chrysene internal standard was added to each algal sample which was then digested for 24 hrs with 150 ml 4N aqueous potassium hydroxide and 50 ml hexane at reflux with stirring. The extracts were partitioned into hexane and dried over sodium sulfate. The dry hexane extract was concentrated to approximately 1 ml for column chromatography. This step and the subsequent gas chromatography were performed as described in Section VIII.

Results and Discussion

Our analyses of subtidal biota (Table IX-IV) show generally low amounts of hydrocarbons in the shrimps and crab examined. Both species of pandalid shrimp contained pristane. However, the species of crangonid shrimp investigated contained no detectable hydrocarbons whatever. *Crangon dalli* may have potential as a monitoring species since its low hydrocarbon background would not obscure even small accumulations of petroleum. However, it may also be that *C. dalli* is low in hydrocarbons because it is metabolically efficient at removing them. An experimental test of these two possibilities would be most interesting.

TABLE IX-I

INTERTIDAL COLLECTIONS MADE FROM SHORE-KACHEMAK BAY
MAY 1977

Material	Date	N. Latitude	W. Longitude	ID
Intertidal sediment	5/4/77	59°39.83'	151°26.00'	IBM
Coal	5/7/77	59°40.22'	151°47.17'	Diamond Gulch
Enteromorpha linza	5/4/77	59°39.60'	151°26.20'	IBM
Constantinea subublifera	5/5/77	59°46.96'	151°52.10'	Anchor Point
Desmarestia aculeata	5/7/77	59°40.22'	151°47.17'	Diamond Gulch
Desmarestia aculeata	5/6/77	59°38.08'	151°30.41'	NW-Spit
Palmeria palmata	5/5/77	59°46.96'	151°52.10'	Anchor Point
Fucus distichus	5/7/77	59°40.22'	151°47.17'	Diamond Gulch
Fucus distichus	5/6/77	59°36.03'	151°52.10'	Homer Spit
Fucus distichus	5/6/77	59°38.03'	151°30.41'	NW-Spit
Fucus distichus	5/4/77	59°39.60'	151°26.20'	IBM
Alaria	5/5/77	59°46.96'	151°52.10'	Anchor Point
Laminaria saccharina	5/6/77	59°38.08'	151°30.41'	NW-Spit
Laminaria saccharina	5/7/77	59°40.22'	151°47.17'	Diamond Gulch
Zostera marina	5/4/77	59°39.60'	151°26.20'	IBM
Flustrella gigantea	5/5/77	59°46.96'	151°52.10'	Anchor Point
Fusitriton oregonensis	5/5/77	59°46.96'	151°52.10'	Anchor Point
Neptunea lyrata	5/6/77	59°38.03'	151°30.41'	NW-Spit
Nucella lamellosa	5/5/77	59°46.96'	151°52.10'	Anchor Point
Nucella lima	5/5/77	59°46.96'	151°52.10'	Anchor Point
Nucella lima	5/4/77	59°39.60'	151°26.20'	IBM
Callosella fenestrata	5/5/77	59°46.08'	151°51.96'	Anchor Point
Callosella pelta	5/5/77	59°46.08'	151°51.96'	Anchor Point
Callosella pelta	5/4/77	59°39.60'	151°26.20'	IBM
Callosella scutum	5/5/77	59°46.08'	151°51.96'	Anchor Point
Callosella scutum	5/7/77	59°40.22'	151°47.17'	Diamond Gulch
Macoma balthica	5/4/77	59°39.60'	151°26.20'	IBM
Modiolus modiolus	5/5/77	59°46.96'	151°52.10'	Anchor Point
Mytilus edulis	5/5/77	59°46.96'	151°52.10'	Anchor Point
Mytilus edulis	5/7/77	59°40.22'	151°47.17	Diamond Gulch
Mytilus edulis	5/6/77	59°38.03'	151°30.41'	NW-Spit
Mytilus edulis	5/4/77	59°39.60'	151°26.20'	IBM
Sea Squirts	5/5/77	59°46.96'	151°52.10'	Anchor Point
Sea Stars	5/5/77	59°46.96'	151°52.10'	Anchor Point
Sea Stars	5/7/77	59°40.22'	151°47.17'	Diamond Gulch
Sea Stars	5/6/77	59°38.03'	151°30.41'	NW-Spit
Strongylocentrotus	5/5/77	59°46.96'	151°52.10'	Anchor Point
Strongylocentrotus	5/7/77	59°40.22'	151°47.17'	Diamond Gulch
Strongylocentrotus	5/6/77	59°38.03'	151°30.41'	NW-Spit

TABLE IX-II

COLLECTIONS MADE DURING CRUISE OF R/V *ACONA* IN LOWER COOK INLET JUNE 1977

Material	Date	N. Latitude	W. Latitude	ID #
Surface water	6/24/77	59°03.1'	153°23.4'	CI-03
Surface water	6/22/77	59°33.2'	151°36.4'	CI-09
Surface water	6/24/77	60°51.2'	151°36.5'	CI-21
Benthic Sediment	6/24/77	59°03.1'	153°23.4'	CI-03
Benthic Sediment	6/22/77	59°33.2'	151°36.4'	CI-09
Intertidal Sediment	6/25/77	59°37.7'	153°40.0'	Cottonwood Bay
Intertidal Sediment	6/26/77	59°05.2'	153°46.4'	Douglas River
Intertidal Sediment	6/25/77	59°43.8'	153°20.7'	Iniskin Bay
Intertidal Sediment	6/23/77	59°23.8'	151°33.6'	Kasitsna Bay
Intertidal Sediment	6/26/77	59°39.0'	153°18.1'	Oil Bay
Phytoplankton	6/24/77	59°03.1'	153°23.4'	CI-03
Phytoplankton	6/22/77	59°33.2'	151°36.4'	CI-09
Phytoplankton	6/24/77	60°51.2'	151°36.5'	CI-21
Surface Tow	6/24/77	59°02.8' 59°06.5'	153°24.0' to 153°25.8'	CI-03
Surface Tow	6/22/77	59°33.2' 59°30.6'	151°36.4' to 151°41.6'	CI-09
Surface Tow	6/24/77	60°51.2' 60°46.9'	151°36.5' to 151°34.0'	CI-21
Fucus distichus	6/25/77	59°37.7'	153°40.0'	Cottonwood Bay
Fucus distichus	6/22/77	59°14.5'	151°52.5'	Dogfish Bay
Fucus distichus	6/26/77	59°05.2'	153°46.6'	Douglas River
Fucus distichus	6/25/77	59°43.8'	153°20.7'	Iniskin Bay
Fucus distichus	6/23/77	59°28.8'	151°33.6'	Kasitsna Bay
Fucus distichus	6/26/77	59°39.0'	153°18.1'	Oil Bay
Halosaccion gladiforme	6/26/77	59°05.2'	153°46.4'	Douglas River
Halosaccion sp. I	6/26/77	59°05.2'	153°46.4'	Douglas River
Cymathere triplicata	6/22/77	59°14.5'	151°52.5'	Dogfish Bay
Zostera marina	6/25/77	59°43.8'	153°20.7'	Iniskin Bay
Zostera marina	6/23/77	59°28.8'	151°33.6'	Kasitsna Bay
Littorina sitkana	6/23/77	59°28.8'	151°33.6'	Kasitsna Bay
Nucella lima	6/25/77	59°43.8'	153°20.7'	Iniskin Bay
Nucella lima	6/26/77	59°39.0'	153°18.1'	Oil Bay
Macoma balthica	6/25/77	59°37.7'	153°40.0'	Cottonwood Bay
Macoma balthica	6/25/77	59°43.8'	153°20.7'	Iniskin Bay
Macoma balthica	6/23/77	59°28.8'	151°33.6'	Kasitsna Bay
Mytilus edulis	6/22/77	59°14.5'	151°52.5'	Dogfish Bay
Mytilus edulis	6/26/77	59°05.2'	153°46.4'	Douglas River
Mytilus edulis	6/23/77	59°28.8'	151°33.6'	Kasitsna Bay
Mytilus edulis	6/26/77	59°39.0'	153°18.1'	Oil Bay

TABLE IX-III

COLLECTIONS MADE ON CRUISE OF NOAA SHIP *SURVEYOR* IN LOWER COOK INLET NOVEMBER 1977

Material	Date	N. Latitude	W. Longitude	ID #
Sediment	11/16/77	59°38.7'	151°43.5'	Bluff Station
Sediment	11/13/77	60°12.8'	152°36.1'	Tuxedni Bay
Sediment	11/15/77	59°41.2'	151°12.8'	Station 37
Sediment	11/16/77	59°34.1'	151°43.5'	Station 40
Coal	11/16/77	59°39.2' 59°39.5'	151°45.7' to 151°46.9'	Bluff Station
Agarum cribosum	11/11/77	59°33.3' 59°33.2'	151°53.9' to 151°56.0'	Station 41
Fusitriton oregonensis	11/10/77	59°01.6' 59°03.4'	153°01.4' to 152°59.3'	Station 5
Fusitriton oregonensis	11/ 7/77	59°26.9' 59°27.5'	153°18.0' to 153°19.9'	Station 35
Neptunea lyrata	11/16/77	59°39.2' 59°39.5'	151°45.7' to 151°46.9'	Bluff Station
Neptunea lyrata	11/11/77	59°35.7' 59°36.4'	151°47.7' to 151°49.0'	Station 40
Clinocardium nuttali	11/11/77	59°35.7' 59°36.5'	151°47.7' to 151°49.0'	Station 40
Macoma nusta	11/15/77	59°41.2' 59°40.6'	151°12.0' to 151°12.9'	Station 37
Mytilus edulis	11/11/77	59°33.3' 59°33.2'	151°53.9' to 151°56.0'	Station 41
Crangon dalli	11/ 8/77	59°16.3' 59°15.7'	153°35.7' to 153°32.4'	Station 27
Crangon dalli	11/11/77	59°37.2' 59°36.6'	151°48.6' to 151°45.1'	Station 40
Crangon dalli	11/14/77	59°46.8' 59°46.0'	152°56.4' to 152°56.5'	Station 62
Pandalus borealis	11/10/77	59°01.6' 59°03.4'	153°01.4' to 152°59.3'	Station 5
Pandalus borealis	11/15/77	59°40.8' 59°40.2'	151°13.6' to 151°14.8'	Station 37
Pandalus hypsinotus	11/15/77	59°40.8' 59°40.2'	151°13.6' to 151°14.8'	Station 37
Paralithodes camtschatica	11/ 7/77	59°27.0' 59°27.6'	153°18.4' to 153°21.5'	Station 35
Paralithodes camtschatica	11/ 7/77	59°31.2' 59°31.3'	153°12.3' to 153°15.1'	Station 53
Paralithodes camtschatica - digestive glands	11/ 7/77	59°31.2' 59°31.3'	153°12.3' to 153°15.1'	Station 53

TABLE IX-III

CONTINUED

Material	Date	N. Latitude	W. Longitude	ID #
Chionoecetes opilio	11/10/77	59°01.6' 59°03.4'	153°01.4' to 152°59.3'	Station 5
Chionoecetes opilio	11/ 8/77	59°16.3' 59°15.7'	153°35.7' to 153°32.4'	Station 27
Chionoecetes opilio	11/15/77	59°40.8' 59°40.2'	151°13.6' to 151°14.8'	Station 37
Chionoecetes opilio	11/11/77	59°35.7' 59°36.4'	151°47.7' to 151°49.0'	Station 40
Chionoecetes opilio	11/11/77	59°33.3' 59°33.2'	151°53.0' to 151°56.0'	Station 41
Chionoecetes opilio	11/ 7/77	59°32.2' 59°31.8'	153°08.8' to 153°10.6'	Station 53
Chionoecetes opilio	11/14/77	59°46.6' 59°46.2'	152°55.3' to 152°56.3'	Station 62
Cancer magister	11/11/77	59°35.7' 59°36.4'	151°47.7' to 151°49.0'	Station 40
Sea Star	11/12/77	59°38.8' 59°37.3'	151°44.4' to 151°46.6'	Station 40A
Strongylocentrotus	11/16/77	59°39.2' 59°39.5'	151°45.7' to 151°46.9'	Bluff Station
Strongylocentrotus	11/ 8/77	59°10.4' 59°12.0'	153°49.5' to 153°51.6'	Station 18
Gadus macrocephalus	11/10/77	59°01.6' 59°03.4'	153°01.4' to 152°59.3'	Station 5
Hippoglossoides elassodon	11/ 7/77	59°27.0' 59°27.6'	153°18.4' to 153°21.5'	Station 35
Hippoglossoides stenolepis	11/11/77	59°37.2' 59°36.6'	151°48.6' to 151°45.1'	Station 40
Platyichthys stellatus	11/ 8/77	59°16.3' 59°15.7'	153°35.7' to 153°32.4'	Station 27
Pleuronichthys decurrens	11/11/77	59°33.3' 59°33.2'	151°53.9' to 151°56.0'	Station 41
Theragra chalcogramma	11/10/77	59°01.6' 59°03.4'	153°01.4' to 152°59.3'	Station 5

TABLE IX-IV

HYDROCARBONS OF COOK INLET BIOTA (μg/g)

Material	Total Saturates	Total Unsaturates	C_{15}	C_{16}	C_{17}	Prist.	C_{18}	Phyt.	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	C_{32}	$C_{19:4}$	$C_{19:5}$	$C_{21:6}$	Sq.
Pandalus hypsinotus 37	2.9	0.5	-	-	-	.09	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pandalus borealis 37	16.6	3.0	-	-	-	13.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Crangon dalli 27	<.01	<.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Crangon dalli 40	<.01	<.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Crangon dalli 62	<.01	<.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chionoecetes opilio	<.01	55	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chionoecetes opilio 37-2	4	5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fucus distichus																										
Cottonwood Bay	22.5	165	22.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.0	-	109	54
Diamond Gulch (1)	594	3420	594	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2800	585
Diamond Gulch (2)	308	1860	308	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1520	335
Dogfish Bay	78.3	229	78.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.0	-	155	70
Douglas River	36.4	109	36.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.6	-	90.6	8.2
I.B.M. (1)	296	1206	296	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	17.2	-	1054	127
I.B.M. (2)	32.5	219	32.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	199	19
Iniskin Bay	28.5	97.9	28.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.6	-	85.2	10.4
Kasitsna Bay	22.7	122.7	22.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.7	-	49.2	50.3
N.W. Spit (1)	18.6	33.7	18.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	21	12.5
N.W. Spit (2)	36.0	46.9	23.3	-	-	-	-	-	-	-	-	.12	.38	.65	.98	1.22	1.65	1.51	2.23	1.33	1.78	.72	-	-	27.4	19.1
Oil Bay	29.2	17.1	29.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.1	-	9.3	6.9
Homer Spit	153	276	22.7	.42	1.06	.79	1.66	.80	3.44	5.70	4.06	3.08	1.74	1.15	.97	.85	.99	.80	-	-	-	-	-	3.0	112	99
Desmarestia aculeata																										
Diamond Gulch	1.42	68.6	.85	-	.57	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.2	51.3	14.1
N.W. Spit	.21	39.1	.05	-	.16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5.3	31.2	2.6
Halosaccion gladiforme																										
Douglas River	2.2	.85	-	-	1.8	-	-	-	-	-	.28	-	-	-	-	-	.16	-	-	-	-	-	-	.03	.44	.38
Palmeria palmata																										
Anchor Point	26.8	.29	.06	.07	26.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.05	-	.24
Constantinea subulifera																										
Diamond Gulch	27.1	40.0	-	-	13.1	-	-	-	.38	-	.26	.17	.48	.19	.48	.21	.97	.26	1.57	-	1.67	.27	-	-	-	1.1

Table IX-IV also shows the results of hydrocarbon determinations of intertidal benthic algae. These include *Fucus distichus* (Phaeophyta) from 10 locations and four species of red algae (Rhodophyta). The qualitative composition of *F. distichus* from most locations is similar to that found in the variability study reported in Section VII of this report. In most the plants analysed here, the absolute concentrations of hydrocarbons are markedly higher than the values reported in Section VII. This is probably a function of the season of collection. The plants whose analyses are reported in this Section were obtained in May and June 1977 while those of Section VII were collected the previous December. Youngblood and Blumer (1973) have already noted that high hydrocarbon concentrations in marine benthic algae are generally associated with rapidly growing tissue. Undoubtedly plants collected in late spring were growing more actively than ones collected in late fall. It is possible that the presence of a nonadecatetraene in these *F. distichus* also is a seasonal effect.

Two of the *F. distichus* samples show qualitatively quite different arrays of hydrocarbons. The N.W. Spit (2) sample contains, in addition to the usual biogenic array, a suite of normal alkanes with chain lengths ranging from 22 to 32 carbon atoms and no odd carbon predominance. We have previously observed this distribution in some samples (Shaw, 1976) as have others (e.g. Calder 1976; Marty and Saliot, 1976). However, the source of this array is unknown. It does not correspond to any fossil or biogenic source of which we are aware. More can be said about the hydrocarbons in the *F. distichus* collected at Homer Spit. The two most abundant compounds are pentadecane and heneicosahexaene, both of which are biogenic. This sample also contains all normal alkanes from hexadecane through octacosane with no odd carbon predominance, pristane, phytane, and substantial unresolved complex mixtures in both the saturated and unsaturated fractions. This array has all the characteristics of fuel oil. This interpretation is all the more convincing in view of the fact that the sample was collected near the small boat harbor of the town of Homer. An interesting aside about this sample is that here the presence of pristane is an indication of petroleum; this compound was detected in no other algal sample.

Among the red algae, most samples analysed show clearly endogenous biogenic distributions, the presence of heptadecane being characteristic of this class (Youngblood and Blumer, 1973). The *Constantinea subulifera*, however, also contained a series of normal alkanes ranging from heneicosane through dotriacontane with a distinct odd carbon dominance. This sample also contained terperoid hydrocarbons not listed in Table IX-IV: retene, 9.9 ppm; simonellite, 6.7 ppm; and cadalene 0.27 ppm. These compounds are associated with coal and peat deposits (Section IV) as are the odd chain length normal alkanes. Diamond Gulch, where the *C. subulifera* was collected, in adjacent to Bluff Point an area of coal outcrops. A nearby subtidal sediment showed most of these same coal associated compounds (Section IV).

While most of the algal materials analysed contained only biogenic hydrocarbons, we were able to recognize fossil hydrocarbons in two samples. Petroleum was present in *Fucus distichus* from the Homer Spit. A complex of compounds associated with coal and peat was found in *C. subulifera* from Diamond Gulch. We do not know whether these fossil hydrocarbons were incorporated into the cellular structure of the algae or present only on tissue surfaces. However, to a herbivore that eats these algae, that may be of little importance.

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Youngblood, W. W. and M. Blumer. 1973. Alkanes and alkenes in marine benthic algae. *Mar. Biol*. p. 163-172.

SECTION X. PERFORMANCE ASSESSMENT

In order to assess the methods we have used in the extraction and analysis of hydrocarbons we have conducted inter- and intralaboratory procedural checks. Environmental samples are run in groups (usually of five) together with a procedural blank (no environmental material) spiked with a quantitative hydrocarbon mixture. As a further intralaboratory exercise all analysts have performed a precision and recovery check procedure adopted by BLM's Hydrocarbon Methodology Review Group:

"Using approximately 1 μℓ equivalent of the BLM reference mixture, spiked with 10 μg of methyl stearate, the analyst should achieve separations such that <1% of each individual alkane added will appear in the aromatic fraction and <1% of each individual aromatic will appear in the aliphatic fraction. The methyl stearate to pyrene ratio in the aromatic fraction shall be less than 0.1. Recoveries of individual hydrocarbons when this mixture is carried through the analytical scheme shall be greater than 70%. This exercise shall be carried out frequently during the analytical period. Additionally, the reference mixture shall be used to spike tissues, sediments and other substances where appropriate in a concentration appropriate for routine analysis of samples normally collected in environmental assessment programs. The precision and percent recovery of the method employed shall be established based on at least three replicates analyzed quarterly. Because of potential interference from indigenous compounds, it will be necessary to first analyze the sample and then prepare the spike in such a quantity as to exceed background by a factor of approximately 5 to 10."

Results of these checks are shown in Table X-I. The composition of the standards used are shown in Table X-II. It was necessary to use this simplified standard since the BLM mixture was unavailable. The column chromatographic methods used in the checks are those described in Section VIII. In no case was any trace of methyl stearate found with the hydrocarbons. The Soxhlet extraction procedure for sediment is described in Section III. The centrifuge procedure for biota is described in Section VIII. We began these checks shortly after beginning the use of SCOT columns for gas chromatography (see Section III). One of the first things that we

TABLE X-I

RECOVERY OF STANDARD HYDROCARBONS IN INTRALABORATORY CHECKS

					Present Recovery of Standard							
Type	Date	Analyst	Standard	Replicate	C_{14}	C_{17}	C_{18}	C_{22}	C_{28}	C_{32}	Naphthalene	Anthracene
Column chromatogr.	2/8/77	1	1	1	88.6	93.6	110.5	100.0	-	82.8	-	39.9
				2	98.7	80.8	85.7	80.1	-	66.7	-	45.6
				3	104.5	90.5	108.6	98.5	-	67.0	-	36.1
Column chromatogr.	4/8/77	2	1	1	80.1	84.7	104.0	72.7	-	92.0	-	90.5
				2	71.5	73.6	91.5	78.7	-	150.0	-	54.5
				3	66.5	76.7	93.5	79.6	-	150.3	-	44.1
Column chromatogr.	9/8/77	2	1	1	80.8	75.8	97.2	101.2	-	92.9	-	10.9
				2	80.4	76.3	89.9	84.1	-	73.6	-	11.9
				3	84.2	83.2	95.6	94.2	-	73.5	-	17.9
Column chromatogr.	10/8/77	2	1	1	109.0	106.8	163.1	86.2	-	85.0	-	107.8
				2	103.2	104.7	161.6	86.4	-	152.6	-	22.1
				3	106.8	102.2	153.1	74.8	-	57.4	-	22.3
Column chromatogr.	8/3/78	3	3	1	92	87	93	87	65	62	56	73
				2	91	85	92	82	64	60	69	80
				3	80	75	79	76	62	59	74	92
Sediment by Soxhlet	15/8/77	1	1	1	100	98	107	100	-	96	-	59
				2	38	91	95	103	-	103	-	71
				3	52	95	97	104	-	92	-	84
Sediment by Soxhlet	25/8/77	2	1	1	59.8	99.6	97.0	98.0	-	111.2	-	110.1
				2	74.4	102.1	98.4	95.6	-	148.7	-	100.0
				3	66.7	102.1	98.1	87.9	-	177.4	-	149.3
Sediment by Soxhlet	14/10/77	3	2	1	21	50	63	83	77	117	-	-
				2	85	92	90	76	59	49	-	-
				3	133	66	65	44	22	11	-	-

TABLE X-I

CONTINUED

Type	Date	Analyst	Standard	Replicate	Present Recovery of Standard							
					C_{14}	C_{17}	C_{18}	C_{22}	C_{28}	C_{32}	Naphthalene	Anthracene
Biota centrifuge	25/8/77	1	1	1	15.2	24.6	27.0	29.9	-	36.6	-	21.0
				2	2.8	4.4	6.1	5.0	-	4.2	-	0
				3	15.7	14.3	18.0	19.4	-	20.0	-	-
Biota centrifuge	29/9/77	1	2	1	22.8	22.8	21.4	18.5	16.1	17.2	0	-
				2	24.1	30.2	26.9	23.7	17.9	16.9	84.4	-
				3	24.9	34.9	30.3	26.9	25.9	28.3	0	-

- Indicates compound not included in standard

TABLE X-II

COMPOSITION OF HYDROCARBON REFERENCE MIXTURES

	Concentration mg/ℓ in hexane							
Standard	C_{14}	C_{17}	C_{18}	C_{22}	C_{28}	C_{32}	Naphthalene	Anthracene
1	46.0	41.7	49.4	40.4	-	65.0	-	42.4
2	43.2	49.0	47.4	34.2	39.1	57.8	34.3	-
3	68.6	42.9	40.7	39.3	43.5	45.9	87.3	92.5

- Indicates compound not included

noticed was low recovery of the least volatile compuunds. We identified the cause of this low recovery as a leak in the gas chromatograph which only occurred at high temperature. We also noticed that our SCOT columns gave moderate to severe tailing for the aromatic hydrocarbons, leading to difficulty in quantification. Modifications in column preparation and conditioning procedures have improved this situation somewhat and work is continuing. We were pleased to find that the recoveries from our complete. sediment procedure were generally as high or higher than for the column chromatography procedure alone. Evidently losses in the extra steps of the Soxhlet procedure are more than offset by matrix effects of sediment lipids. The analyses of euphausids by the centrifuge procedure were not particularly encouraging. Part of the problem was hydrocarbon loss during the digestion step. This has been in part eliminated by the use of tighter fitting centrifuge caps and teflon liners. However, a significant part of the problem seems to be a species dependent variability in the recovery obtained by the centrifuge method. For other species than the euphausids reported here we have consistently obtained better recoveries (often over 50%, see discussion of *Mytilus* samples below) by the centrifuge procedure. Our present opinion is that procedures for biota need to be separately optimized for each species if maximum recoveries are to be obtained.

We have also participated in interlaboratory comparison analyses of a spiked sediment from the Santa Barbara Basin and of tissue homogenates of *Mytilus edulis*. The results of these analyses are shown in Table X-III. *Mytilus* samples were extracted by the use of the centrifuge procedure of Section III. Preliminary extractions with internal standards showed that for the homogenized *Mytilus* tissue the recovery of the procedure was greater than 80%. These samples contained low concentrations of hydrocarbons as noted in the table. Mass spectral analysis clearly identified DDE in both S41 and S50 but no aromatic hydrocarbons above background. The four analyses of sediment are all of the same homogenate. For these samples the total reported concentration of saturates and unsaturates include substantial unresolved complex mixtures which were quantified by planimetry.

TABLE X-III

HYDROCARBONS IN INTERLABORATORY COMPARISON MATERIALS (ppm dry weight)

Material	Analyst	Totals		C_{14}	C_{15}	C_{16}	C_{17}	Prist.	C_{18}	Phyt.	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}
		Saturates	Unsaturates																				
Mytilus S41	1	1.8	<.01	-	-	-	-	-	-	-	-	-	.04	-	.10	.17	.21	.26	.22	-	.17	.36	.07
Mytilus A16	1	1.5	2.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mytilus A38	2	2.61	2.34	-	-	-	-	-	-	-	-	-	-	.09	.08	.13	.22	.25	.11	.91	.14	.11	-
Mytilus S50	2	1.52	.76	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sediment (1)	1	1490	1100	34.3	43.3	40.5	14.2	7.6	15.1	5.5	16.9	12.1	8.5	6.5	4.0	6.4	3.0	1.4	1.6	-	-	-	-
Sediment (2)	1	490	430	13.9	16.8	14.9	6.0	2.8	4.9	1.8	5.3	3.4	2.2	1.6	1.0	1.6	0.5	.22	.42	-	-	-	-
Sediment (1)	2	1235	979	18.3	27.5	28.9	8.8	4.7	9.3	3.4	10.0	7.1	4.0	2.8	-	-	-	-	-	-	-	-	-
Sediment (2)	2	752	500	21.1	21.1	21.7	8.3	3.9	8.6	3.1	11.9	7.6	7.0	3.9	-	-	-	-	-	-	-	-	-

SECTION XI. ACTIVITY SUMMARY FOR THE QUARTER ENDING 31 MARCH 1978

Field Activities: None

Laboratory Activities: We have continued the analysis of environmental materials collected previously. Some attention has been devoted to the improvement of analytical methods for biological materials. Considerable effort has gone into the preparation of the attached annual report. OCSEAP's failure to complete contractual arrangements for FY78 has seriously and adversely affected our ability to complete the analysis of some samples and to prepare for future cruises.

APPENDIX I

SUMMARY OF PREVIOUS DATA COLLECTED FOR OCSEAP

This summary deals with work done for OCSEAP prior to that contained in the accompanying Annual Report. It does not include work performed under other NOAA programs (e.g. NEGOA or SGP) or for other agencies in the principal investigator's laboratory. Neither does it include work performed under R.U. 275 as a sub-contract by I. R. Kaplan.

Table A-1 summarizes the environmental data produced for various lease areas. The numbers shown are substantially correct but not totally accurate. The numbers of samples archived were estimated by subtraction. In some cases only an aliquot of a sample was needed for analysis and the remainder has been archived. In other cases sample pooling has been required or a biological sample has been dissected and tissues separately analyzed. Thus, the number of samples archived is probably an underestimate.

In all study areas the water, sediment, biota and seston show an absence of petroleum and the general presence of only biogenic hydrocarbons. Rather than discuss the biogenic distributions of hydrocarbons on a lease area by lease area basis it seems more germaine to OCSEA program goals to consider the contemporary fossil hydrocarbon inputs to each area. This is worthwhile since it gives information about the various areas' capacity to assimilate these compounds. It is very different if an area has no standing stock of petroleum because there are no inputs, or if there is no standing stock because a substantial input is acted upon by highly efficient degradative mechanisms.

In the Gulf of Alaska the only known natural inputs of fossil hydrocarbons are bands of onshore oil seeps between Puale Bay and Becharof Lake on the Alaska Peninsula and between Katalla and Icy Bay. The seepage rate from these zones is unknown but appears to be low. The only petroleum residues in the marine environment which have been associated with these seeps were in intertidal sediments from the Katalla area. Nearby water samples showed no detectable oil. Seston tows did not reveal elevated amounts of floating tar associated with the seep areas. It appears that the Alaska Gyre effectively moves the seep oil offshore and disperses it quickly to below detectable concentrations. Even the Kayak Island eddy

TABLE A-I

SUMMARY OF STATUS OF OCSEAP SAMPLES THROUGH LAST REPORTING PERIOD (31 MAR 77)

	Water	Sediment	Biota	Seston
Gulf of Alaska	85,85,0,20*	0,0,0,0	28,18,10,0	63,63,0,0
Cook Inlet	17,17,0,0	7,3,4,0	8,10,0,0	20,20,0,0
Bering Sea	0,0,0,0	0,0,0,0	92,54,38,0	20,20,0,0
Chukchi/Norton	11,11,0,0	0,0,0,0	0,0,0,0	25,25,0,0
Beaufort Sea	14,14,0,3	6,4,2,0	0,0,0,0	0,0,0,0

* collected, analyzed, archived, lost

system, which is adjacent to Katalla, has not resulted in oil retention in that area. The dispersive forces in the Gulf of Alaska are more than adequate to dissipate present inputs.

There appear to be three sources of fossil hydrocarbons to the Cook Inlet area. These are coal outcrops in the Anchor Point, Bluff Point area; commercial petroleum production and transshippment in the Nikiski, Trading Bay, Drift River area and onshore oil seeps in the vicinity of Chinitna Bay, Oil Bay and Iniskin Bay. The only indication of accumulation of these fossil hydrocarbons in the marine environment is the presence of aromatic hydrocarbons which are thought to be coal derived in intertidal sediments of Kachemak Bay. Subtidal sediments, water, and intertidal and subtidal organisms show no petroleum residues, only biogenic distributions. Even intertidal sediments taken in the oil seep areas of Oil Bay and Iniskin Bay showed no oil. It would appear that an important contributing factor to the dispersion of fossil hydrocarbons in Cook Inlet is the strong tidal mixing of the region, which also prevents deposition in most of the area and facilitates exchange with the Gulf of Alaska. The finding of coal associated aromatic hydrocarbons in Kachemak Bay raises the possibility that this environment has been exposed to these compounds for a considerable length of time. If that is the case, it may be that the biota have adapted to the presence of these aromatic hydrocarbons. It is also possible that the biota are now stressed making them more vulnerable to further stress. In any case, it should be noted that the number of these coal associated aromatic compounds is small and that they are structurally much less diverse than the aromatic hydrocarbons of petroleum.

We do not know of any inputs of petroleum to the Bering Sea. Thus, it is not surprising that our examination of Bering Sea biota and seston has not revealed any accumulation of fossil hydrocarbons. What has been observed is an abundance of heptadecane and pristane in zooplankton, fish, and marine mammals. These findings, together with the known high productivity of the Bering Sea pelagic ecosystem, indicate that a substantial amount of energy is being stored as hydrocarbon lipids. The adulteration of these lipids with petroleum might seriously upset this system or render it unacceptable for exploitation by man.

Our knowledge of fossil hydrocarbon inputs to the Chukchi/Norton area is limited. While at least one area of gas seepage has been identified off Nome, there is to our knowledge no evidence of heavy hydrocarbon seepage in the area. There is no evidence of fossil hydrocarbons in the water or seston of the area.

There are several potential sources of fossil hydrocarbons to the Beaufort Sea. These include oil seeps, coal outcrops, oil shale, and tar sands. These are discussed in detail in the body of this Annual Report. While fossil hydrocarbons were not found in the water column, fossil aromatic hydrocarbons were found to be widely distributed in nearshore sediments of the region. The nature and significance of these aromatic hydrocarbons is discussed in the body of this report.

Publications:

Gritz, R. L. and D. G. Shaw. 1977. A comparison of methods for hydrocarbon analysis of marine biota. Bulletin of Environmental Contamination and Toxicology. 17:408-415.

Shaw, D. G. 1977. Pelagic tar and plastic in the Gulf of Alaska and Bering Sea. The Science of the Total Environment. 8:13-20.

Shaw, D. G. 1977. Hydrocarbons in the water column. *In* Proceedings of Symposium on Fate and Effects of Petroleum Hydrocarbons in Marine Ecosystems and Organisms. Pergamon, New York. pp. 8-18.

Shaw, D. G. 1977. Aromatic Hydrocarbons of Recent Sediments of the Beaufort Sea: Distribution and Sources, invited paper for the Symposium "Nature and Distribution of Organic Matter in Recent Continental Shelf Sediments", Geological Society of America Annual Meeting, Seattle (abstract).

ANNUAL REPORT

April 1, 1977 to March 31, 1978

to

U.S. Department of Commerce

National Oceanic and Atmospheric Administration

Characterization of Organic Matter in Sediments from Lower Cook Inlet

Contract No. 03-6-022-35250, R.U. No. 480

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Summary

A large portion of the effort in the past contract year has been devoted to the development of reliable extraction and analysis procedures. Satisfactory analysis of sediment samples containing even very small amounts of organic components can now be performed.

All Lower Cook Inlet samples from 1976-1977 cruises have been analyzed and the data processed. Analyses of samples from the other regions of Alaska OCS is nearly complete as well.

Each sample was analyzed for: 1) total carbon content, 2) organic carbon content, 3) sulfur content, 4) aliphatic hydrocarbons, 5) aromatic hydrocarbons.

No signs of petroleum hydrocarbons input were detected, hence the organic content of the sediments is biogenic, derived from terrestrial and marine sources.

Introduction

A. General Nature and Scope of Study

The purpose of this study is to determine the baseline concentrations and distributions of hydrocarbons in surface sediments of Lower Cook Inlet and to characterize the nature of these hydrocarbons with respect to their possible origin, either biogenic (marine or terrestrial) or petrogenic.

B. Specific Objective

A comprehensive report is submitted with regard to Lower Cook Inlet sediment samples obtained during the 1976 and 1977 cruises. The gravimetric results are accompanied by the gas chromatographic analysis of both the aliphatic and aromatic fractions. Several samples were also analyzed by combined gas chromatography-mass spectroscopy.

C. Relevance to Problems of Petroleum Development

Petroleum production and transport has been going on in Upper Cook Inlet for quite some time. Existing oil fields and pipelines reach as far as Kalgin Island near the center of the Inlet. The search for oil in Lower Cook Inlet (LCI) may soon begin after the OCS lease sale (#CI) of 87 tracts (204, 448) hectares) occurred in October, 1977. Therefore, the baseline study of LCI received primary attention in this year's program.

An attempt has been made to determine whether there is any organic material in the sediments which may have originated from petrogenic sources. If present, it may have been transported south by the outflow of turbid, low salinity water originating in Upper Cook Inlet. Because of the detrital content of the water mass in that region, petroleum released into the marine environment from production wells in Upper Cook Inlet could be deposited with sediments. Biodegradation by the marine microorganisms and subsequent dispersion into the Gulf of Alaska through Shelikof Strait may also occur.

Important data regarding the organic content and origin of hydrocarbons in different areas of LCI was acquired. GC and GC-MS were used to determine the composition and distribution patterns of the hydrocarbons. It was possible to distinguish between marine and terrestrial sources of hydrocarbons. This information should allow the prediction of the fate of petroleum introduced into Lower Cook Inlet through routine activity or through accidental spillage.

Sampling and Study Area

In order to acquire information concerning the distribution of hydrocarbons in the sediments of Lower Cook Inlet, the region was sampled during two cruises in 1976 and 1977. Only surface sediments were collected, as it is in this layer that changes due to petroleum exploration and development will initially be observed. The first set of 23 samples was collected in the Sea 2-76WG cruise of R/V SEA SOUNDER which departed Seward on June 18 and arrived at Homer on July 1, 1976. Sediment samples 0-2 centimeters deep were quantitatively collected using a modified aluminum Van Veem grab sampler, constructed of non-contaminating materials. A detailed description of the sampler and its features can be found in the September, 1976 quarterly report. The second set, consisting of 9 samples, was collected by Ms. J.W. Wiggs of the University of Alaska (RU275) during the November, 1977 cruise of the NOAA ship SURVEYOR. These sediments are from a depth of 0-4 cm.

The locations of the sampling stations of the two cruises are given in Fig. 1. Most of them were chosen in the vicinity of the proposed lease area and in the eastern part of LCI including Kachemak Bay. Shipping routes and pipelines from the lease area will probably be directed toward the eastern part of LCI, which is already developed. This area of LCI is also the one of highest biological productivity. Few samples were obtained from the Western part of LCI and Kamishak Bay as this region will be more extensively investigated during the 1978 cruises.

Methods

1. Elemental Analysis*

Elemental sulfur analysis was carried out on freeze-dried sediment samples. 20-40 mg of the powdered sample was combusted with the accelerator (Cu chips and Fe filings) in a LECO (Laboratory Equipment Corporation) induction furnace (Model No. 523). The resulting sulfur gases were titrated according to ASTM procedure E30-47, using a LECO (Model No. 517) titrator. This method involves the measurement of the amount of KIO_3 required to oxidize the SO_2 and SO_4. The completion of the reaction was monitored by colorimetric determination of I_2 in the solution (HCl/starch). The total sulfur content was corrected for sea salt sulfate content (Table 1). Total carbon and organic carbon (that remaining after treatment with 3N HCl) were measured with a LECO acid-base semi-automatic carbon determinator (Figs. 2 and 3, Tables 2 and 3).

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* The details of the procedures are given in the respective manuals of LECO, 3000 Lakeview Avenue, St. Joseph, Michigan 49085

2. Analysis of High Molecular Weight Hydrocarbons

The following method is that recommended by the BLM with necessary modifications. Freeze drying was replaced by wet extraction with methanol because the freeze drier introduced contamination into the sediments. Bieri's (Virginia Institute of Marine Science) column procedure was adopted instead of the original silica gel and alumina chromatography so that aromatic fractions free of methyl esters could be obtained.

A pre-cleaned cellulose thimble of known weight was filled to approximately 2/3 of its capacity with a thawed sediment sample and placed in a beaker-like funnel. The interstitial water was allowed to drain into an Erlenmeyer flask. The sediment was then washed with about 150 ml of organically clean double-distilled water to remove salts. The filtrate and the interstitial water was extracted three times with 25 ml of hexane and saved for later analysis (A).

The wet sample in the thimble was extracted in a Soxhlet extractor with 500 ml of methanol for 24 hours and then with 500 ml of toluene:methanol (3:7) for 76 hours. The methanol extract was concentrated to 100 ml, added to a separatory funnel with clean water and extracted with 100 ml of hexane three times (B). If an emulsion formed, saturated NaCl solution was added before extracting into hexane. The hexane fractions (A and B) were combined with the toluene:methanol extract and concentrated to about 5 ml.

Activated copper wire was dipped into the extract to test for sulfur. If a blackening of the wire was observed, the sulfur was removed by passing the extract through a column of fine copper granules (J.T. Baker). The eluate was concentrated to 5 ml and saponified by refluxing for four hours with 40 ml of 1N KOH in 1:1 water:methanol.

A molecular sieve trap on top of the condenser prevented contamination from external sources. The mixture was then diluted with an equal volume of saturated sodium chloride solution. If no emulsion was observed, the mixture was extracted three or four times with hexane and concentrated with a rotary evaporator. If an emulsion did occur, the extract was centrifuged three times with hexane in a glass jar with a teflon-lined cap. The organic phases were combined and back extracted with an equal volume of saturated sodium chloride solution. The aqueous solution was then re-extracted once with hexane and all the organic phases combined and concentrated to 2 ml. This non-saponifiable fraction was transferred to a 2 ml vial using a glass syringe and the solvent was removed on a sand bath at 40°C under a stream of nitrogen. A subsample of about 5 μℓ was transferred onto the pan of a Mettler ME22 electrobalance and the residue after evaporation of the solvent was weighed. The weight was extrapolated to the total volume of the fraction (Fig. 4).

Pre-cleaned silica gel was activated at 235°C for 16 hours and packed with hexane in a column with a length-to-i.d. ratio of 20. A weight ratio of 200 parts of silica gel to one part of the sample was used. Aliphatics were eluted with 1.5 column volumes of hexane, after the void volume was discarded. Aromatic hydrocarbons were eluted with approximately 2 column volumes of 60:40 hexane:benzene mixture. The fractions were reduced to 100-150 μℓ and weighed on the Mettler as before, prior to gas chromatography.

Materials

1. Solvents

All solvents used were high purity grade solvents (Burdick and Jackson "distilled in glass" grade). The chemicals were of A.R. grade.

2. Water

Trace organics were removed from double-distilled water by passing it through a column of Chromosorb 102, which was prewashed with dichloromethane.

3. Soxhlet Thimbles

Single thickness cellulose (Whatman) thimbles were shaken three times overnight with toluene:methanol 3:7 in glass jars on a shaker table.

4. Glassware

All glassware was cleaned with detergent, dipped in chromic-sulfuric acid solution, and rinsed successively with distilled water and methanol and dried at 110°C. Before use, the glassware was rinsed with dichloromethane as well as the solvent to be used in extraction. Syringes were sonicated three times in dichloromethane and then rinsed once with the same solvent.

5. Silica Gel

Silica gel was first sonicated with dichloromethane-methanol and then with hexane prior to activation.

6. Sodium Chloride

NaCl was heated overnight at 500°C.

7. Potassium Hydroxide

KOH was fused at 500°C for two hours in a nickel crucible.

8. Copper Granules

Copper granules were cleaned successively with 6N HCl, acetone and hexane.

GC Analysis and Processing

The aliphatic fractions were analyzed on a modified Varian 1400 gas chromatograph equipped with a Grob injector. The FID temperature was set at 290°C and the injection temperature at 260°C. The column used was a 20 m/0.34 mm SE-54 glass capillary column produced by Jaeggi (Switzerland). The column was heated from 40°C to 250°C at a rate of 4°C/min and then kept isothermal at 260°C for approximately 60 minutes.

The aromatic fractions were run on a Varian 1520C gas chromatograph also equipped with a Grob injector. The FID temperature was set at 300°C and the injection temperature at 275°C. The column used was a 15 m/0.25 mm OV-101 glass capillary column (J&W). The column used for the aromatic runs was heated from 40°C to 260°C at a rate of 6°C/min and then kept isothermal at 260°C for approximately 60 minutes. The carrier gas in both the aliphatic and aromatic analyses was helium.

Both GC instruments were coupled to an Akai reel-to-reel audio tape recorder, so that chromatograms were recorded on tape as well as on chart paper. Each GC run was recorded at 1 7/8 ips by means of a voltage-to-frequency converter. The recorded data was then read into a PDP 11/10 computer with 16K core and 2 RK05 disks by means of a frequency-to-voltage converter and a filter attached to the computer.

Each GC run consists of about 100,000-150,000 pieces of data which are stored on disks for processing after the tape is read into the computer. This "raw" data is then processed, using GC MAIN. The processing involves the determination of the distance between the solvent peak and the beginning of the data record, finding the baseline and the largest peak (other than the solvent peak), and performing an n-point average of the data (usually n=30). This processed data record replaces the raw data recorded on the disk and is used for the peak integration and plotting.

An advantage of off-line computer processing of the GC data is the flexibility of controlling peak detection and polotting without the need of re-running a sample. The user can select a different slope sensitivity or n-point averaging. In addition, selection of plot sizes and number of copies can be varied by using the Versatec Electrostatic Printer/Plotter.

The GC/MS analyses were carried out on a Finnigan Model 4000 Quadrapole Mass Spectrometer directly interfaced with a Finnigan Model 9610 Gas Chromatograph. The GC is equipped with a 30 m/0.75 mm glass capillary column (J&W, Inc.) which is wall-coated with OV-101. The mass spectrometric data was acquired and processed through the use of a Finnigan Model 2300 Data System. Five aliphatic and six aromatic samples (20% of the total) were analyzed by GC-MS.

Results

Hydrocarbons in Lower Cook Inlet

Gravimetric data for 1976 samples and 1977 samples are presented in Tables 2 and 3, respectively. The GC data and the characteristic parameters calculated from gravimetric and GC data are presented in Tables 4-6.

Investigation began with station 48, the closest to Upper Cook Inlet and just SE of Chisck Island. A moderate (0.5%) content of organic carbon with relatively high amounts of hydrocarbons were found here. The GC pattern of the aliphatic fraction points to a clean environment with a mostly terrestrial input (Eglinton and Hamilton, 1963; Kolattakudy and Walton, 1973)-- exhibiting an odd/even preference together with a small marine-algal input (Clark and Blumer, 1967; Han _et al_., 1968; Winters _et al_., 1969). There are no signs of any petroleum-like hydrocarbons (Burns and Teal, 1971; Blumer and Sass, 1972; Kaplan _et al_., 1976;Farrington and Tripp, 1977) originating from the drilling activity in the upper part of the inlet (Pr/Ph = 4.2). Station 62A is located SW of station 48 at the mouth of Chinina Bay and shows similar parameters to those of station 48 with regard to the organic carbon and hydrocarbon content. The GC trace of the aliphatic fraction indicates mainly terrestrial input of plant waxes with strong odd carbon preference (Pr/Ph = 3.9). Four sample stations (37, 39, 44 and 15) are located further south and west to Anchor Point. The organic carbon content of the samples in the middle of the inlet (44, 15) is relatively lower--0.15 to 0.19%--and increases to 0.92% in the near-shore station (39). Station 14, which is very close to (and just SE of) station 15, had an even smaller organic carbon content (0.09%) and only a very small amount of hydrocarbons was isolated. The GC trace indicates a mixed terrestrial and marine input with Pr/Ph = 2.4.

The above data demonstrate that the surface sediments in Lower Cook Inlet north to Kamishak and Kachemak Bays are free from petroleum contamination.

The second set of samples are from various locations in Kachemak Bay in the eastern part of LCI. Station 37 is at the center of the inner part of the bay and relative to its rather moderate organic carbon content (0.36%), it showed very high concentrations of the nonsaponifiable, aliphatic and aromatic fractions. The GC trace represents a typical example of terrestrial organic matter with extremely high odd/even preference with the main n-alkanes being C_{25}, C_{27}, C_{29} and C_{31}. The contribution from other sources are almost negligible. It seems that the inner part of Kachemak Bay behaves as a closed basin allowing almost no mixing with the western part of the bay. The high vascular plant input from the rivers (mainly the Fox River) and the glaciers accumulates and sinks to the bottom supplying the dominant amount of the organic content of the sediments. The high productivity in this region is more evident in station 43 on the border between the inner and outer parts of Kachemak Bay. This sediment sample contained 1.47% organic carbon, 250 ppm of non-saponifiable lipid fraction, 16 ppm in aliphatics, and 24 ppm in aromatics and was the richest sample in the whole of LCI. In station 43, as in station 37, hydrocarbons from terrestrial sources were dominant in the aliphatic fraction, however, despite the high odd/even preference, the chromatogram between n-C_{27} and n-C_{31} was more complex--probably due to the presence of some triterpenoid derivatives. In addition, there were signs (olefinic hydrocarbons) of some marine input; especially between n-C_{19} and n-C_{20}. The amounts of pristane and phytane were very small with Pr/Ph = 6.0.

Two samples were taken from station 227 located close to station 43 and the analysis of the two gave very similar results, reflecting the homogeneity of the samples and the accuracy of the detection technique. The organic carbon content is above 1% and relatively large amounts of lipids were isolated. The chromatograms of the two samples (227A and 227B) are nearly identical and while the high molecular weight hydrocarbons in the n-C_{25} - n-C_{31} region remain dominant, there is a significant contribution from marine-algal sources with a typical cluster of olefins surrounding n-C_{21}. Pr/Ph = 4.6 at 227A and 4.7 at 227B.

In all five stations at the entrance and the western part of Kachemak Bay (34, 41, 42, 40A, 40B and 41') the organic carbon content is less than 1% and there is a decreasing trend in organic carbon content and the amount of lipids found, from the bay toward the open sea. The GC traces of the aliphatic fractions of all these samples are bimodal and the contribution from terrestrial sources predominantes with various degrees of contribution from marine sources. It seems that this is the region where materials entering the bay from the surrounding land are being diluted by fresh ocean water coming via Kennedy entrance. The amounts of pristane and phytane are small and the ratio Pr/Ph varies from 3.5 to 6.1. There were no signs of petroleum contamination in any of the Kackemak Bay stations.

Five stations with low amounts of organic carbon ($< 0.5\%$) and small concentrations of lipids (< 14 ppm) are located in the SE part of the LCI west of the Kenai Peninsula. From north to south, these stations are 27, 33, 28, 30 and 26. Apparently the counterclockwise motion of the currents entering from Kennedy entrance and the stormy nature of the waves in this area result in a slow rate of deposition. Sample 27 had the lowest amount of extractable lipids (1.7 ppm) among all LCI samples. The hydrocarbons from this group of samples are of mixed terrestrial and marine origins. The normal hydrocarbons above C_{25} show a definite odd/even preference, while those in the lighter molecular weight region usually do not show any preference and maximize at n-C_{23}. The Pr/Ph range is from 2.9 to 7.0, reflecting the biogenic origin of the hydrocarbons (Blumer et al., 1964; Blumer and Sass, 1972).

Stations 16 and 17 are located in the middle of the inlet east of Augustine Island. They both show a low content of organic components. The GC data (available for station 16 only) demonstrate substantial terrestrial input with some marine contribution, no contamination and Pr/Ph = 3.7.

Very few samples were available from the Kamishak Bay area, and efforts this year will be directed toward obtaining a large number of samples from Kamishak Bay and other areas in the western part of LCI. This is necessary in order to determine whether the organic material originating at the northern part of Cook Inlet is being deposited near Kamishak Bay and Augustine Island or carried away and dispersed beyond Shelikof Straight. Station 8, in the southern portion of Kamishak Bay, has an organic carbon content of about 0.5%. Station 27', at the mouth of the bay and just south of Augustine Island, has about the same organic carbon content (0.5%) and the GC analysis shows complete dominance of hydrocarbons of terrestrial origin. Pristane and phytane are low, with Pr/Ph = 4.6.

Stations 18 and 29 are located in the middle of the lease area at the southern end of LCI; they both have the same organic carbon content (0.65%) and similar amounts of extractable lipids (about 23 ppm). Station 29 is richer in hydrocarbons. Even the GC traces of their aliphatic fractions are similar and indicate both marine and terrestrial sources. There are two clusters of peaks, one that probably contains some olefinic hydrocarbons between n-C_{19} and n-C_{21} and the other with triterpenoid derivatives between n-C_{27} and n-C_{31}. Pr/Ph are very high, 18 for station 29 and 11 for station 18.

Four sediment samples were obtained from the SW part of LCI, west of the Barren Islands. Three stations: 19, 23 and 207 have low to moderate organic carbon content and lipid concentrations. Their GC traces show an almost equal input from marine and terrestrial sources. The Pr/Ph ratio varies from 6.9 (Station 207) to 9.4 (Station 19). The fourth station, 24, which is very close to 19 and 23 and east of 207, has an organic carbon content of 0.43%, but a surprisingly high concentration of the non-saponifiable fraction of the lipids (approximately 180 ppm). The GC trace of the aliphatic fraction is characteristic of a mixed marine-terrestrial environment, but in addition to that, very large amounts of pristane were detected. Pristane was the major hydrocarbon in the mixture and Pr/Ph = 37. This station has a unique source of pristane; possibly a benthic organism (shrimp) with a habitat localized at station 24.

The results of the analysis of the aromatic fractions usually correspond to those of the respective aliphatic fractions. The largest concentrations were found in and near Kachemak Bay. In some cases (Stations 43, 40B, 227A, 227B) the amount of aromatics exceeded that of the aliphatic components. Usually the GC traces of the aromatic fractions illustrate a complex mixture. In a few cases, however, very few peaks were resolved because of the small amount of material present (e.g., stations 14, 27 and 33). Analysis of specific aromatic compounds was based upon GC-MS runs of a few samples.

In summary, the following conclusions have been reached from the gas chromatographic study:

1. In all regions investigated, there were no signs of petroleum-derived hydrocarbons in the sediments. This was demonstrated by the high Pr/Ph ratios (generally < 3) and by the GC traces which had straight baselines and lacked the unresolved complex mixture (UCM), which is the common marker of the presence of petroleum hydrocarbons in sediments.

2. The biogenic sources of the hydrocarbons in the sediments are mostly allochthonous (terrestrial) mixed with varying amounts of autochthonous (marine) components.

3. The terrestrial input is predominant in the northern and eastern parts of LCI. The origins of the hydrocarbons are the surface waxes of high plants. A very strong odd carbon number predominance

exists in the n-C_{25} to n-C_{35} range with n-C_{27}, n-C_{29} and n-C_{31} being most abundant. Sometimes those high molecular weight hydrocarbons are accompanied by a cluster of peaks between n-C_{27} and n-C_{31} due to the presence of different triterpenoid derivatives.

4. The marine input of hydrocarbons, which never exceeds that of the terrigeneous source, is more pronounced in the southern and western parts of Lower Cook Inlet. These are regions where plant-wax hydrocarbons are being diluted by hydrocarbons from phytoplankton and zooplankton sources. These sources show a maximum in the C_{19} to C_{23} region and are often accompanied by a cluster of mono- and polyolefins between n-C_{20} and n-C_{21}.

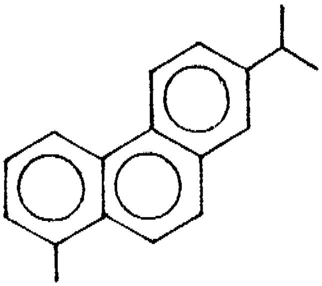
5. In most cases, small amounts of pristane and phytane were detected--pristane always in much larger amounts. In one station (24) pristane was the dominant hydrocarbon, probably due to the presence of a benthic community in the sediment at that location.

GC-MS Analysis

The GC-MS results of the five aliphatic fractions were helpful in the correct assignment of retention times for the straight chain hydrocarbons as well as for pristane and phytane. The information was particularly useful in the n-C_{20} - n-C_{21} region where in some cases, olefinic and unknown components masked the peaks of the normal saturated hydrocarbons. In addition, many olefinic, isoprenoid, and terpenoid compounds have been identified. The detailed GC-MS analysis of five aliphatic fractions (stations 18, 24, 34, 43 and 227A) is submitted in Appendix 3. The mass spectra of individual components is available on request from the authors.

The GC analysis of the aromatic fractions was much more complicated. In a few cases only a small number of peaks was observed, while most of the samples showed a very complex GC pattern. No identification of specific compounds is possible solely on the basis of GC analysis. Six samples (stations 16, 24, 43, 48, 27' and 41') were chosen for GC-MS analysis. As in the case of the aliphatic fractions, the GC-MS traces of these aromatic fractions are included in Appendix 3, together with the corresponding tables.

In general, it was determined that there was virtually no interference from fatty acid methyl esters as has often happened in the past. However, it seems that there is no way to obtain a complete match between the GC traces from the HP instrument with the flame ionization detector and the total ion current plots from the Finnigan GC-MS. It is even more difficult to analyze the GC trace of an aromatic sample based on the GC-MS data of another sample. Therefore, comprehensive data is furnished only for the six samples analyzed by GC-MS. The four major components which were detected in the analysis were:



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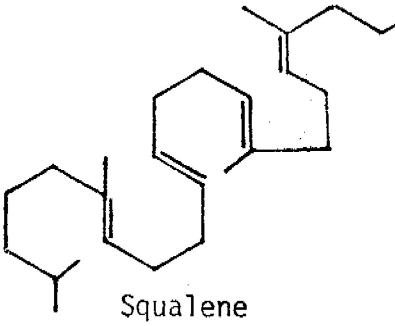
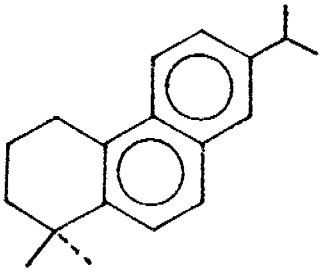
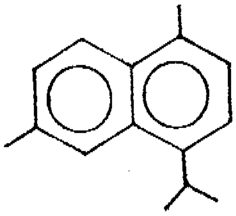


Squalene



Simonellite



Cadalene

None of these four appear on the NOAA aromatic list. Squalene is not an aromatic hydrocarbon but a polyolefinic triterpene, which serves as an important intermediate in the syntheseis of plant and animal steroids.

Cadalene was identified (Bendoraites, 1974) as a major component of the aromatic fraction of two crude oils from Southern Texas and its presence was attributed to either a cyclization reaction of farnesol or to dehydrogenation of sesquiterpenes such as cadinene. Diterpenic acids, such as abietic acid, commonly found in resin acids from various trees, are the possible source of simonellite and retene. Retene is often found in peats, lignites, and brown coal and relatively large amounts of cadalene, retene and simonellite were detected in intertidal samples from several stations in LCI (Shaw, 1978).

These four compounds are almost certainly derived from a biogenic origin of which simonellite and retene are terrigenous (Simoneit, 1977), while cadalene and squalene are probably of a mixed terrigenous and marine origin. As expected, station 43 in the inner part of Kachemak Bay, is the richest in aliphatics and aromatics in LCI (Table 2) and contains extremely large amounts of cadalene, simonellite, retene and squalene (Table 7).

Small amounts of other aromatic compounds such as biphenyl, fluorene, pyrene, fluoranthene and benzpyrene were often detected. Station 24 is unique in that the analysis of its aliphatic fractions showed the presence of an unusually large amount of pristane. The analysis of the aromatic fraction indicated almost no cadalene or retene, very little simonellite and relatively large amounts of PNAH and their derivatives. A large amount of squalene was also observed. More information about the benthic organisms and the plankton in this location, as well as additional sampling of sediments at various depths below the sediment-water interface might be helpful for a better understanding of the distribution of the hydrocarbons at station 24.

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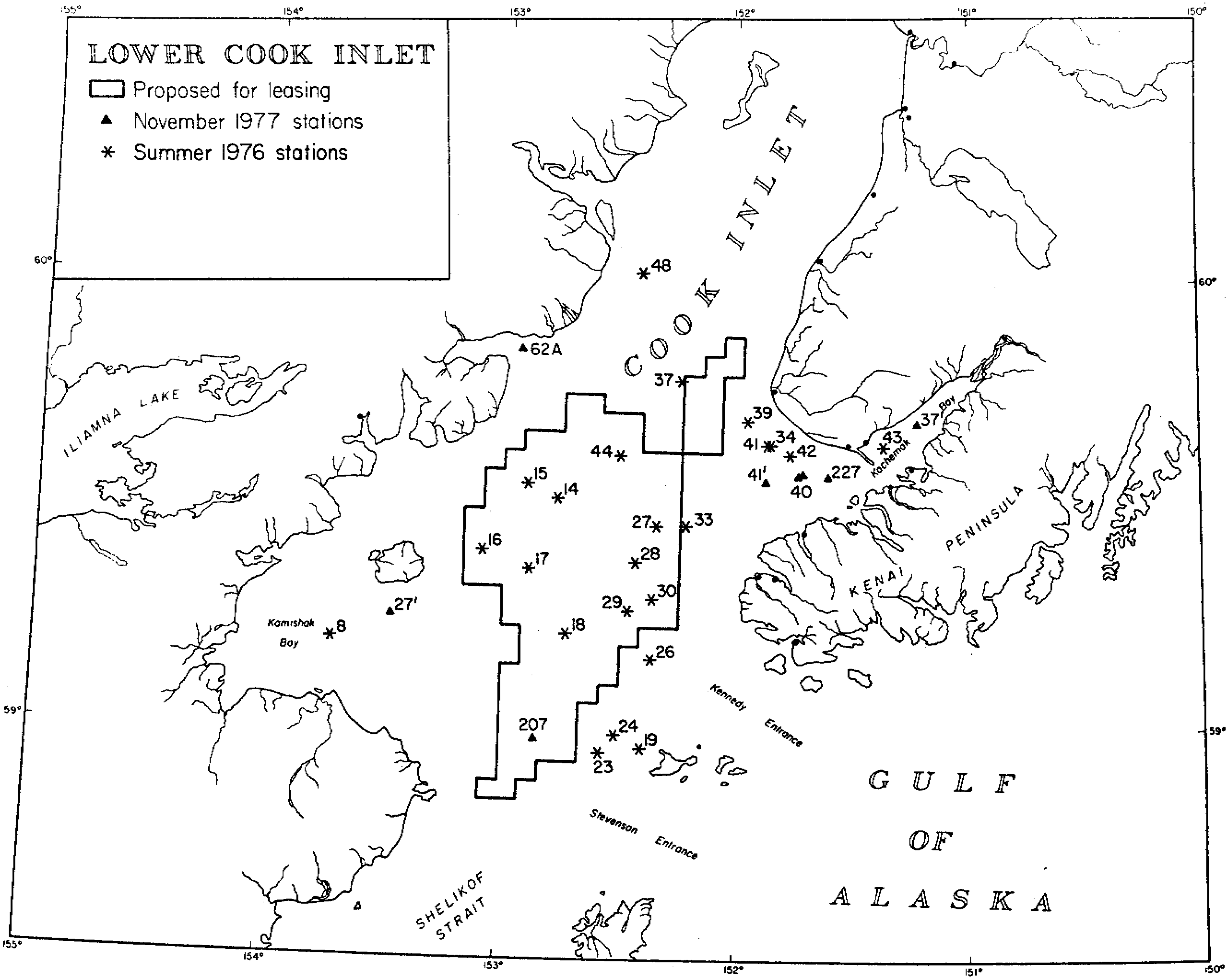
LOWER COOK INLET
Proposed for leasing
▲ November 1977 stations
* Summer 1976 stations
155°
154°
153°
152°
151°
150°
60°
59°
COOK INLET
ILIAMNA LAKE
Kamishak Bay
KENAI PENINSULA
Kachemak Bay
Kennedy Entrance
Stevenson Entrance
SHELIKOF STRAIT
GULF OF ALASKA
48
62A
37
39
41
34
42
43
37
41'
40
227
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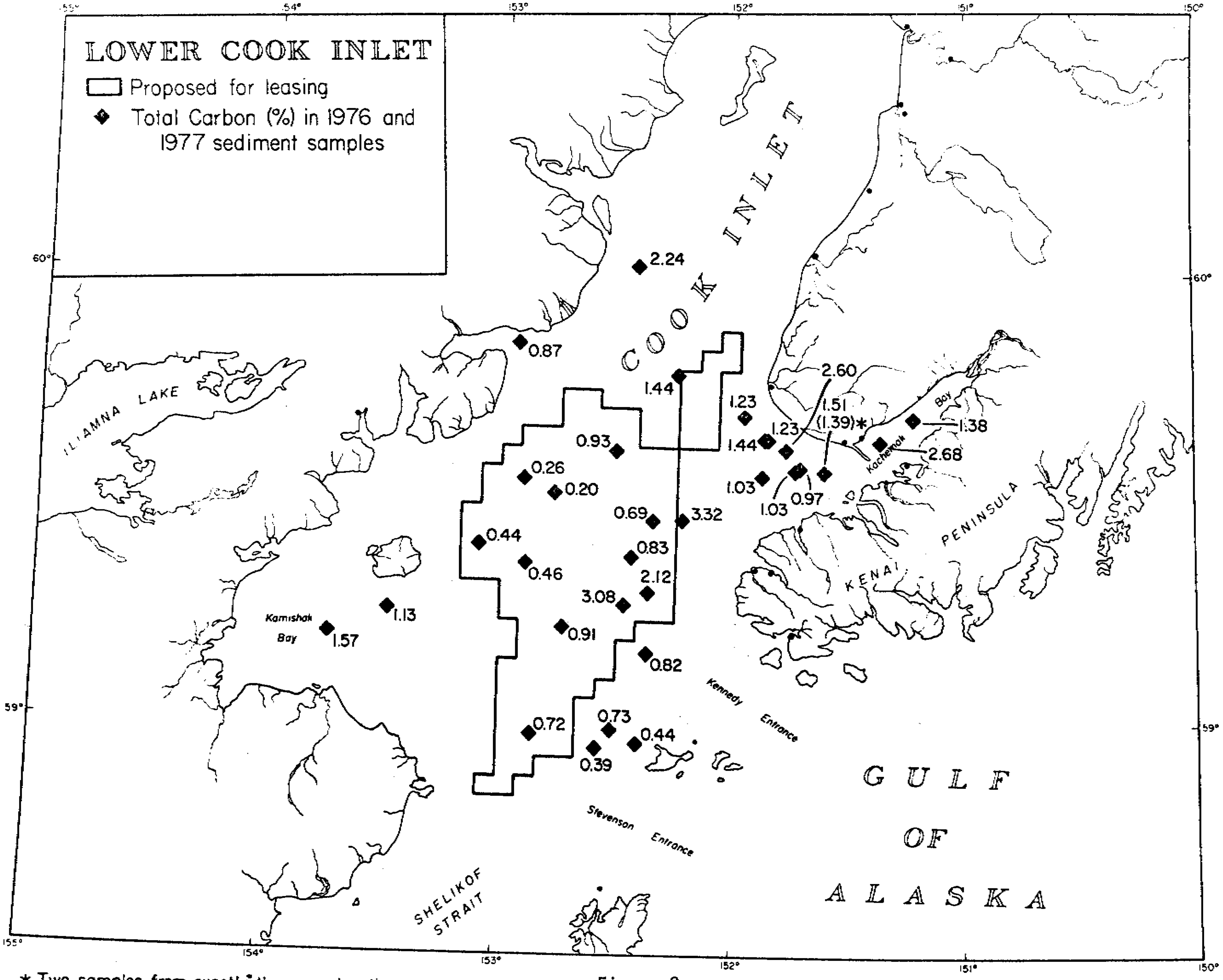
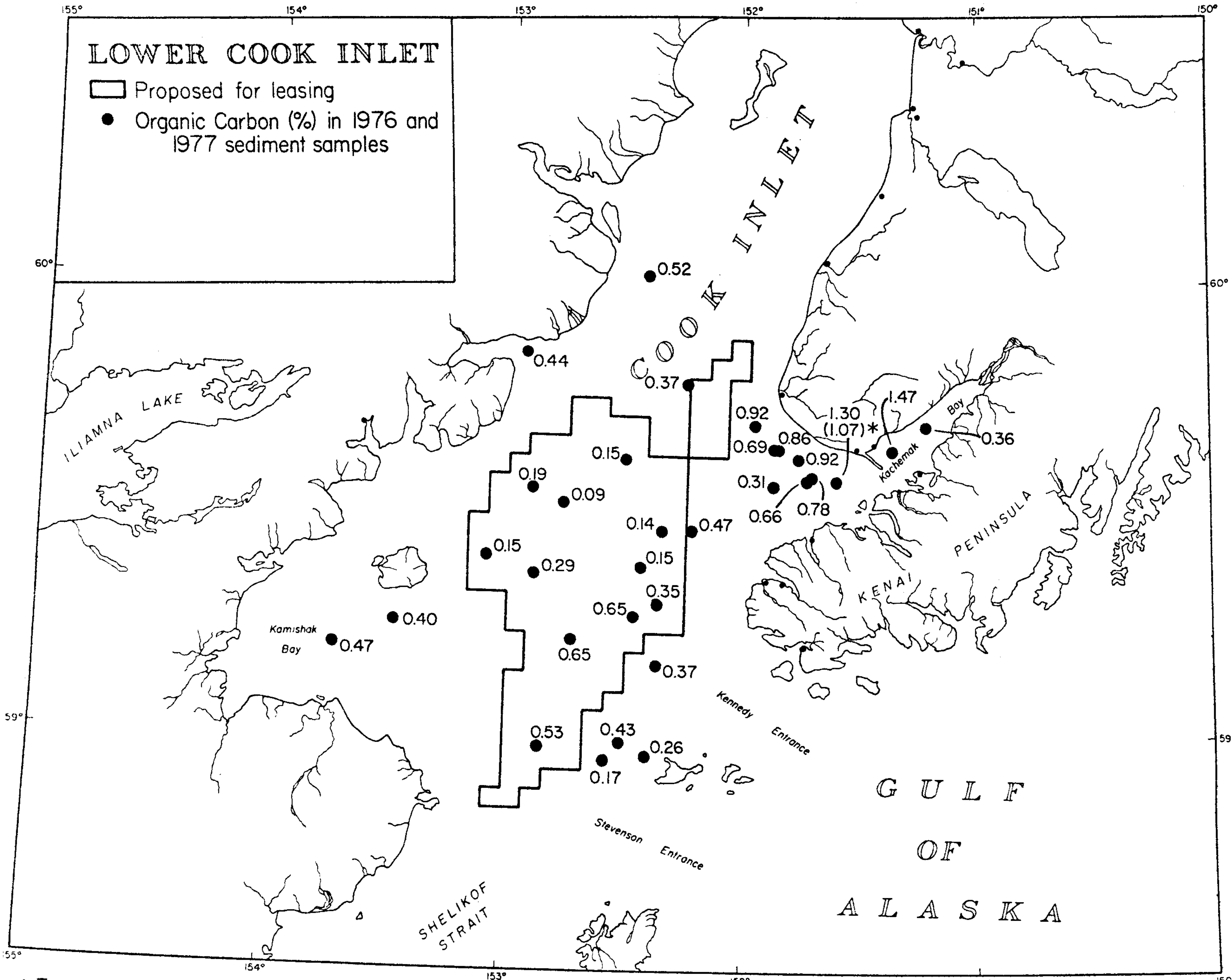
Figure 1



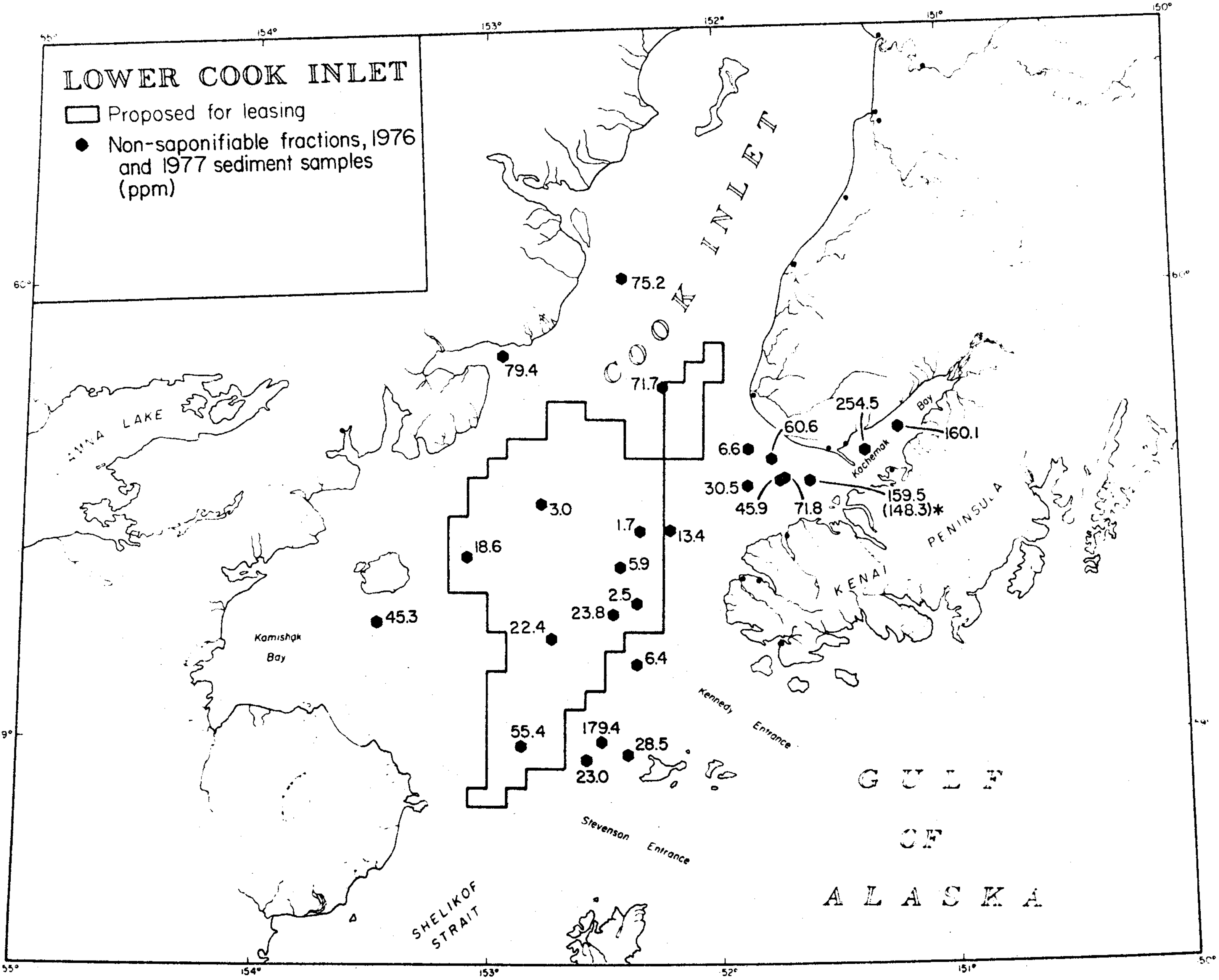
* Two samples from exactly the same location.

Figure 2



* Two samples from exactly the same location.

Figure 3.



* Two samples from exactly the same location

Figure 4

Table 1. Elemental Sulfur in Cook Inlet Sediment Samples 1976 and 1977 Cruises*

Station	8	14	15	16	17	18	19	23	24	26	27
% S	0.038	0.034	0.026	0.009	0.009	0.011	0.034	0.051	0.031	0.0	0.0

Station	28	29	30	33	34	37	39	41	43	44	48
% S	0.0	0.0	0.041	0.014	0.019	0.014	0.031	0.013	0.034	0.006	0.0039

Station	27'	37'	40A	40B	41'	62A	207	227A	227B
% S	0.0	0.0	0.044	0.063	0.023	0.016	0.029	0.037	0.047

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*All the numbers were corrected for the average content of sulfur (0.031%) in sea water sulfates.

Table 2. Gravimetric Data for Cook Inlet Sediment Samples (1976 Cruises) (1)

Station	Lat (N)	Long (W)	Depth (m)	Rating (2)	Total Carbon %	Organic Carbon %	Weight (3) (gr)	Non Saponifiable Fr. (4) (ppm)	Aliphatic Fr. (ppm	Aromatic Fr. (ppm)
8 (5)	59°11.38'	153°44.10'	36	2	1.57	0.47	-	-	-	-
14	59°30.6'	152°46.6'	61	4	0.20	0.09	133.23	3.00	0.435	0.480
15 (5)	59°31.8'	152°54.0'	45	4	0.26	0.19	-	-	-	-
16	59°23.2'	153°06.0'	48	4	0.44	0.15	152.03	18.62	0.868	0.842
17 (5)	59°20.7'	152°53.5'	74	4	0.46	0.29	167.37	-	-	-
18	59°11.90'	152°43.00'	122	3	0.91	0.65	166.33	22.43	0.661	0.992
19	58°56.25'	152°23.36'	75	4	0.44	0.26	157.83	28.51	0.792	0.919
23	58°55.70'	152°34.30'	170	2	0.39	0.17	140.26	22.96	0.563	1.176
24	58°58.49'	152°31.11'	147	4	0.73	0.43	111.45	179.36	2.306	4.845
26	59°08.1'	152°22.1'	119	4	0.82	0.37	151.15	6.42	0.390	0.476
27	59°26.30'	152°20.70'	74	3	0.69	0.14	155.19	1.74	0.509	0.180
28	59°21.35'	152°25.90'	78	2	0.83	0.15	149.33	5.93	0.904	0.603
29	59°14.98'	152°28.15'	89	3	3.08	0.65	142.29	23.83	1.546	1.441
30	59°16.65'	152°21.70'	91	3	2.12	0.35	165.10	2.51	0.121	0.363
33	59°26.35'	152°12.44'	50	4	3.32	0.47	152.27	13.40	0.348	0.585
34	59°36.5'	151°52.0'	28	3	1.23	0.86	144.97	71.74	5.553	3.704
37	59°45.9'	152°13.8'	56	1	1.44	0.37	-	-	-	-
39	59°40.75'	151°57.15'	35	1	1.23	0.92	-	-	-	-
41	59°36.25'	151°56.00'	30	3	1.44	0.69	146.07	6.57	0.815	0.808
42	59°36.20'	151°45.6'	30	2	2.60	0.92	165.41	60.58	1.814	3.265
43	59°36.63'	151°22.07'	52	4	2.68	1.47	131.02	254.54	16.104	23.813
44	59°36.25'	152°29.90'	65	4	0.93	0.15	-	-	-	-
48	60°00.0'	152°24.6'	45	2	2.24	0.52	95.84	75.23	4.539	2.494

(1) All samples but 37,39 and 44 are 0-2 cm. Samples 37,39 and 44 are bulk samples and were not extracted.
(2) Quality of sample recovery based on a subjective scale of 5 (excellent) to 1 (poor).
(3) Extracted (salt free) dry sediment.
(4) No elemental sulfur was detected in this group of samples.
(5) Samples 8, 15 and 17 were analyzed after using a freeze drying and were found to be contaminated.

Table 3. Gravimetric Data for Cook Inlet Sediment Samples (1977 Cruise)

Station	Lat (N)	Long (W)	Depth (m)	Total Carbon %	Organic Carbon %	Weight(1) (gr)	Non Saponifiable Fr.(2) (ppm)	Aliphatic Fr. (ppm)	Aromatic Fr. (ppm)
27'	59°15.0'	153°29.0'	38	1.13	0.40	125.35	45.31	3.191	1.835
37'	59°41.2'	151°12.8'	33	1.38	0.36	100.62	160.11	8.149	6.621
40A	59°33.9'	151°44.5'	82	1.03	0.66	127.74	45.87	2.583	2.583
40B	59°34.1'	151°43.5'	82	0.97	0.78	137.52	71.77	3.345	4.799
41'	59°32.9'	151°53.4'	46	1.03	0.31	142.75	30.47	1.471	1.681
62A	59°50.4'	152°56.5'	16	0.87	0.44	116.45	79.43	5.582	3.349
207	58°59.9'	152°52.8'	165	0.72	0.53	131.34	55.43	2.969	4.188
227A(3)	59°33.6'	151°36.5'	88	1.51	1.30	78.05	159.51	7.687	16.784
227B(3)	59°33.6'	151°36.5'	88	1.39	1.07	88.52	148.78	7.795	9.602

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(1) Extracted (salt free) dry sediment.
(2) No elemental sulfur was detected in this group of samples.
(3) Two samples from exactly the same location.

Table 4. Aliphatic Hydrocarbon Concentrations in Cook Inlet Sediment Samples (ng/g) 1976 Cruise (Part 1, nC_{12}-nC_{22})*

Station	$n\text{-}C_{12}$	$n\text{-}C_{13}$	$n\text{-}C_{14}$	$n\text{-}C_{15}$	$n\text{-}C_{16}$	$n\text{-}C_{17}$	Pristane	$n\text{-}C_{18}$	Phytane	$n\text{-}C_{19}$	$n\text{-}C_{20}$	$n\text{-}C_{21}$	$n\text{-}C_{22}$
14					0.2	0.5	0.4	0.7	0.2	0.9	0.7	1.0	0.9
16			0.2	0.3	0.4	0.9	0.9	1.3	0.2	2.6	2.4	5.7	5.2
18	0.8	0.3	0.3	0.4	0.3	0.5	1.5	0.7	0.1	1.8	1.6	3.2	3.0
19	4.5	2.7	1.8	4.1	4.2	5.6	10.9	5.9	1.2	8.7	8.6	10.7	10.6
23	1.5	1.1	1.3	1.9	1.6	3.3	7.5	4.3	1.1	6.1	9.1	7.3	6.4
24	2.8	1.6	1.5	2.0	2.2	4.2	59.1	5.6	1.4	8.0	12.6	5.5	8.6
26				0.0	0.0	0.1	0.1	0.1	0.0	0.2	0.6	0.4	0.5
27	0.3			0.1	0.1	0.2	0.2	0.3	0.1	0.4	0.7	1.0	1.2
28						0.2	1.0	0.5	0.1	0.9	7.0	2.8	3.9
29	5.4	0.7	0.8	0.9	0.7	1.3	8.1	2.0	0.5	10.4	10.5	10.7	9.7
30				0.3	0.7	1.4	2.1	2.2	0.7	3.4	5.3	6.7	8.5
33	0.1	0.1	0.1	0.3	0.6	1.2	2.0	1.5	0.3	1.9	3.2	2.6	3.0
34	9.2	2.7	8.6	2.7	2.7	5.0	4.0	5.3	1.0	25.0	13.9	24.1	19.5
41						0.7	0.6	0.8	0.1	1.2	0.7	2.5	2.8
42	0.5	0.6	0.6	0.7	1.0	2.4	3.0	3.5	0.7	13.5	7.5	20.6	16.3
43			10.6	6.9	5.1	17.6	40.9	16.9	6.9	52.1	37.4	123.4	91.5
48	6.1	3.8	3.8	7.3	7.3	15.2	13.4	14.7	3.2	20.4	47.5	43.3	36.8

*Concentrations were obtained by comparison of peak heights to those of a known standard mixture and using the appropriate response factors. Based on GC-MS data corrections were made, in many samples, with regard to the concentrations of $n\text{-}C_{20}$ and $n\text{-}C_{21}$.

Table 4 Aliphatic Hydrocarbon Concentrations in Cook Inlet Sediment Samples (ng/g), 1976 Cruise (Part 2, nC_{23}-nC_{34})*

Station	$n\text{-}C_{23}$	$n\text{-}C_{24}$	$n\text{-}C_{25}$	$n\text{-}C_{26}$	$n\text{-}C_{27}$	$n\text{-}C_{28}$	$n\text{-}C_{29}$	$n\text{-}C_{30}$	$n\text{-}C_{31}$	$n\text{-}C_{32}$	$n\text{-}C_{33}$	$n\text{-}C_{34}$
14	1.2	0.9	1.1	0.8	1.2	0.6	1.4	0.5	1.1	0.6	0.5	
16	10.7	5.6	15.4	5.2	>18.0	4.6	> 21.0	4.0	15.6	4.9	6.4	0.8
18	6.4	3.6	7.9	3.1	11.9	2.7	15.1	3.1	10.6	5.8	4.1	0.4
19	11.8	10.3	11.7	8.8	14.2	6.9	16.3	6.5	17.3	4.4	7.5	2.2
23	8.3	6.2	10.0	5.5	15.5	5.0	14.0	4.1	12.0	4.2	4.8	1.1
24	11.1	8.9	13.0	8.7	20.9	8.0	32.5	7.4	36.9	5.6	15.6	2.3
26	0.7	0.6	0.9	0.6	1.2	0.5	1.7	0.9	1.4	0.5	0.7	0.2
27	1.5	1.4	1.5	1.2	1.6	0.9	1.5	0.7	1.1	0.5	0.5	
28	5.3	3.9	6.0	3.4	7.7	5.2	9.8	2.4	6.7	3.3	2.6	0.4
29	24.2	11.7	26.9	10.1	37.0	9.5	39.8	21.6	44.9	34.0	17.6	1.8
30	12.4	9.9	13.8	8.5	15.6	6.6	16.6	4.9	11.1	5.4	4.7	1.4
33	3.4	3.1	3.4	2.4	3.6	1.6	3.0	1.1	2.0	0.9	0.9	0.3
34	70.2	29.9	104.1	33.7	>175.0	34.2	>207.0	44.9	189.9	61.2	70.2	
41	6.5	3.6	10.6	4.2	21.3	4.4	32.8	3.6	25.0	5.3	7.9	0.8
42	41.6	20.0	57.0	19.5	66.2	18.6	> 78.0	27.3	87.3	33.3	32.9	1.8
43	337.1	95.1	>390.0	130.0	>410.0	135.5	>480.0	246.7	666.5	167.2	228.5	7.7
48	89.4	39.8	137.4	39.6	258.4	34.5	161.7	30.0	136.3	26.2	58.9	8.0

*Concentrations were obtained by comparison of peak heights to those of a known standard mixture and using the appropriate response factors.

Table 5 . Aliphatic Hydrocarbon Concentrations in Cook Inlet Sediment Samples (ng/g), 1977 Cruise*

Station	n-C_{12}	n-C_{13}	n-C_{14}	n-C_{15}	n-C_{16}	n-C_{17}	Pristane	n-C_{18}	Phytane	n-C_{19}	n-C_{20}	n-C_{21}	n-C_{22}
27'		1.5	4.1	9.1	8.3	15.2	10.7	11.2	2.3	15.8	8.3	29.8	21.1
37'	6.5	4.2	1.0	7.8	1.6	9.1	15.7	5.7	1.6	20.7	14.8	63.9	54.2
40A		1.1	1.1	2.7	2.5	5.2	5.7	4.9	1.1	10.7	5.9	19.2	15.2
40B		2.2	0.7	3.0	3.2	9.1	9.7	7.6	1.6	14.6	8.1	25.6	19.6
41'	2.3	0.4	1.0	1.4	1.2	2.5	2.2	1.9	0.4	4.1	2.3	6.4	5.6
62A	4.0	0.9	1.5	4.3	5.0	10.7	7.2	9.0	1.8	13.8	32.5	98.0	21.0
207	6.0	6.2	8.1	14.3	10.5	15.9	24.7	15.3	3.6	22.9	15.1	23.0	22.3
227A	7.1	4.1	4.5	12.2	7.5	22.2	20.9	15.2	4.5	29.2	23.0	54.0	40.2
227B	13.8	7.1	6.3	15.0	6.6	15.4	15.2	11.7	3.3	26.4	21.0	48.4	36.4

Station	n-C_{23}	n-C_{24}	n-C_{25}	n-C_{26}	n-C_{27}	n-C_{28}	n-C_{29}	n-C_{30}	n-C_{31}	n-C_{32}	n-C_{33}	n-C_{34}
27'	57.1	29.1	>110.0	33.3	>114.0	30.8	>134.0	25.0	116.7	21.2	48.1	3.7
23'	181.0	73.0	>317.0	87.8	>330.0	84.6	>387.0	47.7	406.4	47.5	136.7	4.6
40A	37.4	18.8	60.2	19.7	> 89.0	19.0	>104.0	22.7	84.8	20.0	32.5	2.5
40B	46.4	23.0	71.9	26.7	141.4	21.9	123.1	19.3	99.2	25.4	37.4	6.9
41'	12.5	7.1	18.1	7.6	33.5	8.6	48.3	7.3	32.5	10.7	14.2	2.9
62A	55.0	104.7	88.0	23.9	187.5	20.2	131.1	22.3	84.6	19.8	35.0	
207	34.8	24.0	46.7	22.0	80.9	19.3	80.5	19.3	62.6	14.9	24.1	3.0
227A	103.1	50.4	166.3	51.6	270.0	55.4	317.0	50.6	237.6	47.5	106.5	7.5
227B	93.4	43.8	152.2	47.2	322.1	48.6	295.1	45.1	227.3	40.6	78.4	4.6

*Concentrations were obtained by comparison of peak heights to those of a known standard mixture and using the appropriate response factors. Based on GC-MS data corrections were made in many samples, with regard to the concentrations of n-C_{20} and n-C_{21}.

Table 6. Characteristic Parameters for Cook Inlet Hydrocarbons.

Station No.	$\frac{\text{Non Saponifiable fr.}}{\text{org. carbon}}$ $(x10^{-4})$	$\frac{\text{Alkanes}}{\text{org. carbon}}$ $(x10^{-4})$	$\frac{\text{Pristane}}{n\text{-}C_{17}}$	$\frac{\text{Phytane}}{n\text{-}C_{18}}$	$\frac{\text{Pristane}}{\text{Phytane}}$	$\frac{\text{Odd}}{\text{Even}}$
14	15.0	2.2	0.8	0.3	2.4	1.5
16	124.1	5.8	1.0	0.2	3.7	>2.8
18	34.5	1.0	2.9	0.2	11.0	2.4
19	109.7	3.1	1.9	0.2	9.4	1.5
23	135.1	3.3	2.3	0.3	7.1	1.7
24	417.1	5.4	14.7	0.3	44.5	2.0
26	17.4	1.1	1.2	0.3	3.7	1.6
27	12.4	3.6	0.8	0.2	3.0	1.3
28	39.5	6.0	4.6	0.3	7.1	1.4
29	36.7	2.4	6.4	0.2	17.6	1.8
30	7.2	0.4	1.6	0.3	2.9	1.6
33	28.5	0.7	1.8	0.2	7.1	1.3
34	83.4	6.5	0.8	0.2	4.0	>3.3
41	9.5	1.2	0.8	0.2	3.9	4.1
42	65.9	2.0	1.3	0.2	4.8	>2.7
43	173.2	11.0	2.3	0.4	6.0	>2.9
48	144.7	8.7	0.9	0.2	4.2	3.2
27'	113.3	8.0	0.7	0.2	4.6	>3.3
37'	444.8	22.6	1.7	0.3	10.1	>4.3
40A	69.5	3.9	1.1	0.2	5.0	>3.4
40B	92.0	4.3	1.1	0.2	6.1	3.6
41'	98.3	4.8	0.9	0.2	5.3	3.0
62A	180.5	12.7	0.7	0.2	3.9	2.7
207	104.6	5.6	1.6	0.2	6.8	2.3
227A	122.7	5.9	0.9	0.3	4.6	>3.1
227B	139.1	7.3	1.0	0.3	4.7	3.9

Table 7. Major aromatic hydrocarbons from GC-MS data (ppb)

Station No.	Cadalene	Simonellite	Retene	Squalene	Phenanthrene Anthracene
16	4	17	12	< 1	6
24	< 1	4	3	20	5
41’	< 1	n.d.*	n.d.*	4	-
43	287	1088	437	103	< 8
48	< 1	< 1	3	96	3
27’	3	6	5	44	10

* Interpretation difficult, but both appear to be < 4.

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